Supporting Information

Electron Transport Dynamics in Redox-Molecule-Terminated Branched Oligomer Wires on Au(111)

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S1 Preparation of Fe(tpy)₂ oligomer wires

Au/mica plates (gold with a thickness of 100 nm was deposited on natural mica) were used as substrates. HPLC-grade ethanol and chloroform were used as solvents. Prior to use, the gold surface was annealed with a hydrogen flame. This treatment gave a Au(111) surface.

Branched wire Au- $[A_H(FeL)_{n+1}]$ was prepared as follows (Figure 1c). An annealed Au/mica plate was first immersed in a solution of phenyl disulfide (1 mM) in chloroform for 5 h, followed by rinsing in chloroform and drying by a nitrogen blow. Next, in order to implant anchor terpyridine ligand molecule (A_H) on the electrode surface sparsely, the modified plate was immersed in a 0.02 mM chloroform solution of $(A_H)_2$ for 5 min, followed by rinsing in chloroform and drying by a nitrogen blow: This process afforded a thiol exchange reaction. In order to attach Fe^{2+} ions, the tpy-terminated surface was immersed in a 0.1 M ethanol solution of $Fe(BF_4)_2$ for 1 h, washed in water and ethanol, and dried by a nitrogen blow. The metal-terminated surface was then immersed in a chloroform solution of L (0.1 mM) overnight to complete the bis(terpyridine)-iron(II) complex motif, followed by washing with chloroform and drying by a nitrogen flow. The last two processes (immersion in a Fe^{2+} ion solution and a L solution) were repeated n+1 times for the preparation of Au- $[A_H(FeL)_{n+1}]$. Au- $[A_H(FeL)_nFeT]$ was prepared using Au- $[A_H(FeL)_n]$ as a scaffold (Figure 1c). The modified electrode was immersed in a 0.1 M ethanol solution of Fe(BF₄)₂ for 1 h, washed in water and ethanol, and dried over a nitrogen blow. The final step was an immersion in a 0.5 mM chloroform solution of T for overnight, followed by washing in chloroform, and drying over a nitrogen blow.

Au- $[A_H(FeL_L)_nFeT]$ (linear wires) was also fabricated using the same method as Au- $[A_H(FeL)_nFeT]$ shown in Figure S1, except that trident bridging ligand L was replaced with two-way bridging ligand L_L .²²⁻²⁵



Figure S1. Stepwise coordination method for the preparation of Au-[A_H(FeL_L)_nFeT].

S2 Surface coverages of $Au-[A_H(FeL)_{n+1}]$



Figure S2. Surface coverages of the $Fe(tpy)_2$ unit in $Au-[A_H(FeL)_{n+1}]$. The dotted line shows the ideal surface coverage, proportional to $2^{n+1}-1$.

S3 Parameters used in the simulation of PSCA, and the other sets of experimental and simulated current-time plots for $Au-[A_H(FeL)_nFeT]$ and $Au-[A_H(FeL_L)_nFeT]$



Figure S3. Other sets of experimental $(i_{exp}-t)$ and simulated $(i_{sim}-t)$ current-time plots for Au-[**A**_H(**FeL**)₁**FeT**]. Legend. Blue solid line: i_{exp} for oxidation with an overpotential of +0.35 V for the ferrocene moiety; red solid line: i_{exp} for reduction with -0.35 V; black dashed line: electric double layer charging current i_{DL} ; green solid line: faradaic current i_F ; orange circles; i_{sim} for the oxidation; light-blue circles: i_{sim} for the reduction.

		k_1 / s^{-1}	<i>k</i> ₋₁ / s ⁻¹	<i>k</i> ₂ , <i>k</i> ₋₂ / s ⁻¹	k ₃ / s ⁻¹	<i>k</i> ₋₃ / s ⁻¹	C_{DL} / μF	α
Sample 1	oxidation	343	4000	17700	4750	18	4.00	0.6
(in the body)	reduction	0	1800	17700	4750	238	5.03	0.6
Sample 2	oxidation	300	4460	17500	4730	90	3.50	0.71
	reduction	32	2220	17500	4730	126	2.81	0.71
Sample 3	oxidation	355	4740	17800	3090	101	4.00	0.63
	reduction	2	1570	17800	3090	19	6.88	0.63

Table S1. Parameters used in the simulation of PSCAs for $Au-[A_H(FeL)_1FeT]$. Sample 1 corresponds to the data represented in the body. The three samples were fabricated independently.



Figure S4. Other sets of experimental $(i_{exp}-t)$ and simulated $(i_{sim}-t)$ current-time plots for Au-[**A**_H(**FeL**)₂**FeT**]. Legend. Blue solid line: i_{exp} for oxidation with an overpotential of +0.35 V for the ferrocene moiety; red solid line: i_{exp} for reduction with -0.35 V; black dashed line: electric double layer charging current i_{DL} ; green solid line: faradaic current i_{F} ; orange circles; i_{sim} for the oxidation; light-blue circles: i_{sim} for the reduction.

Table S2. Parameters used in the simulation of PSCAs for $Au-[A_H(FeL)_2FeT]$. Sample 1 corresponds to
the data represented in the body. The three samples were fabricated independently.

		<i>k</i> ₁ / _s ⁻¹	<i>k</i> ₋₁ / _s ⁻¹	$k_2, k_{-2} / s^{-1}$	<i>k</i> ₃ / _s ⁻¹	<i>k</i> ₋₃ / _s ⁻¹	C _{DL} / μF	α
Sample 1	oxidation	308	3230	17300	5180	132	3.14	0.68
(in the body)	reduction	0.00196	4400	17300	5180	31	4.69	0.68
Sample 2	oxidation	164	3650	16900	3170	15	3.60	0.71
	reduction	0	3230	16900	3170	34	2.55	0.71
Sample 3	oxidation	206	3200	17100	5410	21	3.64	0.94
	reduction	0	4310	17100	5410	128	3.53	0.94



Figure S5. Other sets of experimental $(i_{exp}-t)$ and simulated $(i_{sim}-t)$ current-time plots for Au-[**A**_H(**FeL**)₃**FeT**]. Legend. Blue solid line: i_{exp} for oxidation with an overpotential of +0.35 V for the ferrocene moiety; red solid line: i_{exp} for reduction with -0.35 V; black dashed line: electric double layer charging current i_{DL} ; green solid line: faradaic current i_{F} ; orange circles; i_{sim} for the oxidation; light-blue circles: i_{sim} for the reduction.

		<i>k</i> ₁ / _s ⁻¹	<i>k</i> ₋₁ / s ⁻¹	$k_2, k_{-2} / s^{-1}$	<i>k</i> ₃ / s ⁻¹	<i>k</i> ₋₃ / s ⁻¹	C _{DL} / μF	α
Sample 1	oxidation	208	5000	17900	5210	17	3.99	0.83
(in the body)	reduction	10	5030	17900	5210	5	4.03	0.83
Sample 2	oxidation	163	3600	18500	6080	41	3.70	0.45
	reduction	1	2550	18500	6080	15	3.39	0.45
Sample 3	oxidation	151	3790	18100	6210	33	3.76	0.46
	reduction	2	1460	18100	6210	20	3.51	0.46

Table S3. Parameters used in the simulation of PSCAs for $Au-[A_H(FeL)_3FeT]$. Sample 1 corresponds to the data represented in the body. The three samples were fabricated independently.



Figure S6. Other sets of experimental $(i_{exp}-t)$ and simulated $(i_{sim}-t)$ current-time plots for Au-[**A**_H(**FeL**_L)₁**FeT**]. Legend. Blue solid line: i_{exp} for oxidation with an overpotential of +0.35 V for the ferrocene moiety; red solid line: i_{exp} for reduction with -0.35 V; black dashed line: electric double layer charging current i_{DL} ; green solid line: faradaic current i_F ; orange circles; i_{sim} for the oxidation; light-blue circles: i_{sim} for the reduction.

		k_1 / s^{-1}	<i>k</i> ₋₁ / s ⁻¹	$k_2, k_{-2} / s^{-1}$	k_3 / s^{-1}	<i>k</i> ₋₃ / _s ⁻¹	C_{DL} / μF	α
Sample 1	oxidation	320	4010	16800	5560	31	3.70	0.47
(in the body)	reduction	0	1300	16800	5560	63	3.70	0.47
Sample 2	oxidation	227	3130	17200	3390	10	4.00	0.49
	reduction	18	1400	17200	3390	114	4.00	0.49
Sample 3	oxidation	202	3990	17800	4000	0	4.00	0.48
	reduction	11	2100	17800	4000	132	4.00	0.48

Table S4. Parameters used in the simulation of PSCAs for $Au-[A_H(FeL_L)_1FeT]$. Sample 1 corresponds to the data represented in the body. The three samples were fabricated independently.



Figure S7. Other sets of experimental $(i_{exp}-t)$ and simulated $(i_{sim}-t)$ current-time plots for Au-[**A**_H(**FeL**_L)₂**FeT**]. Legend. Blue solid line: i_{exp} for oxidation with an overpotential of +0.35 V for the ferrocene moiety; red solid line: i_{exp} for reduction with -0.35 V; black dashed line: electric double layer charging current i_{DL} ; green solid line: faradaic current i_{F} ; orange circles; i_{sim} for the oxidation; light-blue circles: i_{sim} for the reduction.

Table S5. Parameters used in t	he simulation of PSCA	s for Au–[A _H (FeL	$_{L})_{2}$ FeT]. Sample 1	corresponds to
the data represented in the body	. The three samples we	re fabricated indep	endently.	

		<i>k</i> ₁ / _s ⁻¹	<i>k</i> ₋₁ / _s ⁻¹	$k_2, k_{-2} / s^{-1}$	<i>k</i> ₃ / _s ⁻¹	<i>k</i> ₋₃ / _s ⁻¹	C _{DL} / μF	α
Sample 1	oxidation	212	5020	16500	5530	14	4.00	0.89
(in the body)	reduction	3	1790	16500	5530	128	4.00	0.89
Sample 2	oxidation	162	4270	17300	4270	34	4.00	1
482	reduction	7	1480	17250	3790	68	4.00	1
Sample 3	oxidation	239	5500	16500	4700	0	4.40	0.48
483	reduction	0	1870	16500	4700	115	4.40	0.48