Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Reliable I/V Characteristics and Long Lifetime of Porphyrin-Based Single-Molecule Junctions

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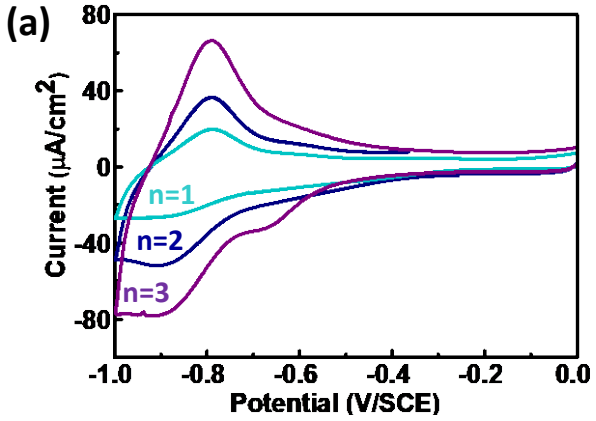
1. Electrochemical grafting on Au and thickness



(b)

Integration Range	Γ(mol·cm^{-2})	Number of Co(porphyrin)
-0.6-(-1.0)	(5.5±1.0)×10^{-10}	n=1-2
	(10.2±1.0)×10^{-10}	n=2-3
	(15.7±1.0)×10^{-10}	n=3-4
-0.8-(-1.0)	(3.8±1.0)×10^{-10}	n~1
	(7.0±1.0)×10^{-10}	n=1-2
	(12.4±1.0)×10^{-10}	n=2-3

Figure S1. (a) Electroactivity (CV) of diamino-CoTPP layers with different thickness in 0.1 M solution of $TBAPF_6$ in acetonitrile with scan rate 0.1 V/s; (b) Calculated surface coverage Γ in different integration range and the number of Co(porphyrin) monomers in grafted layers.

The oligo(porphyrin) were grafted, as free base [TPP]n or Co complexes [CoTPP]n (n=1-3), with controlled thickness on flat gold substrates deposited on Si/SiO_2 wafers by sweeping different scans of potential. The [CoTPP]n modified electrode was also studied by cyclic voltammetry limited to the reductive process centered on the Co ion. The surface concentration of the three films displayed in Figure S1 are 5.5× 10^{-10}, 10.2× 10^{-10} and 15.7 × 10^{-10} mol·cm^{-2} ± 1× 10^{-10} mol·cm^{-2} (assuming a surface concentration of 5× 10^{-10} mol·cm−2 for monolayer)[1] and correspond to estimated thickness of 2.5, 3.2 and 4.8 ±1 nm respectively.

2. Electrochemical grafting on Au and thickness measurements by AFM

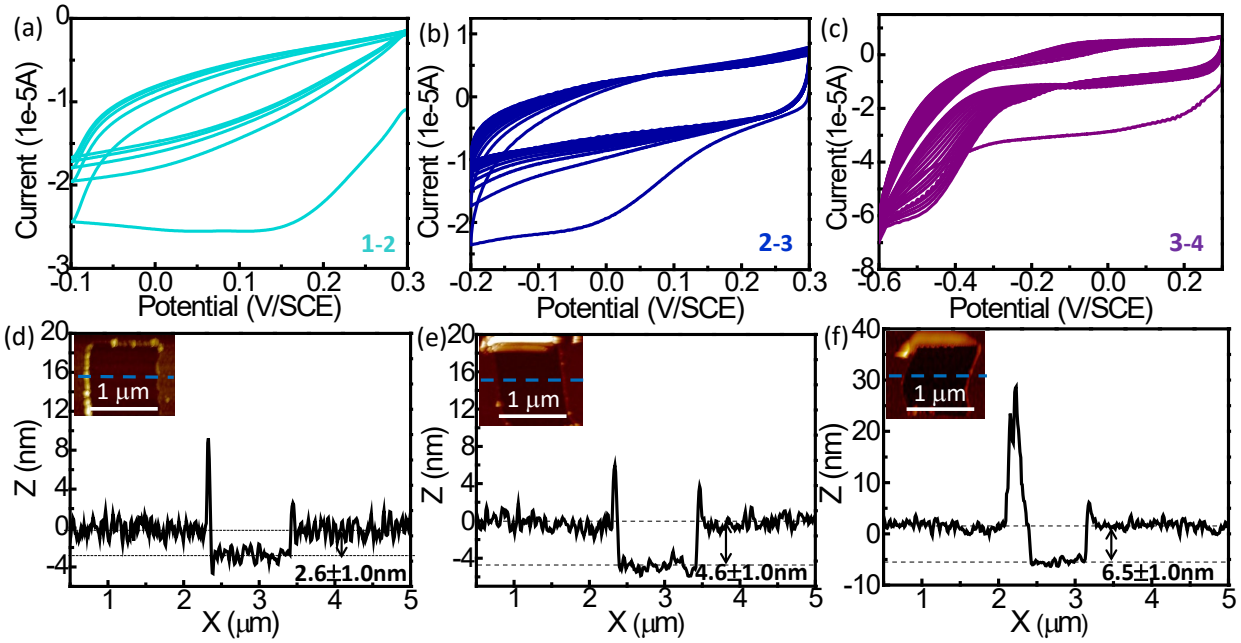


Figure S2. CV of diamino-$[CoTPP]_n$ electrografting on Au substrate (5×10^{-4} M CoTPP with 0.1M $TBAPF_6$ in ACN solution, scan rate 0.1V/s) (a) n=1-2 (b) n=2-3 (c) n=3-4. AFM scratch technique characterizes the film thickness (d) n=1-2 (e) n=2-3. (f) n=3-4.

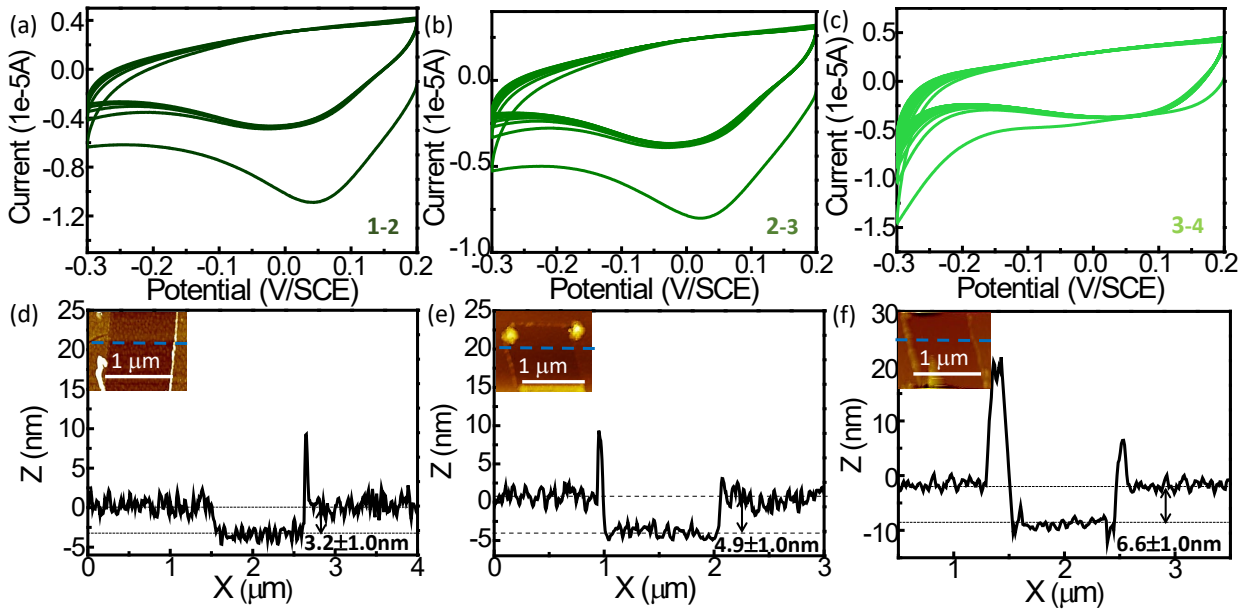


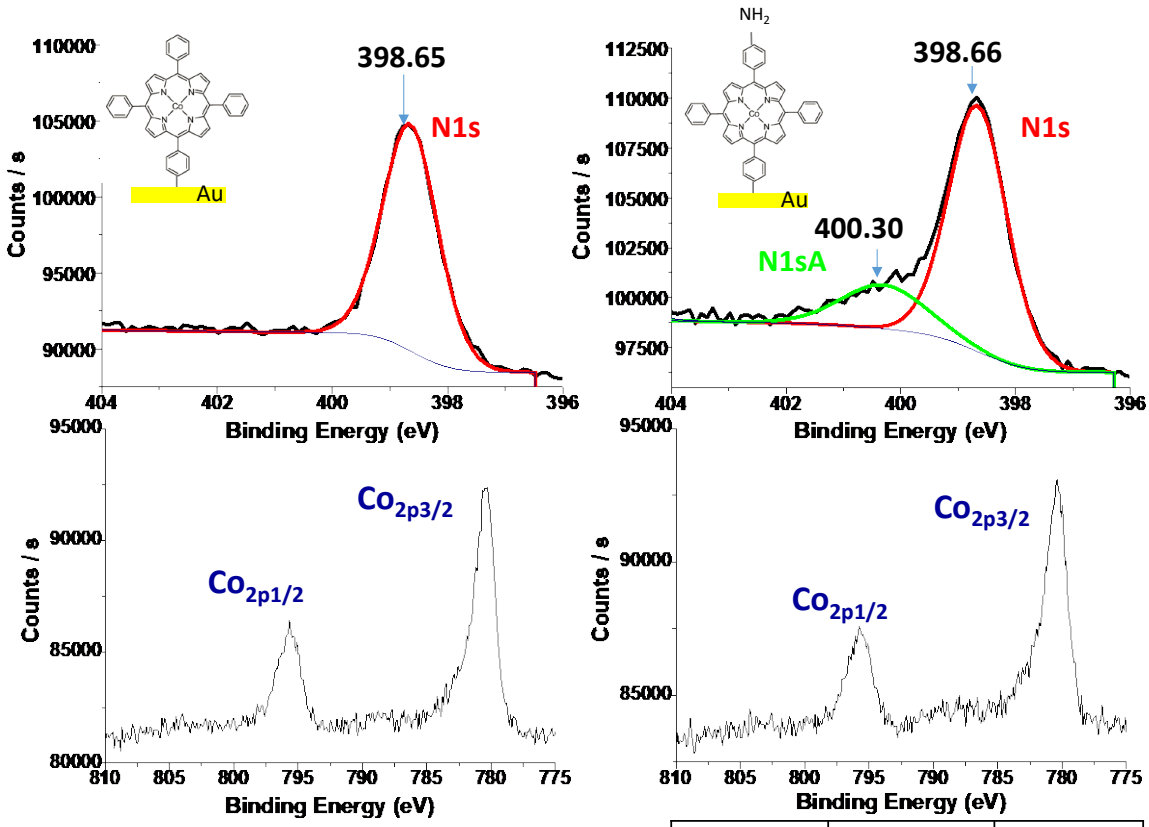
Figure S3. CV of diamino-$[TPP]_n$ electrografting on Au substrate (5×10^{-4} M porphyrin with 0.1M TBAPF6 in ACN solution, scan rate 0.1V/s) (a) n=1-2 (b) n=2-3 (c) n=3-4 Thickness characterization by AFM scratch (d) n=1-2 (e) n=2-3. (f) n=3-4.

Molecules		Scan range (V/SCE)	Cycles	Γ(10^{-10}mol·cm^{-2})	Thickness (nm)
Diamino-$[CoTPP]_n$	n=1-2	0.3-(-0.1)	5	5.5±1.0	2.6±1.0
	n=2-3	0.3-(-0.2)	20	10.2±1.0	4.6±1.0
	n=3-4	0.3-(-0.6)	20	15.7±1.0	6.5±1.0
Diamino-$[TPP]_n$	n=1-2	0.2-(-0.3)	5	--	3.2±1.0
	n=2-3	0.2-(-0.3)	10	--	4.9 ±1.0
	n=3-4	0.2-(-0.3)	20	--	6.6 ±1.0

Table S1. Electrochemical grafting parameters for diamino-$[CoTPP]_n$ and diamino-$[TPP]_n$ grafted on Au substrate: (5×10-4 M with 0.1M TBAPF6 in ACN solution).

The CVs results, shown in Figure S2 and Table S1, indicate that the grafted oligomer films are based on n-mers of [CoTPP] or [TPP]. The AFM scratching technique (Figure S2, S3) measures the [TPP]n or the [CoTPP]n porphyrin oligomer films with average thickness around 2±1 nm (n=1), 4±1nm (n=2), and 6±1 nm (n=3) respectively.

3. XPS analysis



Name	Peak BE	Atomic %
Co2p	780.42	1.5
N1s	398.65	5.4

Name	Peak BE	Atomic %
Co2p	780.41	1.4
N1s	398.66	4.7
N1s A	400.3	1.2

Figure S4. XPS spectra of N1s for monoamino-CoTPP (a) and diamino-CoTPP (b); XPS spectra of Co2p for monoamino-CoTPP (c) and diamino-CoTPP (d) ; The atomic percentage values of Co and N in monoamino-CoTPP (e) and diamino-CoTPP (f).

To verify the existence of -NH2 group on top of the diazonium grafted diamino-porphyrin oligomers, XPS characterizations were performed on modified Au substrate with about one monomer layer of monoamino-porphyrin and diamino-porphyrin, respectively. The peak N 1s, at around 398.65 in both porphyrin complexes, are most likely assigned to the signal of nitrogen in the porphyrin ring. The appearance of the peak N 1sA at around 400.3 eV can be most probably attributed to the additional -NH2 groups in diamino-Co[TPP].[2,3] The atomic ratio between N 1s and N 1sA is around 4 from the result of diamino-Co[TPP], which corresponds to the ratio between the coordinated N in the porphyrin ring and the additional -NH2 groups.

4. STM-bj results and G(t) curves

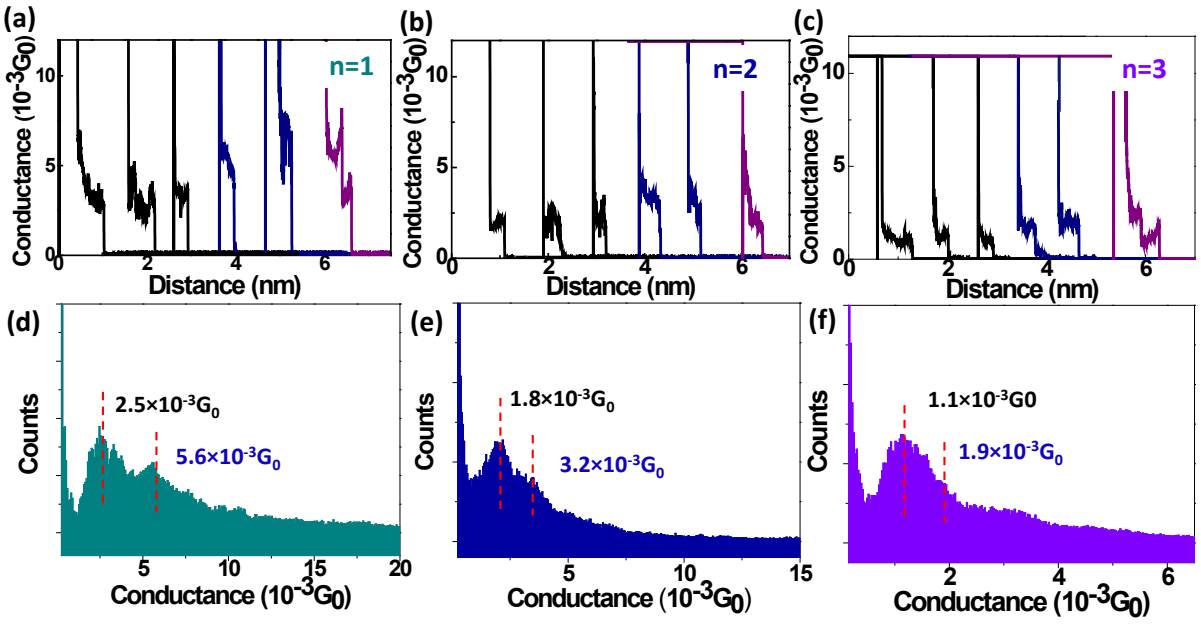


Figure S5. Conductance G(d) traces of Au -[CoTPP]$_n$-Au SMJs (a) n=1 (b) n=2 and (c) n=3 ;and corresponding histograms of Au -[CoTPP]$_n$-Au SMJs (d) n=1 (e) n=2 and (f) n=3. (V_{bias}=20-40mV)

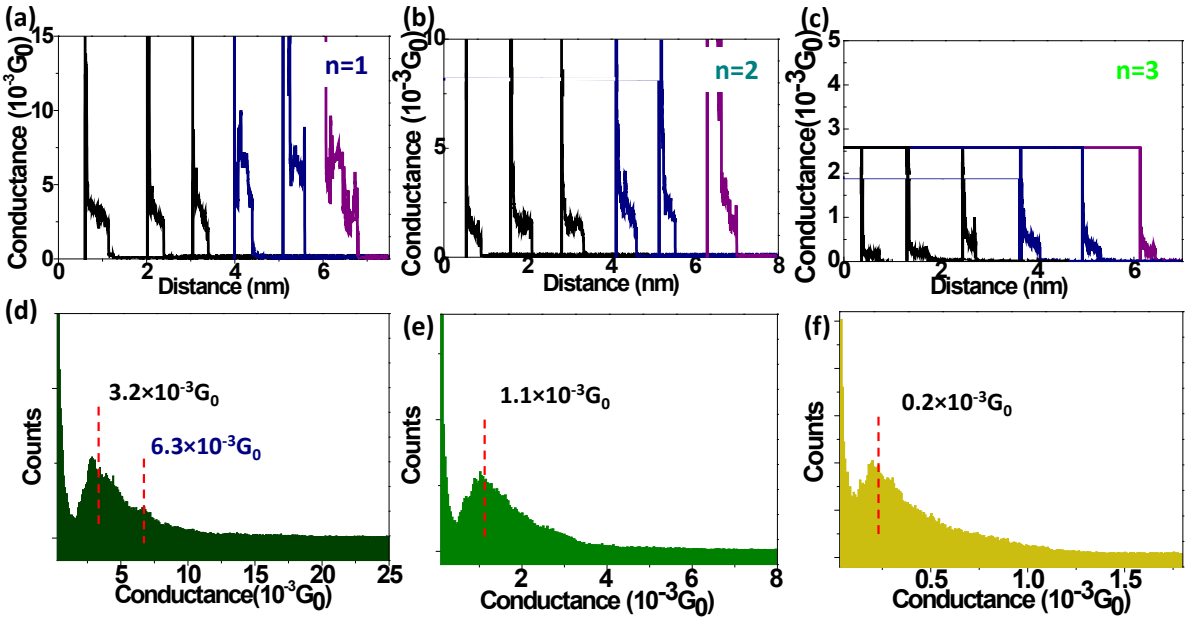


Figure S6. Conductance G(d) traces of Au -[TPP]$_n$-Au SMJs (a) n=1 (b) n=2 and (c) n=3 ; and corresponding histograms of Au -[TPP]$_n$-Au SMJs (d) n=1 (e) n=2 and (f) n=3. (V_{bias}=20-40 mV)

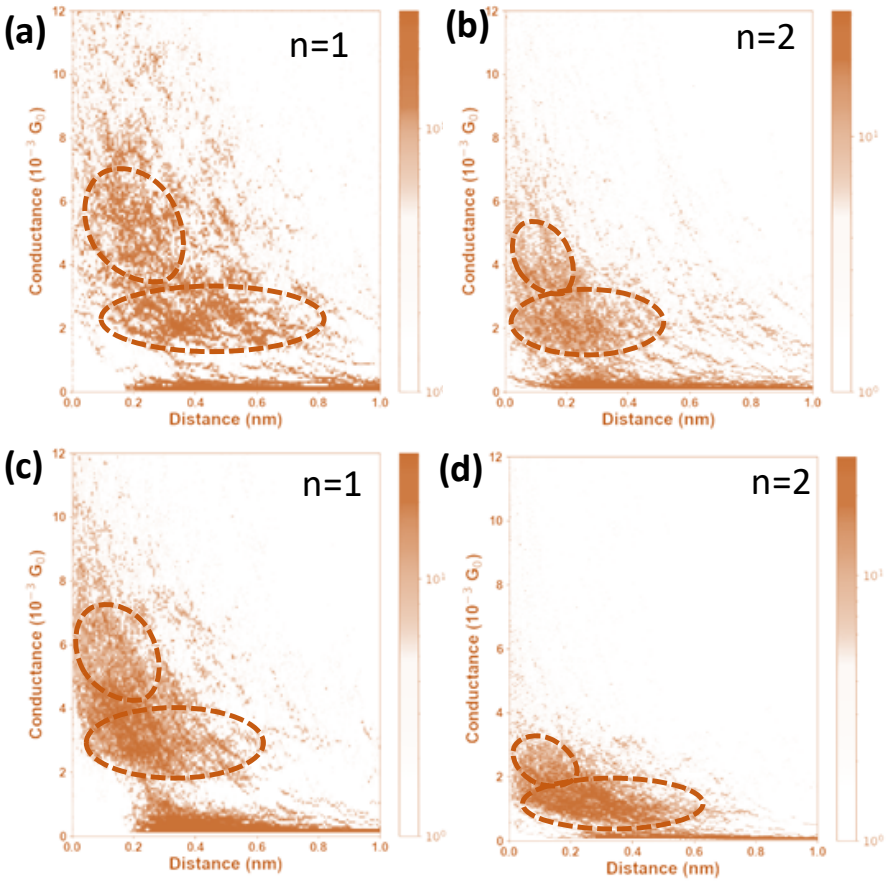


Figure S7 Length-conductance two-dimensional histograms of Au-[CoTPP]n-Au (a, b) and Au-[TPP]n-Au SMJs (c, d) (n = 1, 2)

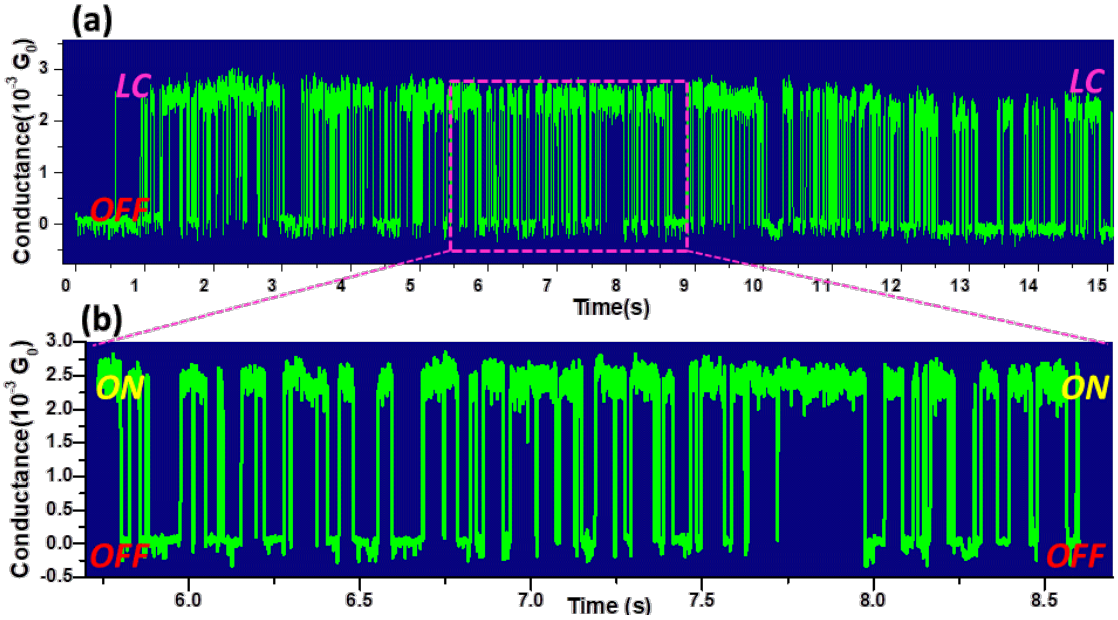


Figure S8. Telegraphic G(t) signal from (a) Au -[CoTPP]$_1$-Au junction and (b) zoom-in images of the G(t) signal showing good signal noise ratio.

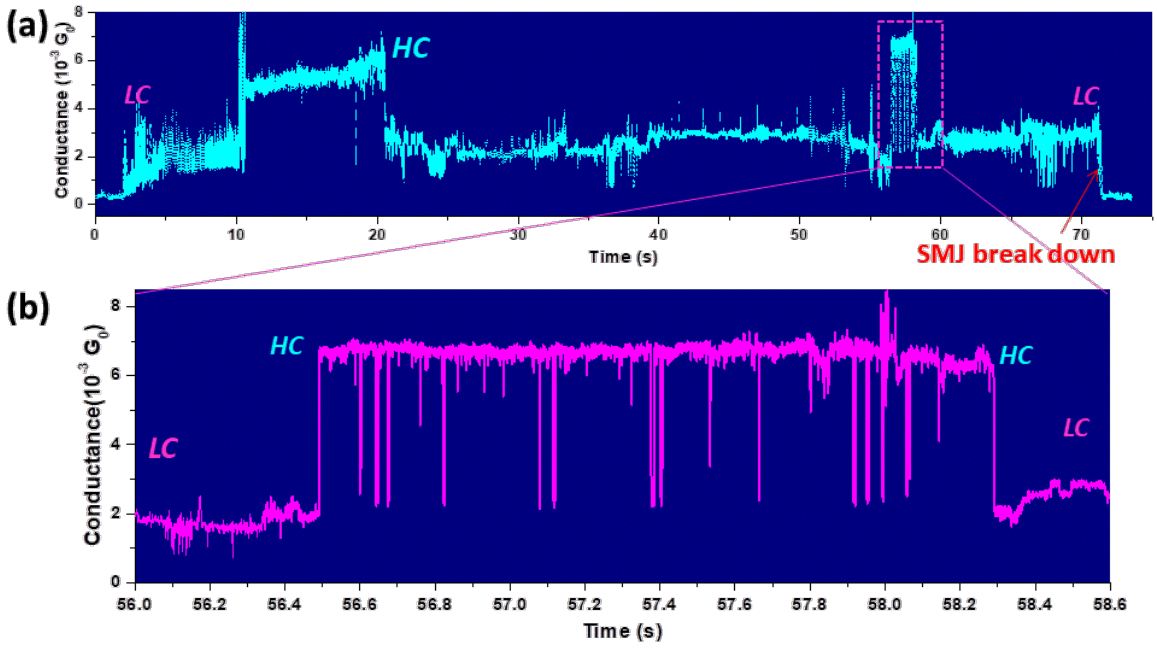


Figure S9. G(t) signal from (a) Au- -[CoTPP]$_1$-Au junction. Long life time of around 1 min is recorded and (b) zoom-in G(t) in (a) where the LC and HC signals alternate.

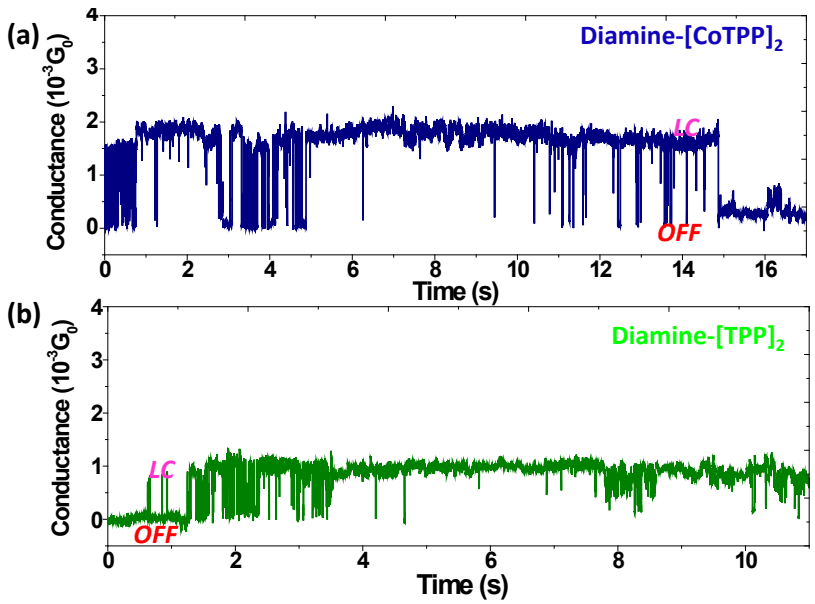


Figure S10. Conductance vs. time G(t) traces from (a) Au -[CoTPP]$_2$-Au junction and (b) Au- -[TPP]$_2$-Au junction, with stabilized LC states lasting as long as 10 s.

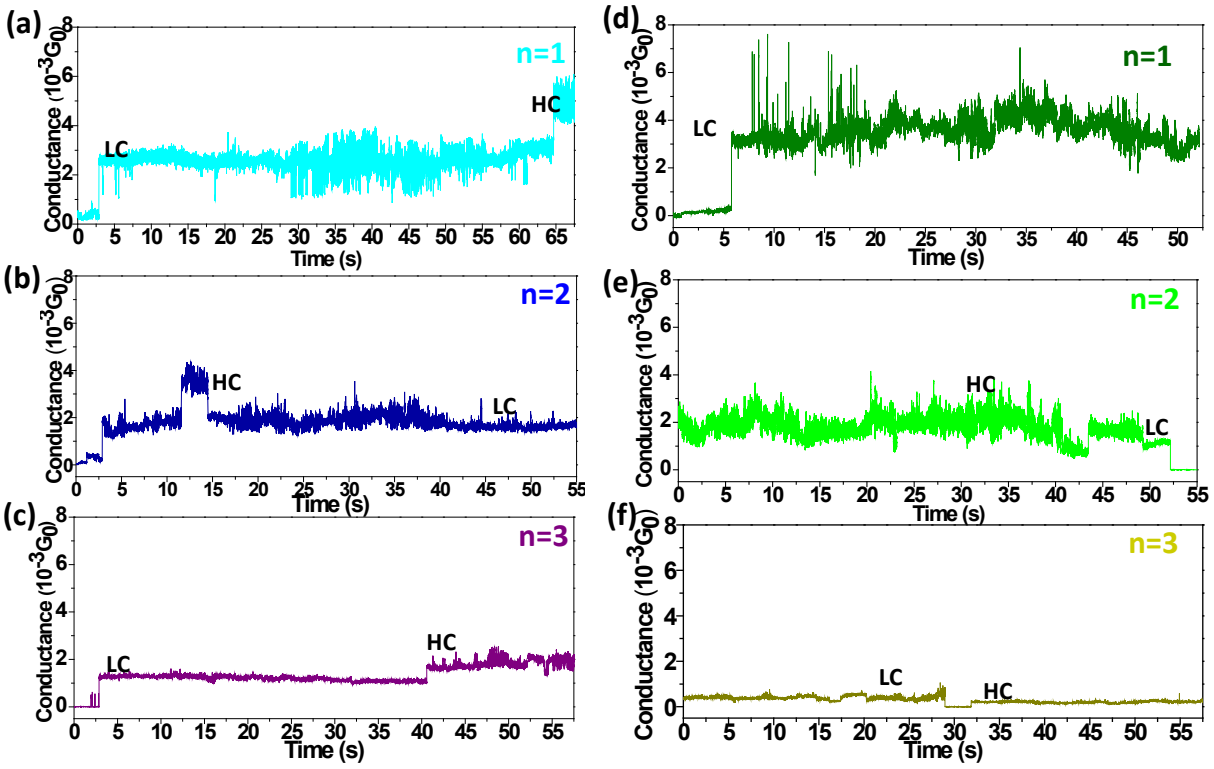


Figure S11. Conductance vs. time G(t) traces from Au-$[CoTPP]_n$-Au junction , n=1(a), n=2(b), n=3(c); and (b) Au-$[TPP]_n$-Au junction , n=1(a), n=2(b), n=3(c);, with LC and HC states lasting as long as 50 s.

5. Energy diagram

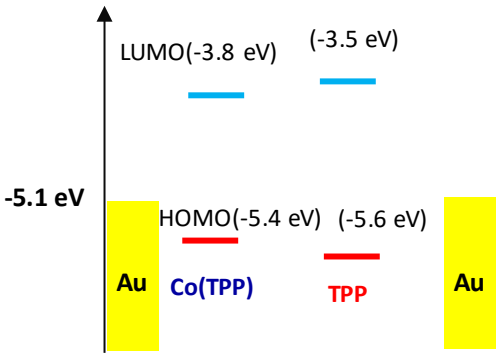


Figure S12 Molecular orbital levels of the molecules (diamino-CoTPP and diamino-TPP) and Fermi levels of the Au electrode in vacuum. HOMO and LUMO levels of the molecules are deduced from their redox potential measured and using an energy level for SCE reference electrode of -4.60 eV in acetonitrile solutions compared to vacuum level following recommendation from (4)

6. STM I(V) measurements

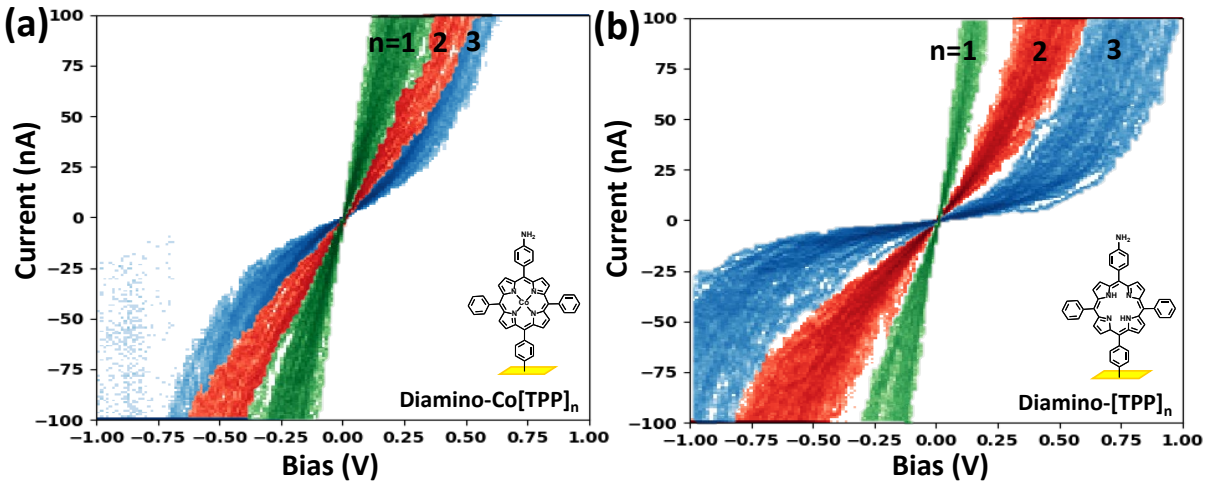


Figure S13. Combined 2D heat maps of Au-[CoTPP]$_n$-Au (a) and Au-[TPP]$_n$-Au SMJs (b) with different molecular lengths.

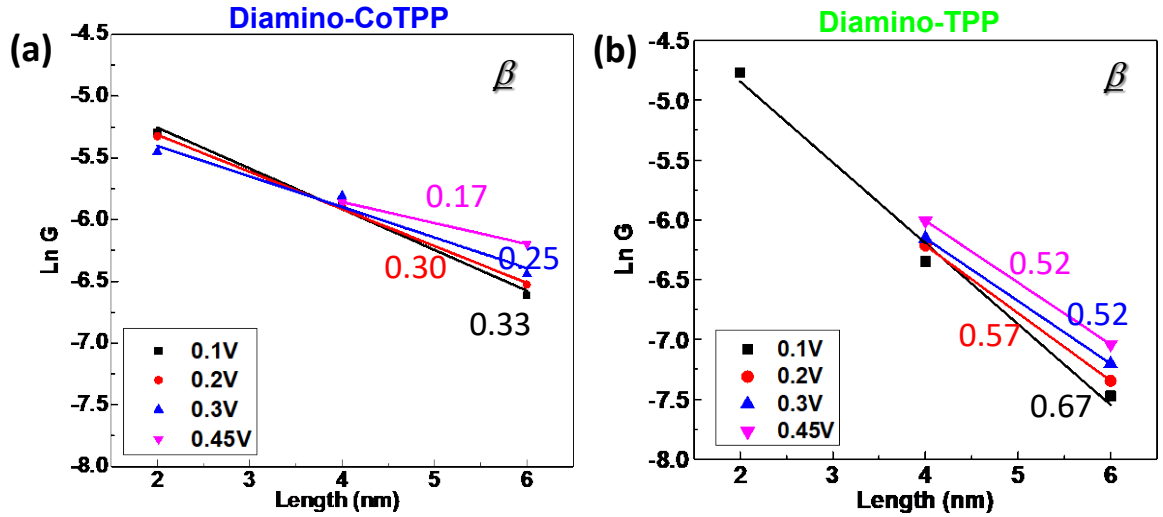


Figure S14. β plots at four different bias voltage for Au-[CoTPP]$_n$-Au SMJ (a); β plots at four different bias voltage for Au-[TPP]$_n$-Au SMJs (b).

Attenuation β plots are expected to change with the applied bias voltages in SMJs. The β values, from diamino- Au-[CoTPP]$_n$-Au and Au-[TPP]$_n$-Au SMJ SMJs, are calculated at four different applied voltages (0.1V, 0.2V, 0.3V, 0.4V). Both SMJs show that the β values decrease when the applied voltages increase.

(1) Brooksby, P. A.; Downard, A. J. *Langmuir* 2004, 20 (12), 5038–5045.

(2) Panighel, M.; Di Santo, G.; Caputo, M; Lal , C.; Taleatu, B.; Goldoni, A. *J. Phys.: Conf. Ser.* 2013, 470, 012012

(3) Ederer, J.; Ecorchard, P.; Tolasz, J.; Perchacz, M.; Pop-georgievski, O. *RSC Adv.* 2017, 7, 12464–12473.

(4) Trasatti, S.. The absolute electrode potential: an explanatory note (Recommendations 1986). *Pure and Applied Chemistry*, 1986, *58*(7), 955-966.