Supplementary Information

Abundant Organic Dye as an Anolyte for Aqueous Flow Battery with Multi-Electron Transfer

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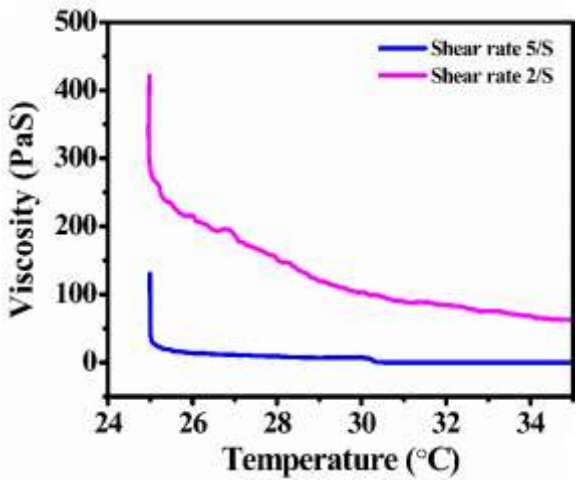


Figure S1: Dynamic viscosity at varying temperature for 0.7 M IC-H at two different shear rates of 5/s and 2/s.

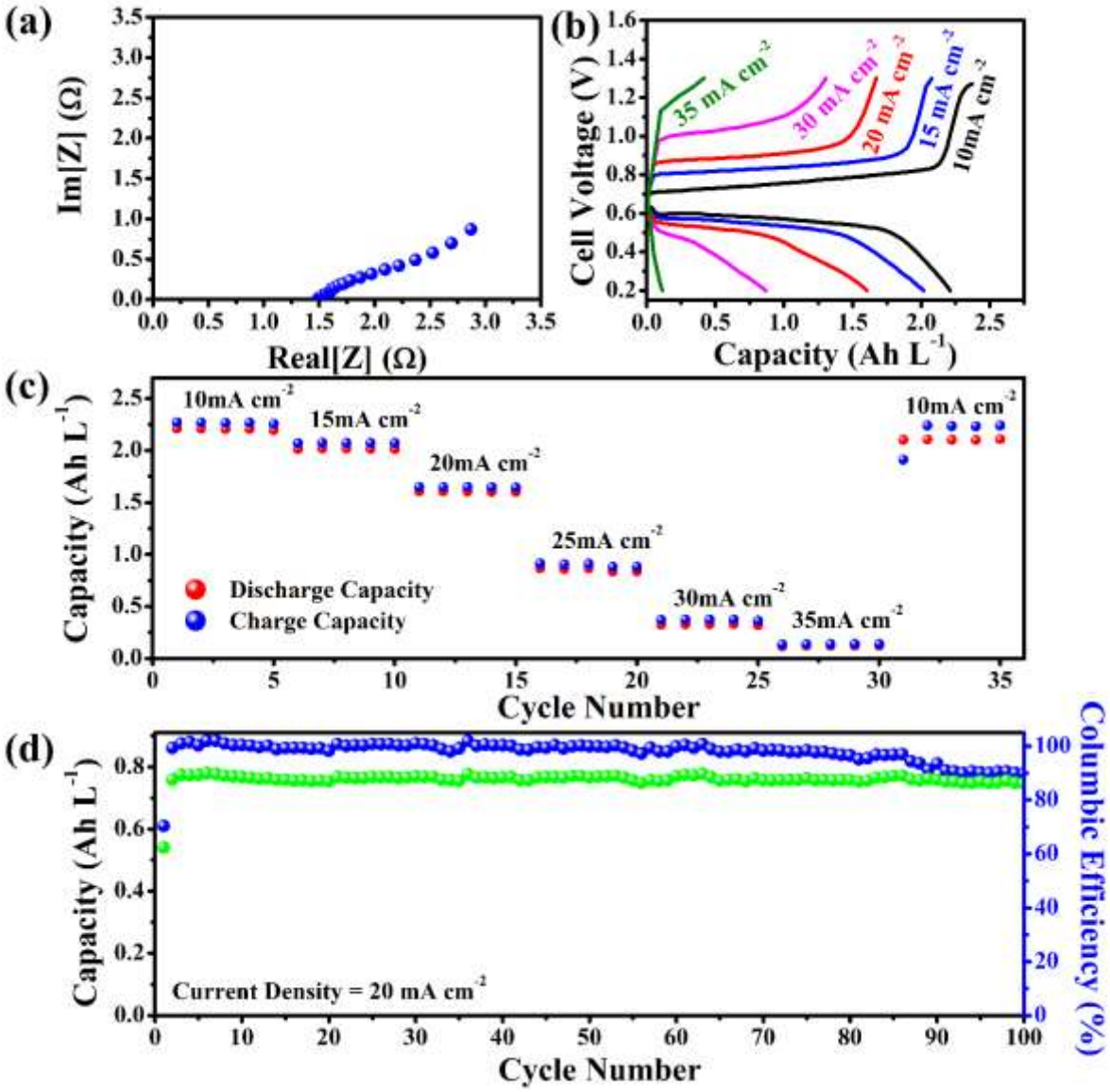


Figure S2: Demonstration of full cell performance of 0.035 M IC-Na in 0.1 M $HClO_4$ against 0.25 M 4-acetamidoTEMPO in 0.1 M $HClO_4$. (a) Electrochemical Impedance Spectrum of IC-Na/ TEMPO cell. (c) Capacity versus cell voltage traces at different current densities. (b) Cycle number versus capacity plot at various current densities. (d) Constant current cycling of IC-Na/TEMPO cell at a current density of 20 mA cm^{-2} with a cut off voltage of 1.3 V during charge and 0.2 V during discharge.

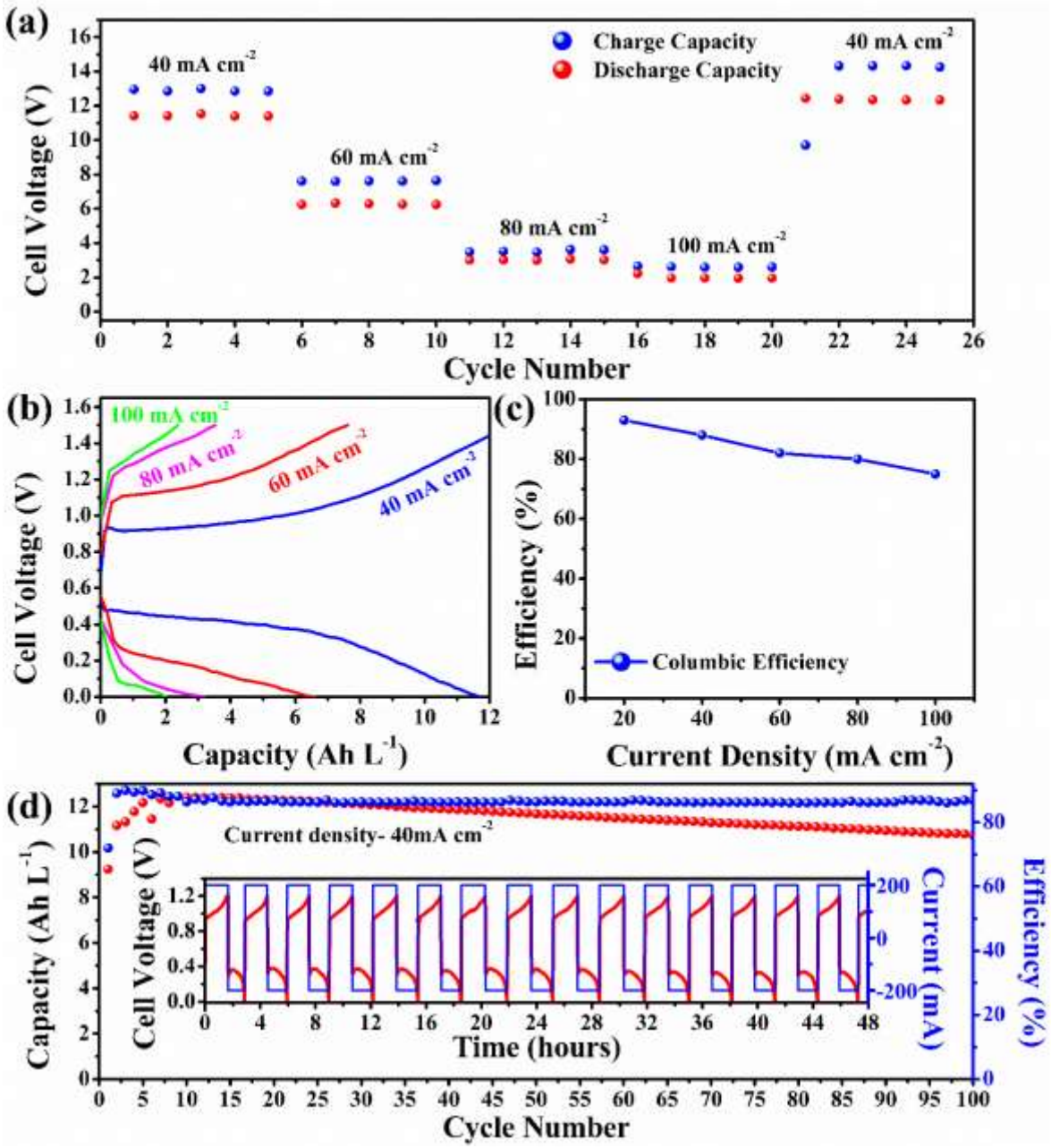
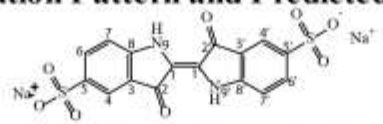


Figure S3: Demonstration of full cell performance of 0.7 M IC-H in 0.2 M $HClO_4$ against 0.5 M TEMPO in 0.1 M $HClO_4$. (a) Cycle number versus capacity plot at various current densities. (c) Capacity versus cell voltage traces at different current densities. (d) Variation in coulombic efficiency with current density. (e) Constant current cycling of IC-H/TEMPO cell at a current density of 40 mA cm^{-2} with a cut off voltage of 1.2 V during charge and 0.2 V during discharge.

Table 1: Substitution Pattern and Predicted Redox Potential



Index No.	Functional Groups	Positions			Solvation Energy (eV)	Redox potential (E_0 V vs. Ag/AgCl)
		4, 4'	5, 5'	7,7'		
Indigo Carmine Na	No Substitution				-3.32	-0.40
	R = OH	1 Substituent				
1		R	H	H	-3.12	-2.27
2		H	R	H	-3.47	-2.32
3		H	H	R	-2.71	-1.91
		2 Substituent				
4		R	R	H	-3.10	-2.09
5		R	H	R	-2.75	-1.84
6		H	R	R	-3.06	-2.35
	R = CH3	1 Substituent				
7		R	H	H	-3.10	-2.02
8		H	R	H	-3.02	-2.08
9		H	H	R	-3.00	-2.06
		2 Substituent				
10		R	R	H	-3.01	-2.11
11		R	H	R	-3.00	-2.28
12		H	R	R	-2.94	-2.30
	R = OCH3	1 Substituent				
13		R	H	H	-3.12	-2.08
14		H	R	H	-4.20	-2.49
15		H	H	R	-2.72	-1.81
		2 Substituent				
16		R	R	H	-3.20	-2.14
17		R	H	R	-2.67	-1.91
18		H	R	R	-2.89	-2.02
	R = COOH	1 Substituent				
19		R	H	H	-3.24	-1.37
20		H	R	H	-3.42	-1.37
21		H	H	R	-2.58	-0.01
		2 Substituent				
22		R	R	H	-3.72	-1.07
23		R	H	R	-2.84	-0.91
	R = HSO3	1 Substituent				
24		R	H	H	-3.47	-1.21
25		H	R	H	-3.02	-2.99
26		H	H	R	-3.24	-0.68
		2 Substituent				
27		R	R	H	-3.58	-0.48
28		R	H	R	-3.55	-0.22
29		H	R	R	-3.58	-0.48
		3 Substituent				
30		R	R	R	-4.92	-0.68

Table S 2		
Methods		**Deviation in redox Potential (mV)**
PBE 6-31 G		47
B3LYP	6-21G	49
	6-31G	42
	6-31+G	44
	6-31+G**	24
	6-311G	28
	6-311G**	8
	6-311+G	22
	6-311+G**	12

Solvation Free Energy Calculation:

$$\Delta \boldsymbol{G_{Solvation}} = \in_s - \{\in_g + \boldsymbol{G_{correction}}\}$$ **.....Equation S 1**

Where, $\Delta G_{Solvation}$ is the solvation energy (Hartree)

$\in_s$ is the free energy of the solvated phase using the CPCM solvation model (Hartree)

$\in_g$ is the free energy of the gas phase (Hartree)

$G_{correction}$ *is the thermal correcton to the gibbes free energy* (Hartree)

Nernst Equation:[1]

$$\boldsymbol{E} = \boldsymbol{E^0} + \frac{\boldsymbol{RT}}{\boldsymbol{nF}} \ln \frac{[Q][H^+]^m}{[H_m\, IC]} = \frac{RT}{F}\frac{m}{n}\, pH + C \quad \text{.....Equation S 2}$$

Where R is the gas constant

T is the temperature

F is the Faraday constant

Q is the reaction quotient

m and n is the number of protons and electrons involved in the reaction, respectively.

H^+: Proton Concentration

H_m: Thermodynamic activity of protons present in the solution

IC: Concentration of IC

C: Arbitrary constant

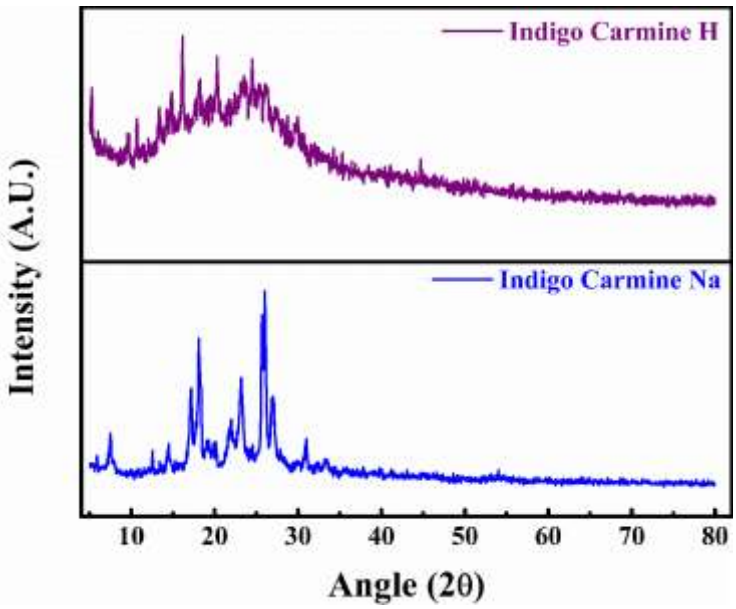


Figure S4: XRD of IC-Na and IC-H indicating a change in the crystalline structure of IC-Na and IC-H

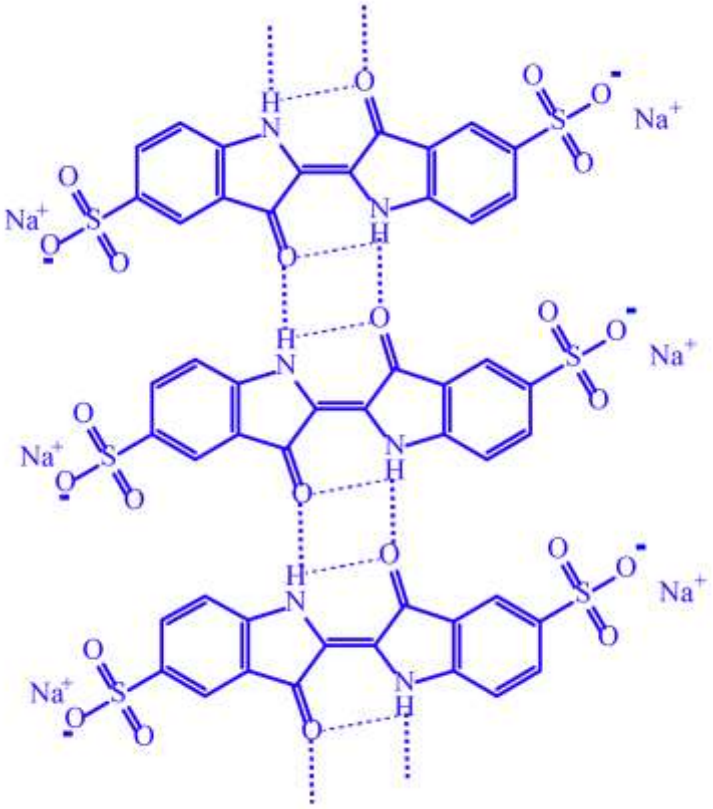


Figure S5: Schematic representation of Hydrogen bonding between amine hydrogens and carbonyl groups of indigo carmine. It is the dominant intermolecular interaction governing the crystallization of indigo.

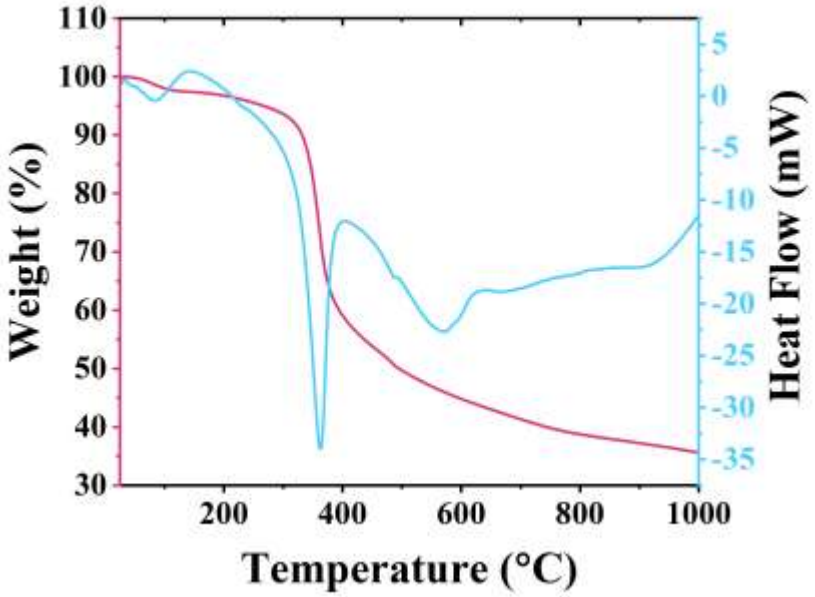


Figure S6: Thermogravimetric analysis of indigo carmine-H in argon atmosphere

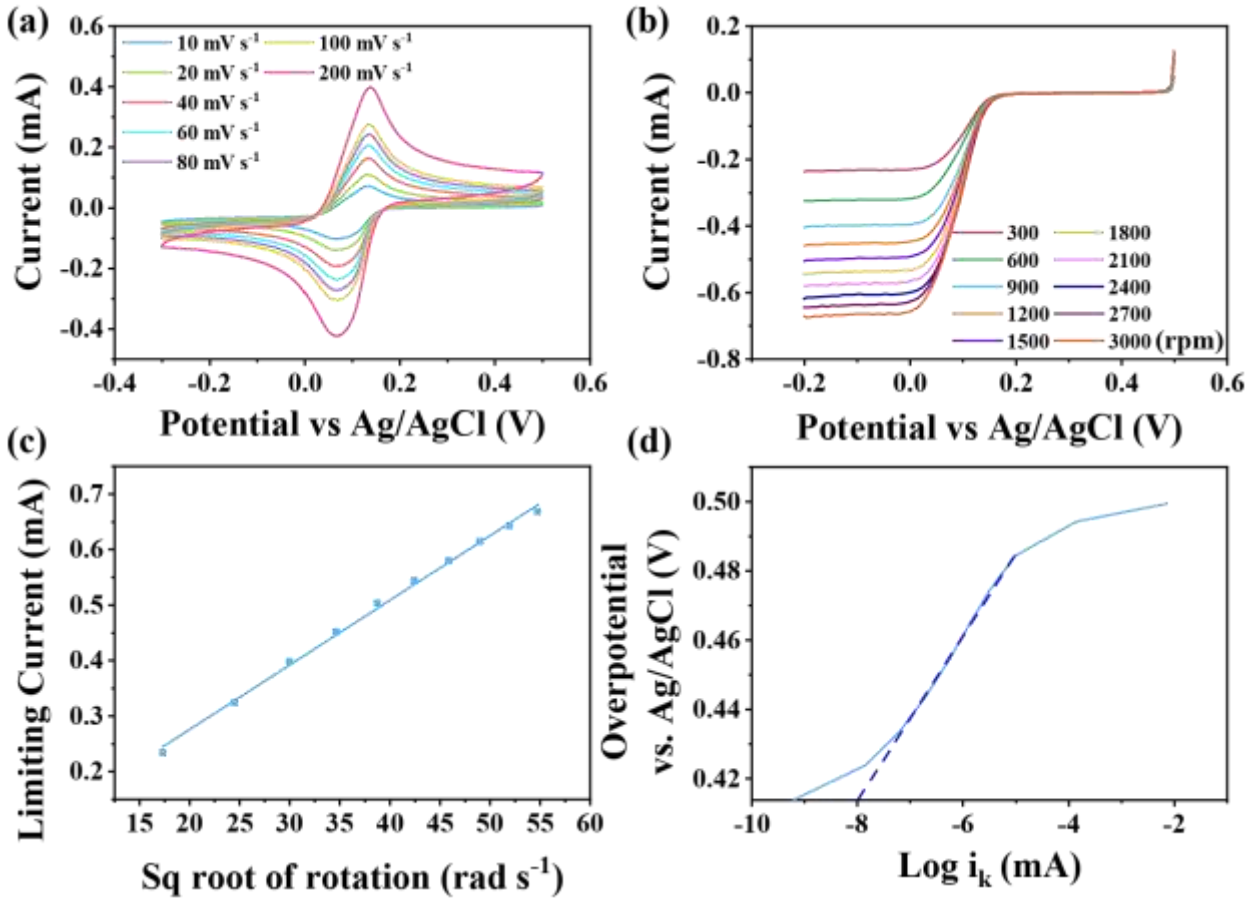


Figure S7: Electrochemical half-cell measurements of 10 mM IC-H in 3 M H_2SO_4. (a) CV of IC-H recorded between -0.3 V to 0.5 V vs. Ag/AgCl at scan rates ranging from 10 mV s^{-1} to 200 mV s^{-1}. (b) Rotating disk electrode measurements of 10 mM IC-H solutions in 3 M H_2SO_4 at nine rotation speeds ranging from 300 rpm to 3000 rpm with an increment of 300. (c) Levich plot (limiting current vs. sq. root of rotation) of IC-H, which is derived from (b). (d) The plots of overpotential versus the logarithm of kinetic current and the corresponding fitted Tafel plots for IC-H.

References:

1. Tong, L. Development of Organic Molecules for Aqueous Redox Flow Battery. 2018.