Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Cu(III)Triarylcorroles with Asymmetric Push-Pull meso-Substitutions: Tunable Molecular Electrochemically Catalyzed Hydrogen Evolution

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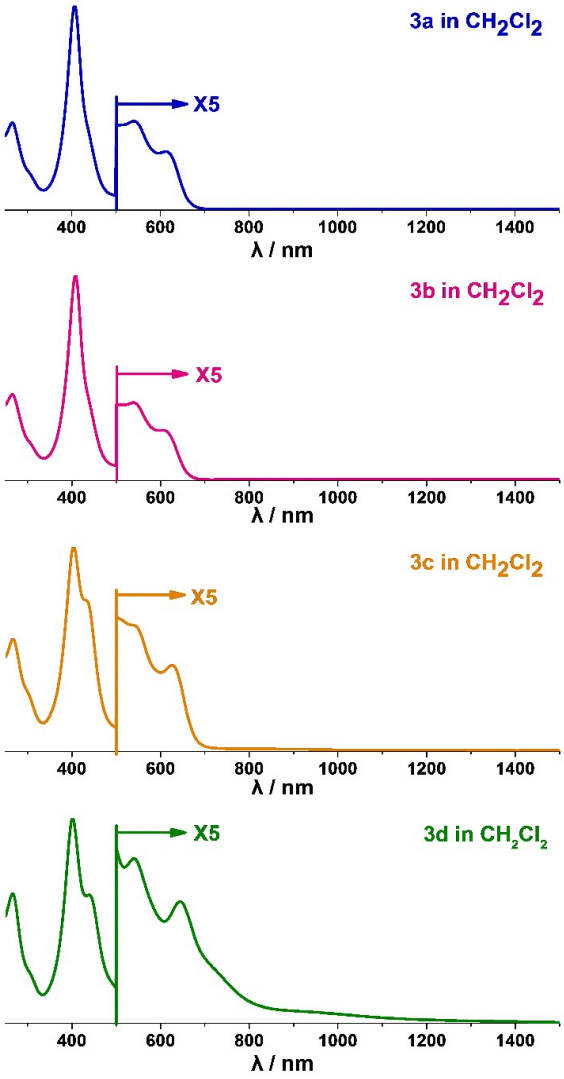

Figure S1 UV-visible-NIR absorption spectra of Cu(III)corroles **3a**-**d** at room temperature in CH_2Cl_2.

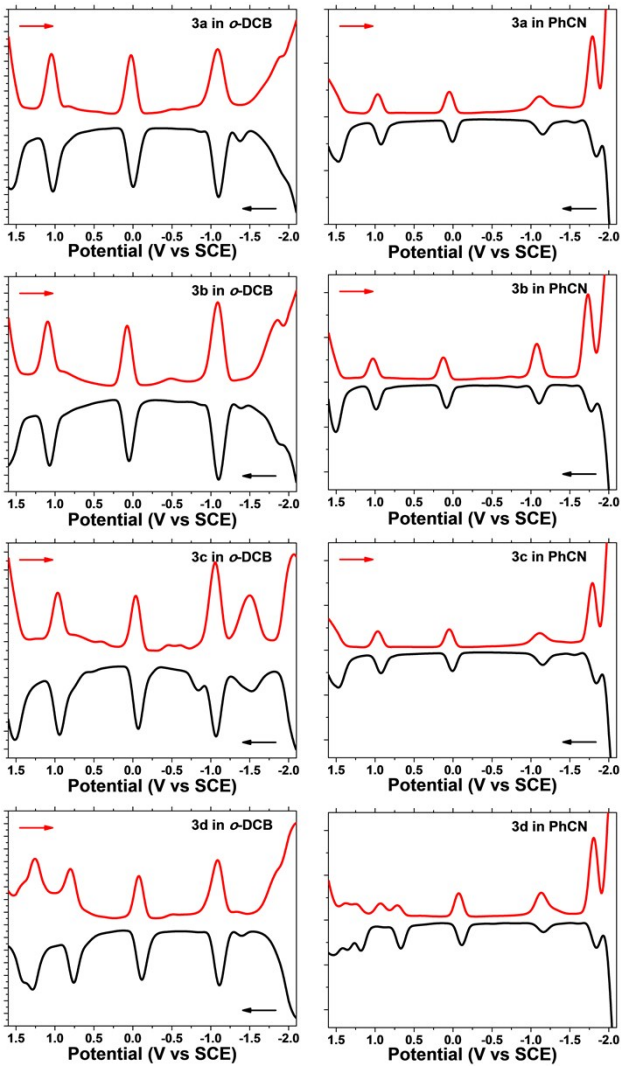

Figure S2 DPV measurements of **3a**-**d** in *o*-DCB (left) and PhCN (right) containing 0.1 M $[NBu_4]^+[ClO_4]^-$ (TBAP) as a supporting electrolyte.

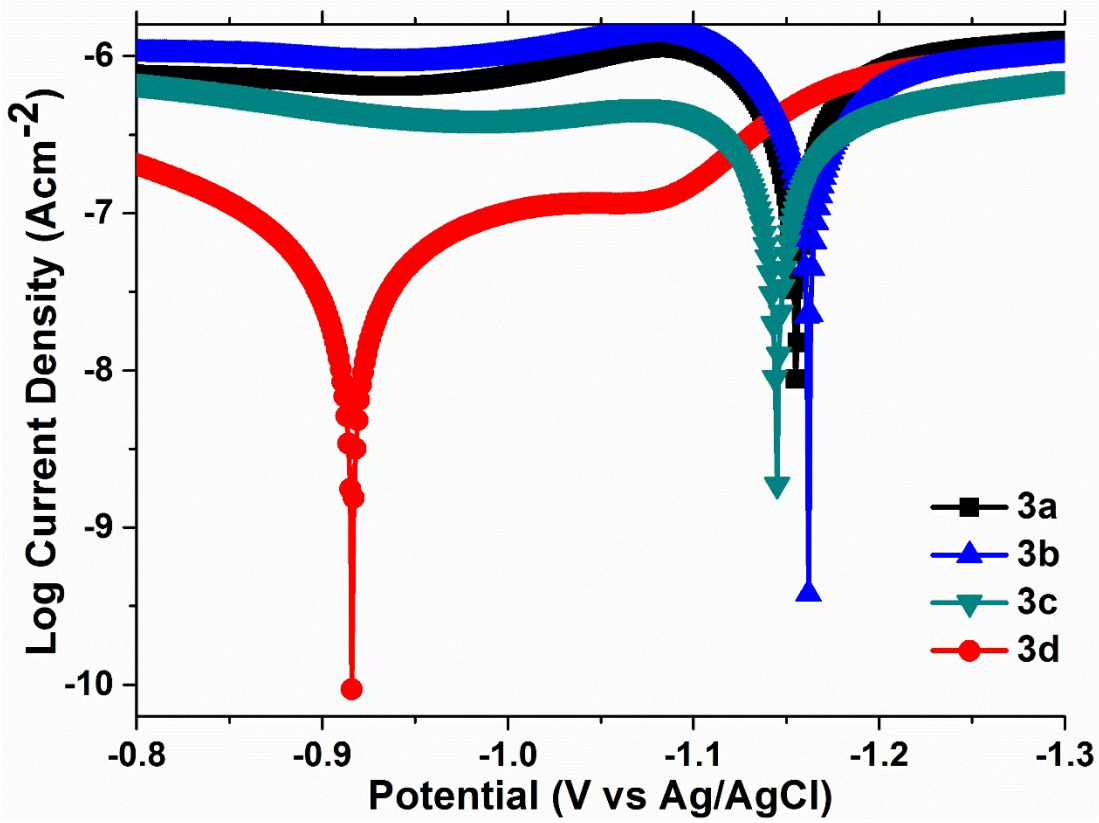

Figure S3 Tafel plot of **3a**-**d** in PhCN containing 0.1 M $[NBu_4]^+[ClO_4]^-$ (TBAP) as a supporting electrolyte.

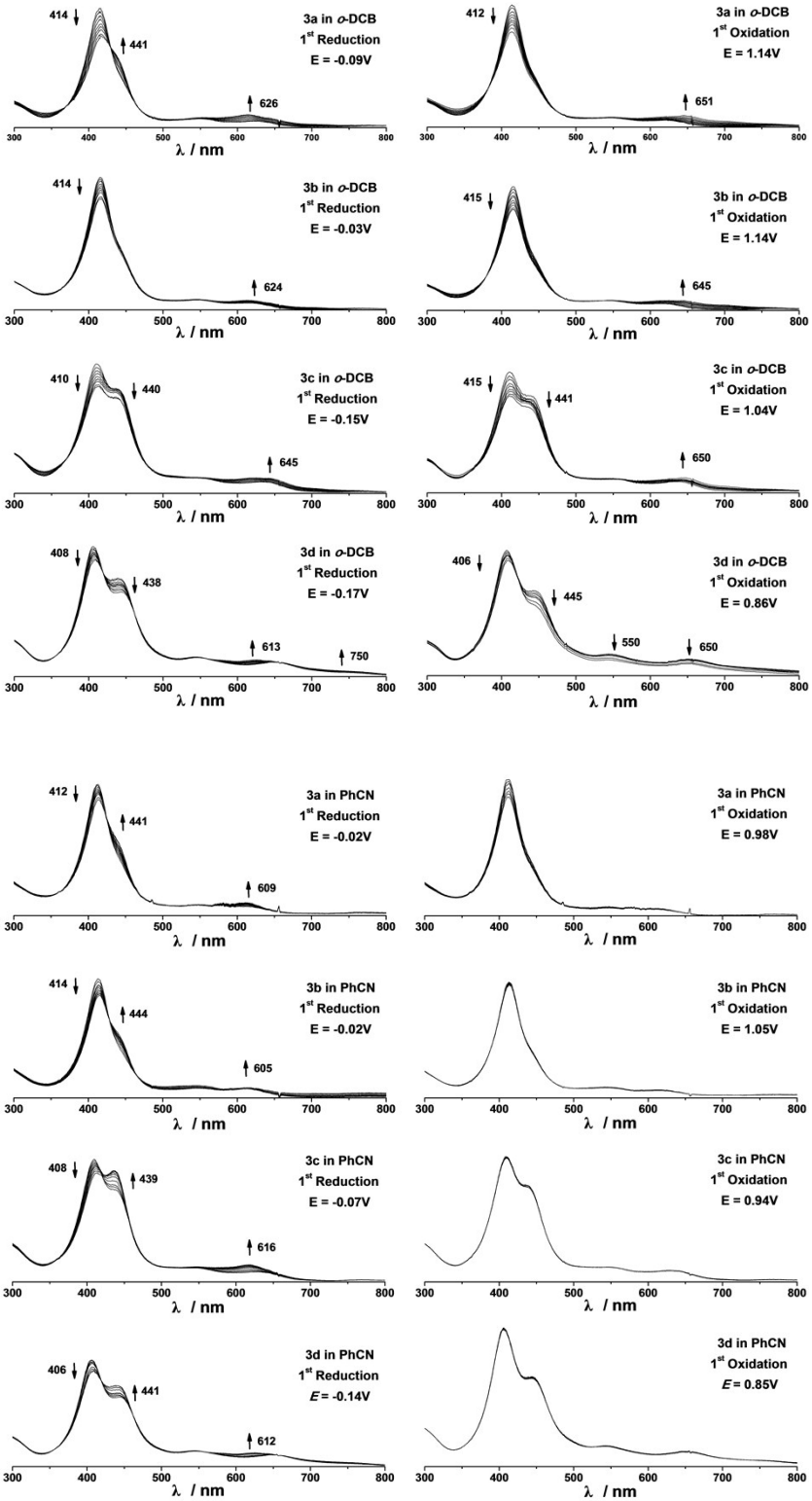

Figure S4 *In situ* spectroelectrochemical measurements of **3a**-**d** in o-DCB containing 0.1 M $[NBu_4]^+[ClO_4]^-$ (TBAP) as a supporting electrolyte.

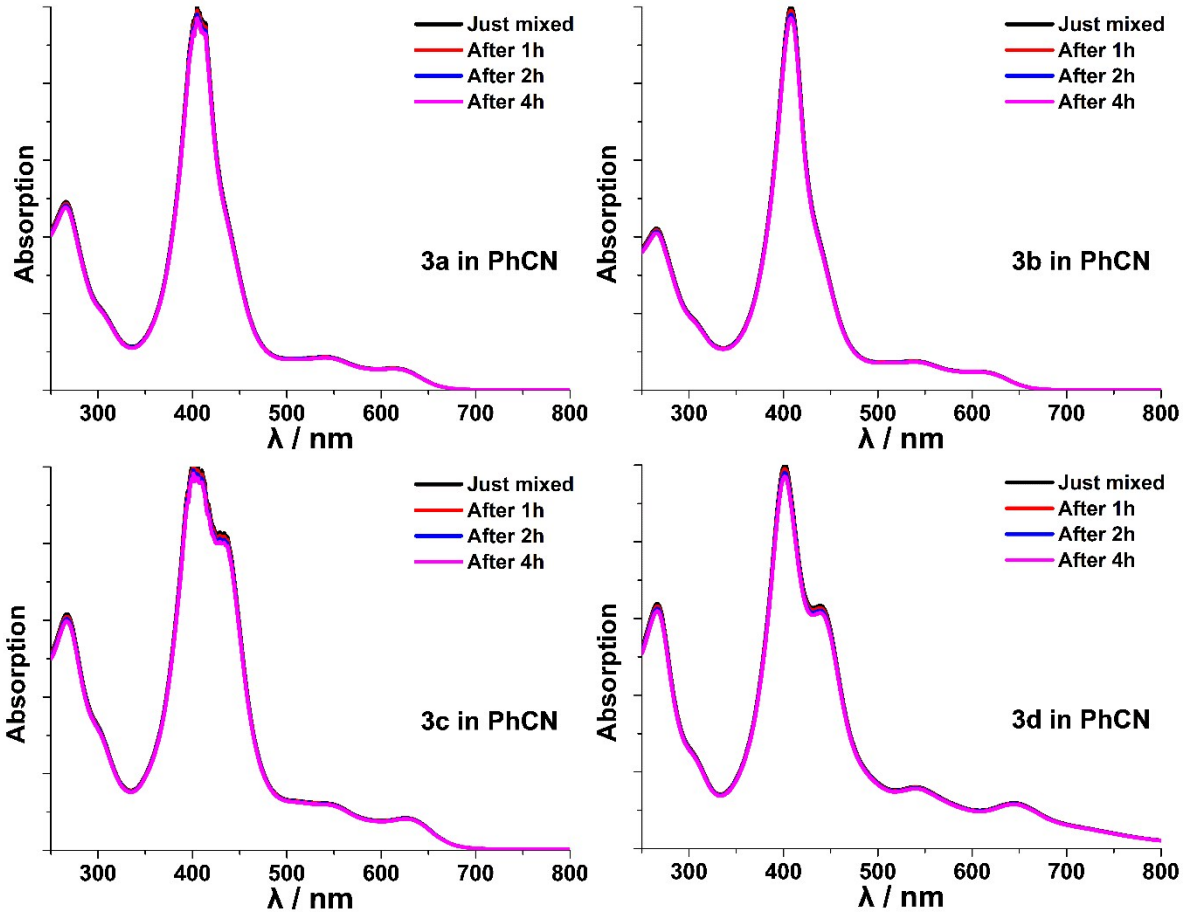

Figure S5 Stability test of **3a**-**d** in PhCN containing 10.0 eq TFA.

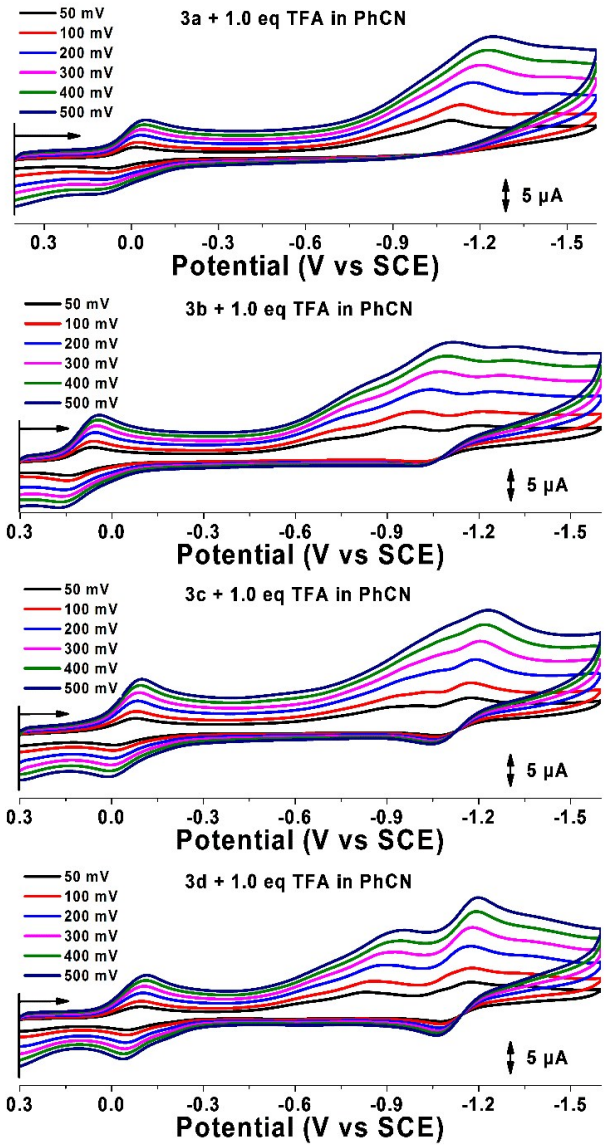

Figure S6 Reductive electrochemical measurements at 50–500 mV/s scanning speed of Cu(III)corroles **3a**-**d** in the presence of 1.0 eq of TFA in PhCN containing 0.1 M $[NBu_4]^+[ClO_4]^-$ (TBAP) as a supporting electrolyte.

1. X-ray Crystallography

Table S1. Crystal data of **3d**.

Sample-Temperature (K)	Data
Space group	P-1
a (Å)	8.525(2),
b (Å)	12.695(17),
c (Å)	18.656(15)
α, β, γ (˚)	71.59, 82.11, 80.69
V (Å^3)	1882.6(9)
Z	2
F(000)	840.0
μ (mm^{-1})	0.637
Observed reflections (*I*>2*σ*(*I*))	20148
Independent reflections	6602
R_1	0.0689
wR_2	0.1634

2. TD-DFT Calculations

Table S2. The calculated UV-visible absorption spectra of the B3LYP optimized geometry of **3a-d** and the 3Ph and 1Ph model complexesobtained by using the CAM-B3LYP functional of the Gaussian 09 software package with 6-31G(d) basis sets.

				3Ph			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
----	**1**	----	----	----	----	----	Ground State
Q	**4**	20.2	495	(0.10)	----	----	**74% s → -a**; **19% a → -s**; …
	5	21.2	471	(0.03)	----	----	**62% a → -a**; **33% s → -s**; …
B	**10**	27.1	369	(0.52)	----	----	**59% s → -s**; **30% a → -a**; …
	11	27.8	360	(0.55)	----	----	**66% a → -s**; **17% a → -s**; …
				1Ph			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
----	**1**	----	----	----	----	----	Ground State
Q	**4**	20.0	500	(0.11)	----	----	**72% s → -a**; **17% a → -s**; …
	5	20.9	478	(0.03)	----	----	**62% a → -a**; **28% s → -s**; …
B	**10**	27.0	371	(0.48)	----	----	**48% s → -s**; **27% a → -a**; 14% s → LUMO+2; …
	11	27.5	364	(0.60)	----	----	**53% a → -s**; **18% a → -s**; 15% a → LUMO+2; …
				3a			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
----	**1**	----	----	----	----	----	Ground State
Q	**4**	20.4	491	(0.09)	16.3	612	**70% s → -a**; **18% a → -s**; …
	5	20.9	478	(0.02)	18.5	541	**61% a → -a**; **27% s → -s**; …
B	**10**	26.9	372	(0.52)	23.1	432	**48% s → -s**; **29% a → -a**; 12% s → LUMO+2; …
	11	27.3	366	(0.62)	24.5	408	**52% a → -s**; **19% a → -s**; 15% a → LUMO+2; …
				3b			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
----	**1**	----	----	----	----	----	Ground State
Q	**4**	20.0	501	(0.10)	16.4	610	**71% s → -a**; **20% a → -s**; …
	5	21.0	477	(0.02)	18.5	542	**60% a → -a**; **32% s → -s**; …
B	**10**	26.6	375	(0.51)	23.0	434	**59% s → -s**; **30% a → -a**; …
	11	27.2	368	(0.63)	24.4	410	**66% a → -s**; **20% a → -s**; …
				3c			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**

----	**1**	----	----	----	----	----	Ground State
Q	**4**	19.9	502	(0.12)	16.0	626	**73% s → -a**; **17% a → -s**; …
	5	20.9	478	(0.02)	18.4	544	**62% a → -a**; **29% s → -s**; …
B	**10**	26.9	372	(0.52)	23.5	426	**48% s → -s**; **28% a → -a**; 14% s → LUMO+2; …
	11	27.5	364	(0.59)	24.9	402	**53% a → -s**; **17% a → -s**; 15% a → LUMO+2; …

3d

Band[a]	**#**[b]	**Calc**[c]			**Exp**[d]		**Wave Function**[e] **=**
----	**1**	----	----	----	----	----	Ground State
Q	**4**	19.8	505	(0.13)	15.5	644	**73% s → -a**; **16% a → -s**; …
	5	20.9	479	(0.02)	18.2	548	**60% a → -a**; **31% s → -s**; …
B	**10**	26.6	376	(0.28)	23.0	435	**25% s → -s**; 17% s → LUMO; **16% a → -a**; 10% s → LUMO+2; …
	12	27.4	365	(0.51)	24.8	403	**48% a → -s**; **18% a → -s**; 15% a → LUMO+2; …

a − Band assignment described in the text. b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation. c − Calculated band energies ($10^3.cm^{-1}$), wavelengths (nm) and oscillator strengths in parentheses (f). d − Observed energies ($10^3.cm^{-1}$) and wavelengths (nm) in **Figure 2**. e − The wave functions based on the eigenvectors predicted by TD-DFT. One-electron transitions associated with the four frontier π-MOs of Gouterman's 4-orbital model[S1] are highlighted in bold. Michl's **a**, **s**, **-a** and **-s** nomenclature[S2] for the four frontier π-MOs is used to facilitate comparison of the transition of porphyrinoids with differing symmetries.

References

[S1] Gouterman, M. Optical Spectra and Electronic Structure of Porphyrins and Related Rings. In *The Porphyrins*, vol. III, Dolphin D. (Ed.) Academic Press: New York, 1978, 1-165.

[S2] (a) Michl, J. *J. Am. Chem. Soc.***1978**, *100*, 6801-6811. (b) Michl, J. *J. Am. Chem. Soc.***1978**, *100*, 6812-6818. (c) Michl, J. *Pure Appl. Chem.***1980**, *52*, 1549-1563. (d) Michl, J. *Tetrahedron***1984**, *40*, 3845-3934.