

## Supporting Information

### I. Synthesis.

*General:* Unless specifically notified, all starting materials were obtained from commercial suppliers (Aldrich or Acrös) and were used without further purification. Hexane, dichloromethane were distilled prior to use. Dry triethylamine and THF were obtained by vacuum transfer from sodium benzophenone. All environmental-sensitive reactions were performed under nitrogen gas. Analytical thin layer chromatography (TLC) was performed on precoated sheets of silica gel 60 F<sub>254</sub> (Merck). Column chromatography was carried out with silica gel (200~400 mesh).

The <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on Varian Unity 400 NMR (400 M Hz). Chemical shifts were recorded in parts per million (  $\delta$  ), and splitting patters were designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants, J was reported in hertz (Hz). The residual proton signal of the solvent was used as an internal standard for spectra record in d-chloroform (  $\delta$  7.26 for <sup>1</sup>H,  $\delta$  77.0 for <sup>13</sup>C), CD<sub>3</sub>CN (  $\delta$  2.00 for <sup>1</sup>H). Electron impact mass spectra were obtain on VG-Quarttro. MALDI-TOF MS was recorded on a LDI-1700. The purity of I-Gn-(TMS)<sub>2n</sub> was found to be higher than 99% by HPLC on Gilson HPLC System. Elemental analyses were performed by the Elemental Analysensystem GmbH VarioEL. Infrared spectra were recorded on a Bio-Rad FTS135 FTIR. Infrared analysis of the polymer support was performed by placing the polymer beads between two KBr plates, swelling the beads by adding a drop of carbon tetrachloride and

immediately recording an FTIR spectrum.

**3,5-diiodo-4-ethoxyl-nitrobenzene (1).** A mixture of 2,6-diiodo-4-nitrophenol (31.28 g, 80 mmol) and potassium carbonate (6.072 g, 44 mmol) in acetone (100ml) was heated to 60°C at reflux under nitrogen for 30 min. Then iodoethane (149.76 g, 960 mmol) was added, and the mixture was stirred at this temperature for another 11h. The potassium iodide was filtered, the solvent was evaporated under reduced pressure, and the residue was washed with 0.5mol/L aqueous NaOH (6 x 500 mL) and water by suction filtration, dried under vacuum to give 3,5-diiodo-4-ethoxyl-nitrobenzene (1) as a light yellow powder (31.82 g, 95%yield).  $R_f = 0.83$  ( $\text{CH}_2\text{Cl}_2$ ); IR: 3083, 3069, 2981, 2924, 1777, 1574, 1558, 1515, 1426, 1385, 1342, 1243, 1122, 1012, 910, 898, 743, 737, 708, 670, 496  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.64 (s, 2H), 4.13 (q,  $J = 14$  Hz, 2H), 1.58 (t,  $J = 7.2$  Hz, 3H).

**3,5-Diiodo-4-ethoxyl-aniline (2).** A homogeneous solution of 3,5-diiodo-4-ethoxyl-nitrobenzene (33.2 g, 79.2 mmol) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (89.42 g, 396 mmol) in EtOH (190 mL) was heated at 70°C for ca. 100 min under nitrogen gas. Upon cooling, the solvent was removed by rotary evaporation under reduced pressure and the residue was diluted with excess 25% aqueous NaOH, the aqueous layer was extracted with ether (4 x 120 mL). The Organic extracts were washed with saturated aqueous brine, dried ( $\text{MgSO}_4$ ), filtered, and concentrated under reduced pressure to give a light yellow solide of analytically pure (2) (30.2 g, 98% yield):  $R_f = 0.45$  (1:1 dichloromethane/hexane); FT-IR: 3427, 3339, 2966, 2932, 2883, 1697, 1619, 1579, 1538, 1474, 1452, 1440, 1411, 1385, 1262, 1224, 1110, 1043, 1024, 912, 884, 848,

802, 710, 593, 545  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 (s, 2H), 3.95 (q,  $J=14$  Hz), 3.53 (br s, 2H), 1.48 (t,  $J=7.2$  Hz, 3H).

**(3,5-diiodo-4-ethoxyl) diazonium tetrafluoroborate (3).** A round-bottom flask was charged with  $\text{BF}_3 \cdot \text{OEt}_2$  (316 mmol, 40.1 mL) and cooled to  $-20^\circ\text{C}$ . Then 3,5-diiodo-4-ethoxyl-aniline (**2**, 30 g, 77.12 mmol in dry THF (155 mL) ) was added dropwise into the mixture to form a homogeneous solution. After stirring for 10 min, *tert*-butylnitrite (316.2 mmol, 37.91 mL) in dry THF (51.25 mL) was added dropwise using an addition funnel so as to maintain the temperature at  $-20^\circ\text{C}$ . After stirring for 30min, the reaction was warmed to  $5^\circ\text{C}$  and dry hexane (100mL) was added. The resulting diazonium tetrafluoroborate salt was isolated by suction filtration, washed with cold ether (100 mL), and dried in air to give 33.9g of title product **3** (90% yield). FT-IR: 3384, 3103, 3060, 2984, 2939, 2902, 2559, 2278, 1538, 1474, 1420, 1400, 1383, 1358, 1276, 1256, 1064, 1007, 901, 771, 717, 676, 587, 564, 522, 499, 452  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.92 (s, 2H), 4.34 (q,  $J=14$  Hz, 2H), 1.62 (t,  $J=7.2$  Hz, 3H).

**Procedure to Link (3) onto the polymer to give (4).** To a chilled ( $0^\circ\text{C}$ ) suspension of propylaminomethyl polystyrene: 1% divinylbenzene copolymer beads (24.28 g, 0.6736 mequiv/g of nitrogen, 200-400 mesh), potassium carbonate powder (5.88 g, 42.6 mmol), and DMF (170 mL) was added (3,5-diiodo-4-ethoxyl) diazonium tetrafluoroborate (**3**, 10.37 g, 21.3 mmol) in portions over 100 min, and reacting continued at  $0^\circ\text{C}$  for 2h. The suspension was transferred to a suction filter using DMF and washed sequentially with the solvents ( $3 \times 30$  mL/g of the polymer) MeOH,  $\text{H}_2\text{O}$ , MeOH, THF, MeOH, and dried in vacuum to a constant mass to give 30.24 g (0.503

mequiv/g ,93% yield). Elemental analyses . Found: C, 76.71; H, 7.40; N, 2.11; O, 0.805.

***P-GI-(TMS)<sub>2</sub> (5).*** A heavy-walled tube was filled with polymer (4), Pd(dba)<sub>2</sub> (0.05 equiv), copper (I) iodide (0.05 equiv), and triphenylphosphine (0.2 equiv), degassed, and back-filled with nitrogen three times. Then degassed triethylamine and THF (2:1, ca, 8 mL/g of the polymer) and (trimethylsilyl)-acetylene (2.2 equiv) were added. The contents were sealed and heated at 70°C for 48h with periodical stirring, Then the mixture was cooled, and washed with the solvents (3 x 30 mL/g of the polymer) methanol, DMF, dichloromethane, methanol, sodium diethyldithiocarbamate in DMF (550 mg of sodium diethyldithiocarbamate in 50 mL of DMF and 0.25 mL of *N,N*-diisopropylethylamine), dichloromethane, and methanol, and dried in vacuum to constant mass to give polymer beads (5): FT-IR (beads in CCl<sub>4</sub> between two KBr plates) 2157 cm<sup>-1</sup>; Elemental Analyse Found: C, 85.03; H, 8.16; N, 2.09; O, 0.80.

***Deprotection of resin-bound (trimethylsilyl)-acetylenes.*** To a suspension of resin-bound (trimethylsilyl) acetylene (1.0 equiv) and THF (9mL/g of polymer) was added a solution of tetrabutylammonium fluoride (1.0M in THF, 2 equiv). The suspension was stirred at room temperature under nitrogen for 30 min. The polymer was filtered, washed with THF, MeOH, CH<sub>2</sub>Cl<sub>2</sub>, and MeOH (3 x 30 mL/g of the polymer), and dried in vacuum to constant mass to give the resin-bound terminal acetylene as yellow polymer beads: FT-IR (beads in CCl<sub>4</sub> between two KBr plates) 3311, 2111cm<sup>-1</sup>.

***General Procedure for the Solid-supported Heck-Cassar-Sonogashira-Hagihara Reaction.*** A heavy-walled flask was charged with the resin-bound terminal acetylene

(1.0 equiv.), iodo-terminated monodendron (1.1 equiv. per acetylene), Pd (dba)<sub>2</sub> (0.05 equiv. per acetylene), copper (I) iodide (0.05 equiv. per acetylene), and triphenylphosphine (0.2 equiv. per acetylene), degassed, and back-filled with nitrogen three times. Degassed triethylamine and THF (2:1, ca, 9mL/g of the polymer) were added, and the contents was heated at 70°C for 48h with stirring. The suspension was cooled and washed with the solvents (3 × 30 mL/g of the polymer) methanol, DMF, dichloromethane, methanol, sodium diethyldithiocarbamate in DMF (550 mg of sodium diethyldithiocarbamate in 50mL of DMF and 0.25 mL of *N, N*-diisopropylethylamine), dichloromethane, and methanol, and dried in vacuum to constant mass to give the resin-bound terminal (trimethylsilyl) acetylenes as golden polymer beads : FT-IR (beads in CCl<sub>4</sub> between two KBr plates) 2156 cm<sup>-1</sup>.

***General Procedure for Deprotection of the Triazene Linkage from the Solid Support.***

A heavy-walled tube was charged with monodendron-attached polymeric beads, and iodomethane was added to wet the polymer (ca. 9mL/g of the polymer). The contents was degassed and back-filled with nitrogen, sealed, and heated to 110°C. After 48h at this temperature the reaction mixture was cooled, and the excess iodomethane was removed under reduced pressure. The monodendron product was extracted from the crude polymer by refluxing in dichloromethane for 30min and filtering. The residue was washed with dichloromethane, and the washing were combined and concentrated. The monodendron was purified by column chromatography.

***I-G1-(TMS)<sub>2</sub>*** : FT-IR 2959, 2899, 2156, 1559, 1477, 1442, 1385, 1249, 1002, 843, 759, 700, 651 cm<sup>-1</sup> ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 7.67 (s, 2H), 4.24 (q, J=14

Hz, 2H), 1.41 (t,  $J=7.2$  Hz, 3H), 0.24 (s, 18H); EI-MS. Calcd. for  $[M]^+$  : m/e 440.

Found: m/e 440.

**I-G2-(TMS)<sub>4</sub>**: FT-IR 2959, 2899, 2217, 2156, 1561, 1478, 1447, 1384, 1249, 1033, 1006, 843, 759, 698, 649  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.71 (s, 2H), 7.52 (s, 4H), 4.33 (overlapping q,  $J=14$  Hz, 6H), 1.46 (overlapping t,  $J=7.2$  Hz, 9H), 0.26 (s, 36H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 162.08, 160.78, 141.59, 136.62, 119.81, 118.22, 117.99, 99.87, 99.79, 92.93, 85.31, 84.08, 70.31, 69.95, 15.94, 15.76, -0.221; EI-MS . Calcd. for  $[M]^+$  : m/e 920. Found: m/e 919.

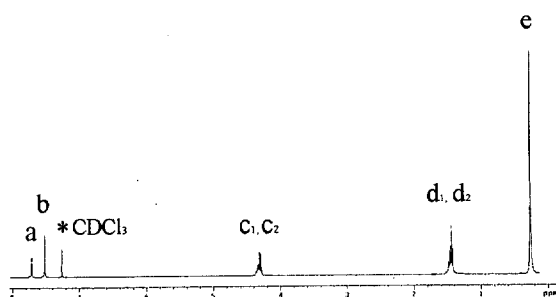
**I-G4-(TMS)<sub>16</sub>**: FT-IR 2960, 2898, 2216, 2156, 1588, 1558, 1478, 1446, 1384, 1249, 1104, 1034, 1008, 842, 758, 698, 649, 615  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.81 (s, 2H), 7.64 (s, 4H), 7.60 (s, 8H), 7.56 (s, 16H), 4.37 (overlapping q,  $J=14$  Hz, 30H), 1.50 (overlapping t,  $J=7.2$  Hz, 45H), 0.265 (s, 144H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 162.06, 161.06, 146.60, 136.67, 136.30, 118.23, 99.86, 92.41, 84.78, 70.38, 69.97, 29.66, 16.00, 15.77, -0.213; MALDI-TOF MS: Calcd for  $[M]^+$  :m/e 3805.7. Found: m/e 3804.4.

**Fc-Gn-(TMS)<sub>2n</sub>**. A heavy-walled flask was charged with **I-Gn-(TMS)<sub>2</sub>**<sup>n</sup>, ferrocene acetylene<sup>[1]</sup> (1.2 equiv.),  $\text{Pd}(\text{dba})_2$  (0.05 equiv.), copper (I) iodide (0.05 equiv.), and triphenylphosphine (0.2 equiv.), degassed, and back-filled with nitrogen three times, Degassed triethylamine and THF (1:1) were added, and the contents was heated at 50 °C for 36h with stirring. The solvent was then removed by rotary evaporation under reduced pressure, the residue was purified by column chromatography to give Fc-Gn-( $\text{SiMe}_3$ )<sub>2n</sub> (n=1, 2, 4) as yellow crystal powders.

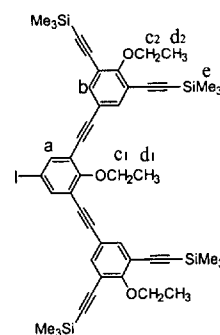
***Fc-G1-(TMS)<sub>2</sub>***. FT-IR 2960, 2927, 2899, 2218, 2160, 1559, 1442, 1248, 1104, 1027, 1005, 845, 804, 759, 702, 648, 495, 483 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 7.49 (s, 2H), 4.55 (t, J=1.6 Hz, 2H), 4.28 (q, J=14 Hz, 2H), 4.26-4.22 (m, 7H), 1.43 (t, J=7.2 Hz, 3H), 0.251 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 161.27, 136.47, 119.30, 118.07, 100.15, 99.45, 88.58, 83.82, 71.41, 69.98, 69.90, 68.86, 64.91, 29.68, 15.76, -0.160 ppm; EI-MS calcd. for [M]<sup>+</sup> : m/e 522. Found: m/e 522.

***Fc-G2-(TMS)<sub>4</sub>***. FT-IR 2960, 2927, 2899, 2160, 1559, 1444, 1249, 1034, 1005, 845, 759, 693, 648, 520 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (overlapping s, 6H), 4.50 (d, J=1.6 Hz, 2H), 4.41-4.23 (m, 13H), 1.51-1.43 (overlapping t, J=7.2 Hz, 9H), 0.262 (s, 36H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.98, 136.66, 136.14, 118.31, 118.21, 117.97, 99.84, 92.07, 85.00, 71.43, 70.33, 70.00, 69.75, 68.91, 29.68, 16.00, 15.79, -0.190; EI-MS . calcd for [M]<sup>+</sup> : m/e 1002. Found: m/e 1002.

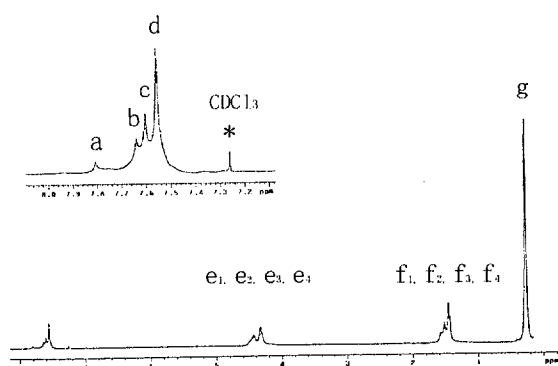
***Fc-G4-(TMS)<sub>16</sub>***. FT-IR 2960, 2898, 2216, 2155, 1588, 1560, 1479, 1446, 1384, 1359, 1249, 1095, 1034, 1007, 884, 845, 759, 693, 649, 616, 520 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.50 (overlapping s, 30H), 4.52 (m, 39H), 1.50 (overlapping t, J=7.2 Hz, 9H), 1.44 (overlapping t, J=6.8 Hz, 36H), 0.251 (s, 144H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.07, 161.07, 136.69, 136.29, 118.23, 99.88, 92.41, 84.81, 71.45, 70.39, 69.99, 68.91, 16.01, 15.79, -0.198; MALDI-TOF MS: calcd. for [M]<sup>+</sup> : m/e 3887.7 Found: m/e 3888.3.



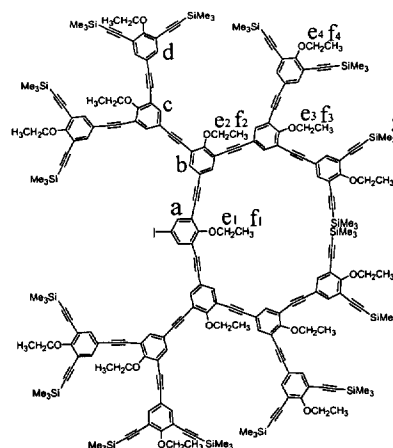
$^1\text{H}$  NMR spectra of **I-G2-(TMS)<sub>4</sub>**



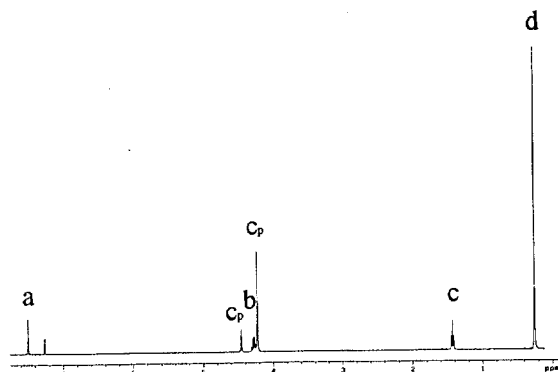
**I-G2-(TMS)<sub>4</sub>**



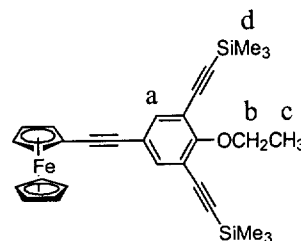
$^1\text{H}$  NMR spectra of **I-G4-(TMS)<sub>16</sub>**



**I-G4-(TMS)<sub>16</sub>**

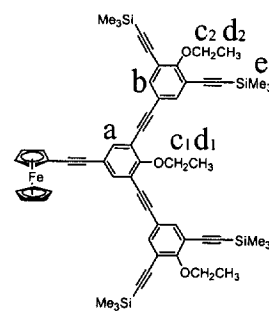


$^1\text{H}$  NMR spectra of **Fc-G1-(TMS)<sub>2</sub>**

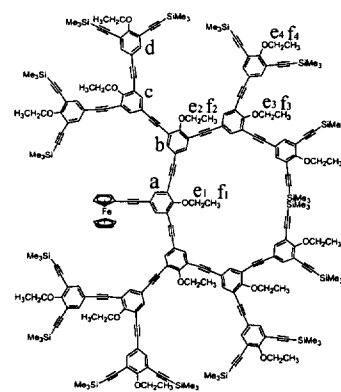


**Fc-G1-(TMS)<sub>2</sub>**

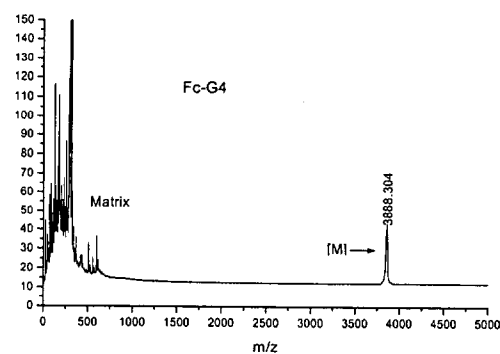


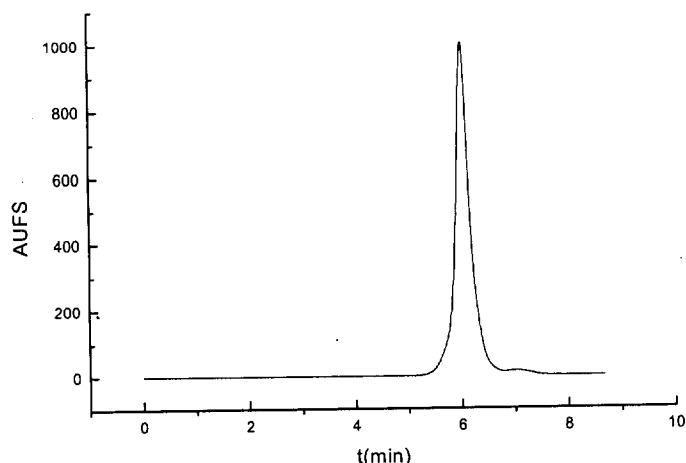


**Fc-G2-(TMS)<sub>4</sub>**



**Fc-G4-(TMS)<sub>16</sub>**





**Fig.3** HPLC trace of **I-G4-(TMS)<sub>16</sub>** (RT: 6.035 min, purity: 99.35%)

Gilson HPLC System; 306 pump, 117UV detector,  $\lambda = 254\text{nm}$ , 0.01 AUFS;  
 Column: Hypersil, C18,  $5\ \mu\text{m}$ ,  $250 \times 4.6\text{mmid}$ ; mobile phase: 100% THF, flow rate:  
 0.4ml/min.

## II. Electrochemical Experiments.

### 1. Apparatus.

Electrochemical experiments were carried out on CHI660A Electrochemical Workstation. Three-electrode cell was employed with a Pt wire as counter electrode, AgCl/Ag in saturated KCl (aq.) as reference electrode and polycrystalline gold wire (1.0 mm-diameter) sealed in Teflon as working electrode. The gold working electrodes were consecutively polished with 1.0, 0.6, and  $0.3\ \mu\text{m}$  alumina powder, rinsed with water and sonicated for 10 min in third distilled water after each polishing, followed by cyclic voltammetry scanning in 1.0 M  $\text{H}_2\text{SO}_4$  between  $-0.1$  and  $+1.5\ \text{V}$  at a scanning rate of  $0.1\ \text{V/s}$  until a characteristic cyclic voltammogram was found. The real area of gold electrode was determined from the cathodic peak area<sup>[2]</sup>. All

electrochemical experiments were carried out in argon atmosphere. Analytes were dissolved in water-free dichloromethane which contained 0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte to form 1.0 mM solution.

## 2. Chronoamperometry.

Chronoamperometry was used to determine the diffusion coefficient ( $D_0$ ). A Pulse width of 500 ms and a potential step height of 800mv centered around  $E_{1/2}$  for each molecule was chosen so as to obtain good Cottrell plots. Linear portion of Cottrell plot were fit using the following Cottrell equation to yield the reported diffusion coefficient for each analyte:  $I(t) = nFAD_0^{1/2}C_0 * (\pi t)^{1/2}$ . The experiment  $I(t) \sim t$  curves was shown in Fig. 3.

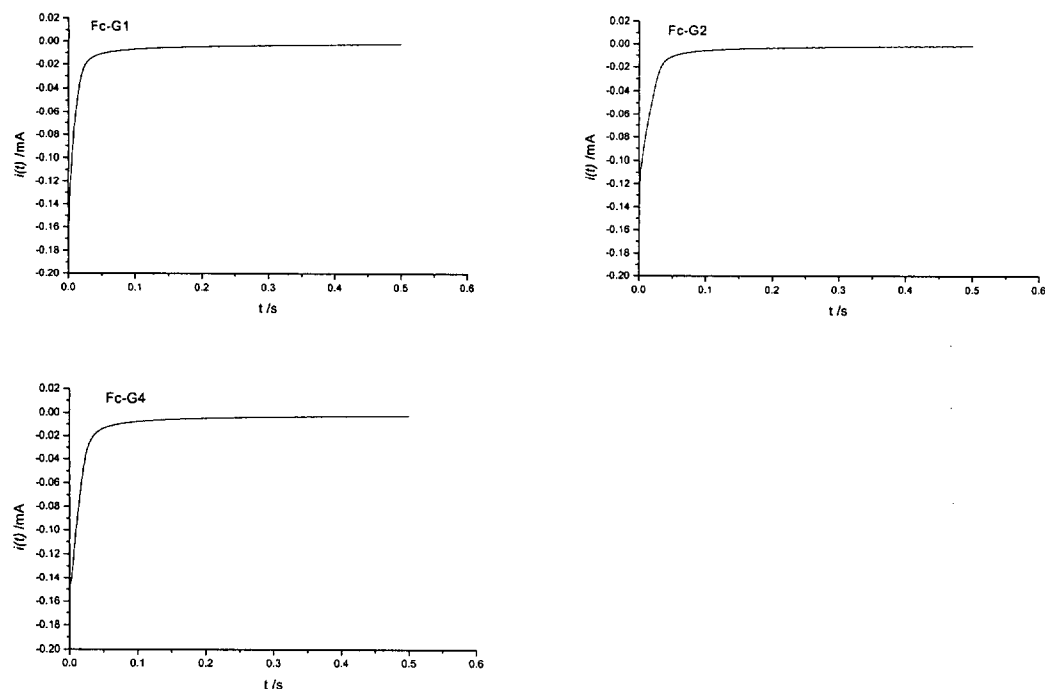


Fig. 3. Chronoamperometry plots of Fc-G1, Fc-G2, and Fc-G4.

## Reference:

[1] Wu, J. S.; Chi, C. Y.; Wang, X. H.; Zhao, X. J.; Li, J.; Wang, F. S. "A One-Pot Procedure to Prepare Ferrocenylethynylenes and Iodoferrocenylethynylenes". submitted to *Synth. Commun.* for publication.

[2] Gopez, M. M.; Vazquez, L.; Salvarezza, R. C.; Vam, J. M. *J. Electroanal. Chem.*

**1999**, 317, 125.