

Supporting Information

Molecular Engineering of Metalloporphyrins and Phthalocyanines for Homogeneous and Heterogeneous CO₂ Electroreduction

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Table. S1 Performance of the molecular catalysts on flow-cell configuration

Molecular catalysts	Catalyst immobilization method	Catalyst loading (mg/cm ²)	Products	Catholyte	Cathodic overpotential (V vs RHE)	Cell voltage (V)	Current density (mA/cm ²)	FE at this current density (%)	TOF (s ⁻¹)	TON	Durability	Cathodic reaction energy efficiency (%)	Energy efficiency of the cell (%)	Productivity (mmol/h)	Ref.
CoPc	Spray coating	4	CO	-			150	>95	0.21						1
							2.7	200	~60	0.18		100 h			
CoPc+phenol	Spray coating	4	CO	-		2.52	200	88	0.26						1
FeTPP[Cl]/carbon			CO	1 M KHCO ₃	<-0.41			60							2
FeTPP[Cl]/Cu	Spray coating		Ethanol	1 M KHCO ₃	-0.82			41				23			
				-		3.7	600	41			12 h		13		
CoTMAPc@CNT	Drop casting	0.069	CO	1.0 M KOH	-0.7		239	95.6		373 000	15 h				3
CoPc/NH ₂ -CNT	Drop casting	0.1	CO	1.0 M KOH	-0.67		225.5	~100			100 h				4
CoPc/OH-CNT	Drop casting	0.1	CO	1.0 M KOH	-0.67		212.0	96.9							
CoPc/COOH-CNT	Drop casting	0.1	CO	1.0 M KOH	-0.67		181.1	93.8							
CoPc/CNT	Drop casting	0.1	CO	1.0 M KOH	-0.67		97.9	90							
CoPc	Drop casting	0.1	CO	1.0 M KOH	-0.67		32	88.8							
CoPc2	Deposition		CO												
					-0.55		30	96			10 h				
[Ni(cyclam)] ²⁺	Homogeneous		CO												5
FeP	Deposition	2.08	CO	0.5 M CsHCO ₃	-0.75		50	98.9			3 h		41		6
				1 M KHCO ₃	-0.86		50	>98		3 h		38			
				1 M KOH	-0.16		27	99.7	1.0	8719	1 day	71	0.5		
[Co(PyPc)] with KOtF	Coating	0.06-0.24	CO	NEt ₄ ⁺ BF ₄ ⁻		1.89	100	98.2	6.4	3 859	7 days		69.5		7
						2.03	200	95.2		745			62.8		
Ag(I) bis-BIANs		0.002-0.5	CO	0.1 M KHCO ₃	-1.39	2.5-3.0	300-900	59-90	0.49-57.5		100 h		30-51		DOI: 10.1016/j.joule.2023.03.015

