Electronic Supplementary Information

Orthogonal bis(terpyridine)-Fe(II) metal complex oligomer wires on a tripodal scaffold: Rapid electron transport

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Materials.

Trichlorosilane, 2-acetylpyridine, 4-bromobenzaldehyde and acetyl chloride were purchased from TCI. Aluminum chloride, 3-bromothiophenol, ethylene glycol, boron tribromide in CH₂Cl₂, Sodium hydrogen carbonate and sodium sulfate were purchased from Wako Chemicals. N-Butyl lithium, 2-chloro-2-methylpropane, 4-toluenesulfonic acid monohydrate, potassium hydroxide and ammonia aqueous solution and all of HPLC grade solvents (CHCl₃, CH₂Cl₂, and EtOH) were purchased from Kanto Chemicals. **L**_H and Iron(II) tetrafluoroborate hexahydrate were purchased from Aldrich. Magnesium was purchased from Nakalai tesque. All regents were used as received. Hexane (Kanto Chemicals), ethyl acetate (Yamaichi), methanol (Godo) and dichroromethane for column chromatography (AGC) were purchased from commercial source and used as received. Water was purified by passage through a Milli-Q purification system (Millipore). The dehydrated solvents for syntheses were purchased from Kanto Chemicals, and purified by organic solvent purifier (Nikko Hansen). For NMR measurement, chloroform-d1 99.8 atom% D containing 0.03 v/v% tetramethylsilane as an internal standard was purchased from Acros Organics. **T**¹¹ and 2-(4-Bromophenyl)-1,3-dioxolane **5**² were synthesized according to previous literatures.

Syntheses.



Synthesis of 3-bromo-tert-butylthiobenzene (2).

Under a nitrogen atmosphere, 3-bromothiophenol **1** (6.0 mL, 58 mmol) was added to a stirred solution of aluminum chloride (0.32 g, 2.4 mmol) in 2-chloro-2-methylpropane (30 mL). After stirring for 6 h, water was poured to the mixture to quench the reaction. The solution was extracted by dichloromethane and the organic layer was dried over Na₂SO₄. After the solvent was removed, the residue was purified by silica column chromatography, eluting with hexane. The product was obtained as yellow liquid. Yield: 13 g (53 mmol, 92%) ¹H NMR (400 MHz, CDCl₃) : δ 7.70 (1H, t, J=2.0 Hz), 7.50 (1H, dq , J=8.0, 0.98 Hz), 7.46 (1H, dq, J=7.8, 1.2 Hz), 7.22 (1H, t, J=3.7 Hz),

1.30 (9H,s).

Synthesis of tris(3-*tert*-butylthiophenyl)silane (3).

Under a nitrogen atmosphere, magnesium tunings (1.1 g, 47 mmol) was mashed, and added dry diethyl ether (70 mL) and a piece of iodine. Then **2** (9.9 g, 40 mmol) in diethyl ether (50 mL) was added dropwise to the stirring solution for 1 h. Then the mixture was heated to 50°C and stirred for 5 h. Then trichlorosilane (1.5 mL, 15 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. Then the solution was allowed to cool to room temperature. After the mixture was stirred for 13 h, the precipitation and remaining magnesium was removed by filtration, and water was poured to the mixture to quench the reaction. The solution was removed by dichloromethane and the organic layer was dried over Na₂SO₄. After the solvent was removed, the residue was purified by silica column chromatography, eluting with hexane/dichloromethane (4:1 v/v). The product was obtained as colorless oil. Yield : 3.9 g (7.5 mmol, 56 %) ¹H NMR (400 MHz, CDCl₃) : δ 7.71 (3H,s), 7.60 (3H, dt, J=7.6, 1.2 Hz), 7.54 (3H, dt, J=7.3, 1.2 Hz), 7.35 (3H, t, J=7.6 Hz), 5.47 (1H, s), 1.24 (27H, s), FAB-MS(m/z) 524.

<u>Synthesis of 4-(tris(3-*tert*-butylthiophenyl)silylphenyl)-1,3-dioxolane (6)</u>.

Under a nitrogen atmosphere, "BuLi (1.6 M in hexane, 4.7 mL, 7.7 mmol) was added dropwise to the stirred solution of **5** (1.6 g, 7.4 mmol) in dry THF (50 mL) at -78°C. After stirring for 4 h, **3** (3.3 g, 6.4 mmol) in dry THF (50 mL) was added dropwise to the reaction mixture for 20 min. Then the solution was allowed to warm to room temperature. After stirring for 15 h, water was poured to the mixture to quench the reaction. The solution was extracted by dichloromethane and the organic layer was dried over Na₂SO₄. After the solvent was removed, the residue was purified by silica gel column chromatography, eluting with hexane/dichloromethane (2:1 v/v). The product was obtained as colorless oil. Yield : 2.8 g (4.2 mmol, 66 %) ¹H NMR (400 MHz, CDCl₃) : δ 7.71(3H, s), 7.60 (2H, dt, J=7.8 Hz, 1.5 Hz), 7.52-7.48 (6H, m), 7.33 (3H, t, J=7.3 Hz), 5.84 (1H, s), 4.16-4.03 (4H, m), 1.22 (27H, s), FAB-MS(m/z) 673.

Synthesis of 4-(tris(3-tert-buthylthiophenyl)silylphenyl)aldehyde (7).

6 (2.6 g, 3.8 mmol) was dissolved in the mixture of THF (50 mL) and water (5 mL) and 4-toluenesulfonic acid monohydrate (0.71 g, 3.7 mmol) was added to the stirred solution. After stirring for 15 h, saturated solution of NaHCO₃ aq. was added to the reaction solution to quench the reaction. The solution was extracted by dichloromethane and the organic layer was dried over Na₂SO₄. After the solvent was removed, the residue was purified by silica gel column chromatography, eluting with hexane/ethyl acetate (4:1 v/v). The product was obtained as colorless oil. Yield : 2.2 g (3.6 mmol, 92 %) ¹H NMR (400 MHz, CDCl₃) : δ 10.06 (1H, s), 7.87 (2H, d, J=8.1 Hz), 7.73 (2H, d, J=8.1 Hz), 7.70 (3H, s), 7.64 (3H, dt, J=7.8, 1.4 Hz), 7.51 (3H, dt, J=7.3, 1.1 Hz), 7.37 (3H, t, J=7.4 Hz), 1.23 (27H, s), FAB-MS(m/z) 673.

Synthesis of 4-(4-(tris(3-tert-buthylthiophenyl))silylphenyl)-2,2':6',2-terpyridine (8).

7 (1.5 g, 2.4 mmol), 2-acetylpyridine (0.80 mL, 7.0 mmol) and potassium hydroxide (0.40 g, 7.2 mmol) were dissolved in the mixture of methanol (25 mL), dichloromethane (25 mL) and 30 % NH₃ aq (12 mL). The mixture was stirred for 41 h. Then water was poured to the mixture. The solution was extracted by dichloromethane and the organic layer was dried over Na₂SO₄. After the solvent was removed, the residue was purified by alumina column chromatography, eluting with hexane/dichloromethane (4:1 v/v) twice. The product was obtained as white oil. Yield : 0.46 g (0.55 mmol, 23 %) ¹H NMR (400 MHz, CDCl₃) : δ 8.75 (2H,s), 8.73 (2H, d, J=3.9 Hz), 8.68 (2H, d, J=8.1 Hz), 7.92-7.87 (4H, m), 7.76 (3H,s), 7.70 (2H, d, J=8.3 Hz), 7.63 (3H, dt, J=7.7, 1.5 Hz), 7.56 (3H, dt, J=6.3, 1.2 Hz), 7.39-7.34 (5H, m), 1.25 (27H, s), FAB-MS(m/z) 832.

<u>Synthesis of 4-(4-(tris(3-acetylthiophenyl))silylphenyl)-2,2':6',2-terpyridine (A_T -Ac).</u>

Under a nitrogen atmosphere, acetyl chloride (0.60 mL, 8.4 mmol) and 1 M boron tribromide in dichloromethane (0.80 mL, 0.80 mmol) were added to the stirred solution of **8** (0.15 g, 0.18 mmol) in dry toluene. After stirring for 6 h, cool water was poured to the mixture to quench the reaction. The solution was extracted by dichloromethane and the organic layer was dried over Na₂SO₄. After the solvent was removed, the residue was purified by flush short alumina column chromatography, eluting with hexane/dichloromethane (1:1 v/v) and recrystalization from hexane/dichloromethane. The product was obtained as pale yellow solid. Yield : 78 mg (0.099 mmol, 54 %) ¹H NMR (400 MHz, CDCl₃) : δ 8.76 (2H, s), 8.73 (2H, d, J=4.2 Hz), 8.68 (2H, d, J=7.8 Hz), 7.94 (2H, d, J=8.1 Hz), 7.89 (2H, dt, J=1.6 Hz, 7.7 Hz), 7.72 (2H, d, J=8.0 Hz), 7.62-7.60 (6H, m), 7.53 (3H, d, J=7.8 Hz), 7.48 (3H, t, J=7.4 Hz), 7.36 (2H, dd, J=4.9, 6.4 Hz), 2.41 (9H, s), FAB-MS(m/z) 790.

Preparation of SAMs of A_T.

Au/mica plates, where gold (100-nm thickness) was deposited on natural mica, were used for the preparation and measurement of SAMs of A_T . The Au/mica plate was annealed with hydrogen flame just before use. The SAM of A_T was prepared by immersion of the Au/mica plate into a chloroform solution of A_T -Ac (0.1 mM) at 25°C, followed by rinsing with chloroform and drying with nitrogen blow. The immersion time was optimized to be 3 days (Fig. 1c) so that all S atoms of A_T were bound chemically to the Au(111) surface.

Preparation of bis(terpyridine)-Fe(II) oligomer wires on the SAM of AT.

The bis(terpyridine)-Fe(II) complex wire on the SAM of A_T was constructed in three steps (Scheme 1a). The first step was the attachment of Fe(II) ions to the terpyridine terminus of the SAM of A_T . The typical procedure is as follows: The terpyridine-terminated Au/mica plate was immersed into a solution of Fe(BF₄)₂ (0.1 M) in ethanol for 1 h. After the immersion, the modified substrate was washed with ethanol and water, and dried by nitrogen blow. The second step was involved in the completion of the bis(terpyridine)-Fe(II) complex motif: The Fe(II)-terminated substrate was

immersed in a chloroform solution of L_H (0.1 mM) overnight, which was then washed with chloroform and dried over nitrogen blow. The two processes were repeated *n* times so that *n*-layer wire Au-[A_T(FeL_H)_n] was constructed. The third step was optional: Ferrocene-teminated wire Au-[A_T(FeL_H)_{n-1}FeT¹] was prepared by the immersion of the Fe(II)-terminated substrate into T¹ in chloroform (0.1 mM) overnight.

Electrochemical measurements.

Electrochemical measurements were carried out using the Au/mica substrate modified with the bis(terpyridine)-Fe(II) oligomer wire (electrode area: 0.264 cm²) as a working electrode, a Pt-wire as a counter electrode, and an Ag/Ag⁺ (10 mM AgClO₄ in 0.1 M Bu₄NClO₄-MeCN) reference electrode in a standard one-compartment cell. Cyclic voltammetry and potential-step chronoamperometry (PSCA) were performed using either ALS 750A or ALS 650B electrochemical analyzer. All experiments were carried out in 1 M Bu₄NClO₄-CH₂Cl₂ under an Ar atmosphere. Ferrocene was used as an internal standard. In the PSCA experiment for Au-[A_T(FeL_H)_{*n*-1}FeT¹], the working electrode potential was first kept -0.40 V from the formal potential (\mathcal{E}^{0}) of the terminal redox site (ferrocene), then a potential step to $\mathcal{E}^{0'}$ +0.40 V was applied to observe the oxidation current of the ferrocene. In the case of Au-[A²(FeL_H)_{*n*-1}FeT¹], the electrode potential was first kept at $\mathcal{E}^{0'}$ -0.20 V. The first-order interfacial electron-transfer rate constant, k_{et} , was estimated using the equation, λ (t) = $\hat{P}\exp(-k_{et}\hat{\tau})$. More than four films were prepared in the same condition, so that the average values and standard deviations were obtained. The error bar in Fig. 6 show the standard deviation.

Molecular modeling of Au-[A_T (FeL_H)_n] (n = 5 and 40).

The distance between the redox site and electrode was calculated by molecular modeling with DFT calculation at the B3LYP/6-31g(d)-LanL2DZ level (6-31g(d) for C, H, N, and LanL2DZ for Fe).

X-ray photoelectron spectroscopy.

X-ray photoelectron spectra were measured with PHI5000 VersaProbe (ULVAC-PHI). Monochromatic Al K_{α} (20 kV, 100 W) was used as the X-ray source. Exit angle was set to 45°. All spectra were calibrated according to the peak for Au 4f_{7/2} at 83.8 eV.

SPM measurement.

AFM and STM measurements were conducted using Aglient 5500 under an ambient condition. AFM was performed in the high amplitude mode (trapping mode) with a silicon cantilever PPP-NCL (Nano World). Probes for STM (Pt-Ir alloy, 4:1, 0.25 mm) were cut off using a nipper to get a sharp edge.

Molecular modeling.

DFT calculation using the B3LYP functional and the 6-31g(d) basis set was conducted. Gaussian 09W Revision-A.02 was implemented.

Other apparatus.

¹H NMR spectra were acquired using JEOL AL-400. FAB mass spectroscopy (HRMS) was carried out using JEOL JMS-700P (matrix: polyethyleneglycol). SEM images were collected using JEOL JSM-7400FNT. IR spectra were recorded using Shimadzu IRPrestige-21.



Fig. S1 (a) IR spectrum of A_T-Ac in a KBr pellet. (b) IR-ATR spectrum of a SAM of A_T on a gold substrate (immersion time: 3 days). (c) IR-ATR spectrum of a bare gold substrate.



Wire height = $1.6 + 1.61 \times n$ (nm)

Au-**[A_T(FeL_H)**₅] = 9.65 nm Au-**[A_T(FeL_H)**₄₀] = 66 nm

Fig. S2 Molecular modelling of $\operatorname{Au}[\mathbf{A}_{T}(\mathbf{FeL}_{H})_{n}]$ (n = 5 and 40).



Fig. S3 Current (*i*) – time (*t*) and (b) $\ln i - t$ plots for Au-[**A**_T(**FeL**_H)_{*n*-1}**FeT**¹] [(a,b) n = 1; (c,d) n = 2; (e,f) n = 3; (g,h) n = 4].



Fig. S4 Current (*i*) – time (*t*) and (b) ln *i* - *t* plots for Au-[$A^{2}(FeL_{H})_{n-1}FeT^{1}$] [(a,b) n = 1; (c,d) n = 2; (e,f) n = 3].

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