

Supporting information

Bioinspired flavin analogue as an organic electrode material for supercapacitor applications

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1. Calculation formula

The calculation formula for specific capacitance (C , F g^{-1}), energy density (E , W h kg^{-1}) and power density (P , kW kg^{-1}) based on the galvanostatic discharge curves of samples are shown as following:

Specific capacitances derived from galvanostatic tests can be calculated from the equation:

$$C = I\Delta t / m\Delta V \quad (1)$$

where I is the discharging current, t is the discharge time, ΔV is the potential drop during discharge, and m is the mass of active material in the working electrode.

$$\text{Capacitance} = I \times t / m \times V \quad (1)$$

Energy density (E) and power density (P) derived from galvanostatic tests can be calculated from the following equations:

$$\text{Energy density, } E = \frac{1}{2} \times CV^2 \times 1000/3600 \quad (2)$$

$$\text{Power density, } P = E/t \times 3600 \quad (3)$$

Where C is specific capacitance ($F g^{-1}$), t is discharge time (s), V is voltage applied, E is energy density ($Wh kg^{-1}$), P is power density ($W kg^{-1}$).

2. Experimental

2a. Materials

Beta alanine was purchased from SRL (98%). Fluoronitro benzene was obtained from Avra with 98% purity. 5% Pd/C was purchased from SRL. Alloxan monohydrate was obtained from SRL (98%). Other chemicals and reagents are purchased from commercial sources Sigma Aldrich, SRL, Alfa Aesar and TCI chemicals and used without purification. Nuclear magnetic resonance spectra were collected using a Bruker DRX-400 spectrometer. ^{13}C NMR spectra were collected at 100 MHz, and 1H NMR spectra were collected at 400 MHz. Resonances are reported in parts per million (ppm) and coupling constants, J, are reported in hertz (Hz). High resolution mass spectra was obtained by Electron Spray Ionization method (ESI) using Agilent QTOF 6538. UV-Visible spectral measurements were obtained from JASCO Spectrophotometer V730 and Fluorescence measurements were taken from JASCO Spectrofluorometer FP-8300. SEM samples were recorded using JEOL JIB-4700F instrument. For cross-sectional image recording, the cFI and FI based electrodes were used. All electrochemical measurements were performed on an Autolab PGSTAT 302 coupled with a frequency response analyzer (FRA) and NOVA 1.1 software for data analysis. X-ray photo electron spectra (XPS) were acquired on an Axis Supra K-ALPHA surface analysis

spectrometer that employed a monochromatic, micro focused Al-K α radiation of 1486.6 eV energy. BET data recorded on Micrometrics ASAP 2020 surface area and porosity analyzer.

2b. Experimental section

The chemical properties were qualitatively evaluated by ultraviolet-visible (UV-vis), Fluorescence, Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) and mass spectroscopy. The physical property of were characterized by FE-SEM.

2c. Details of device fabrication.

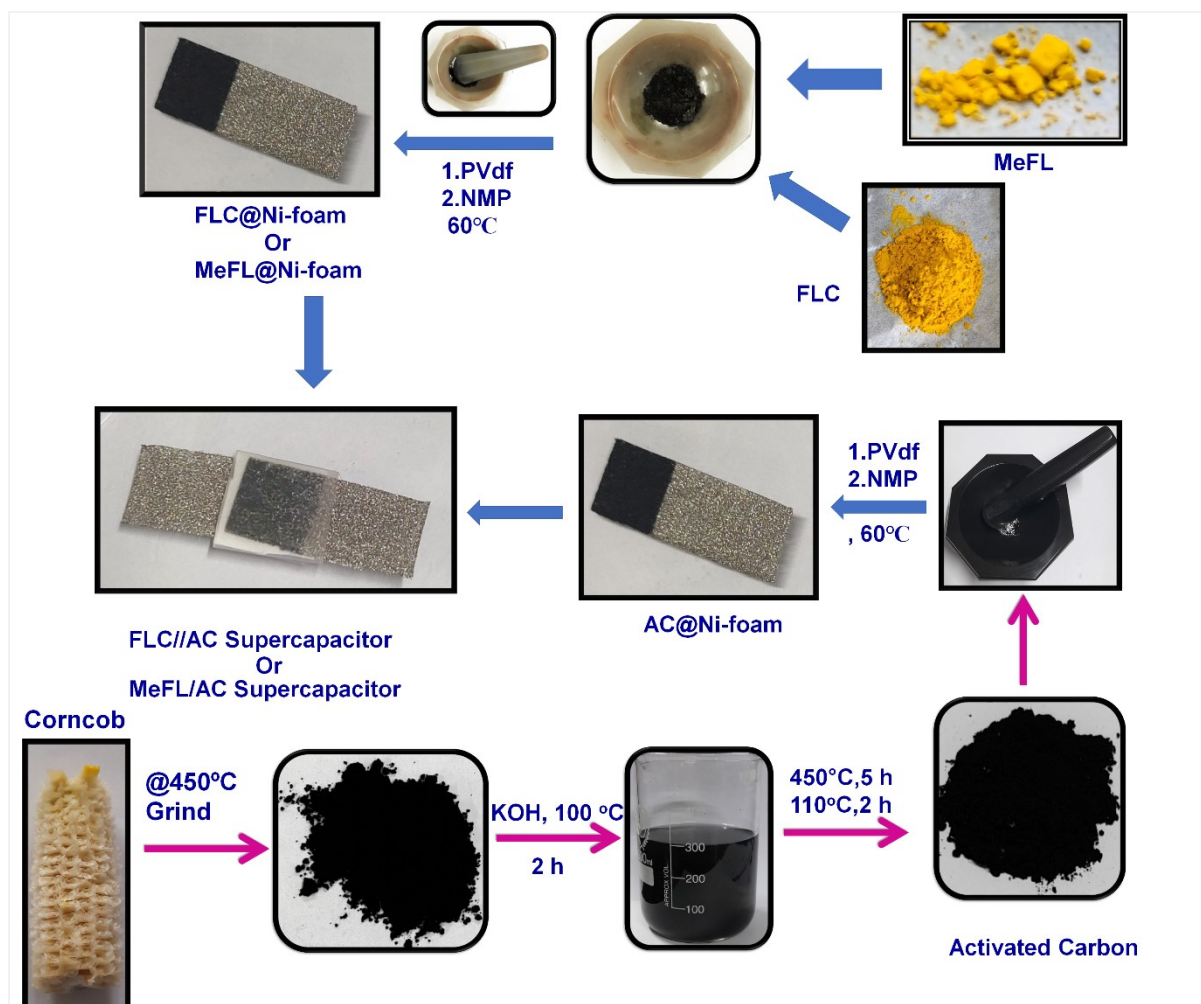


Figure S1. Fabrication pathway of flavin based asymmetric supercapacitor (*cFI//AC@NF* and *FI//AC@NF*).

The corncob was washed with deionized water and dried at 80°C overnight in a vacuum oven. The corncob derived hard carbon samples were prepared by pyrolysis of the cleaned corncob under argon flow in a tubular furnace at 450°C for 6h. The synthesized carbon was activated

by KOH solution (1 g of carbon was dispersed in a solution of 2 g KOH in 200 mL of ultrapure water) at 100°C for 2 h. Moreover, typically corncob precursor then kept immersed into KOH solution in room temperature for 24h, and then dried at 80°C. The dried corncob was carried out in a tubular furnace at 450°C for 5h. The carbonized corncob was first ground and then washed with 2M HCl and deionized water and dried at 110°C for 2 h in a vacuum oven, as shown in scheme S1 and was labelled as AC. The AC or **cFI** or **FI** electrode was fabricated by taking AC powder or **cFI** or **FI**, CB and PVdF in a weight ratio of 60:30:10 in a mortar, mixed thoroughly and dry ground with a pestle for a half an hour. A few drops of NMP were added and the mixture was ground for another half an hour resulting in the formation of a smooth homogeneous slurry. The slurry was coated on Ni-foams over an area of 1 cm × 1 cm and dried at 60°C in a vacuum oven for 12 h, to obtain the AC@Ni-foam electrodes. A few drops of an aqueous solution of the electrolyte were applied over a Whatman filter paper which was used as a separator. The electrolyte coated filter paper was sandwiched between the active electrodes, which yielded ASCs in the following configurations: **cFI//AC@NF** and **FI//AC@NF**. The cells were kept at rest for 12 h at room temperature. Figure S1 shows the fabrication of the **cFI//AC@NF** and **FI//AC@NF** electrodes.

3. Characterization

Compound 5

^1H NMR (400 MHz, DMSO-*d*6) δ 11.46 (s, 1H), 8.13 (d, $J = 7.9$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 7.95 (t, $J = 7.6$ Hz, 1H), 7.65 (t, $J = 7.5$ Hz, 1H), 4.88 – 4.74 (m, 2H), 3.66 (s, 3H), 2.91 – 2.74 (m, 2H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ 171.28, 160.14, 156.08, 150.84, 139.02, 135.57, 135.28, 132.74, 132.29, 126.56, 116.69, 52.21, 40.56, 30.79. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_4$: 323.0756 Found 323.0738.

cFl

^1H NMR (400 MHz, DMSO-*d*6) δ 11.45 (s, 1H), 8.14 (dd, $J = 8.1, 1.4$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 7.98 – 7.90 (m, 1H), 7.69 – 7.62 (m, 1H), 8.08 (t, $J = 8.08$, 2H), 2.73 (t, $J = 8.04$, 2H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ 172.38, 160.20, 156.15, 150.86, 139.10, 135.55, 135.31, 132.80, 132.27, 126.53, 116.73, 40.69, 31.02. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4$: 287.0702 Found 287.0771.

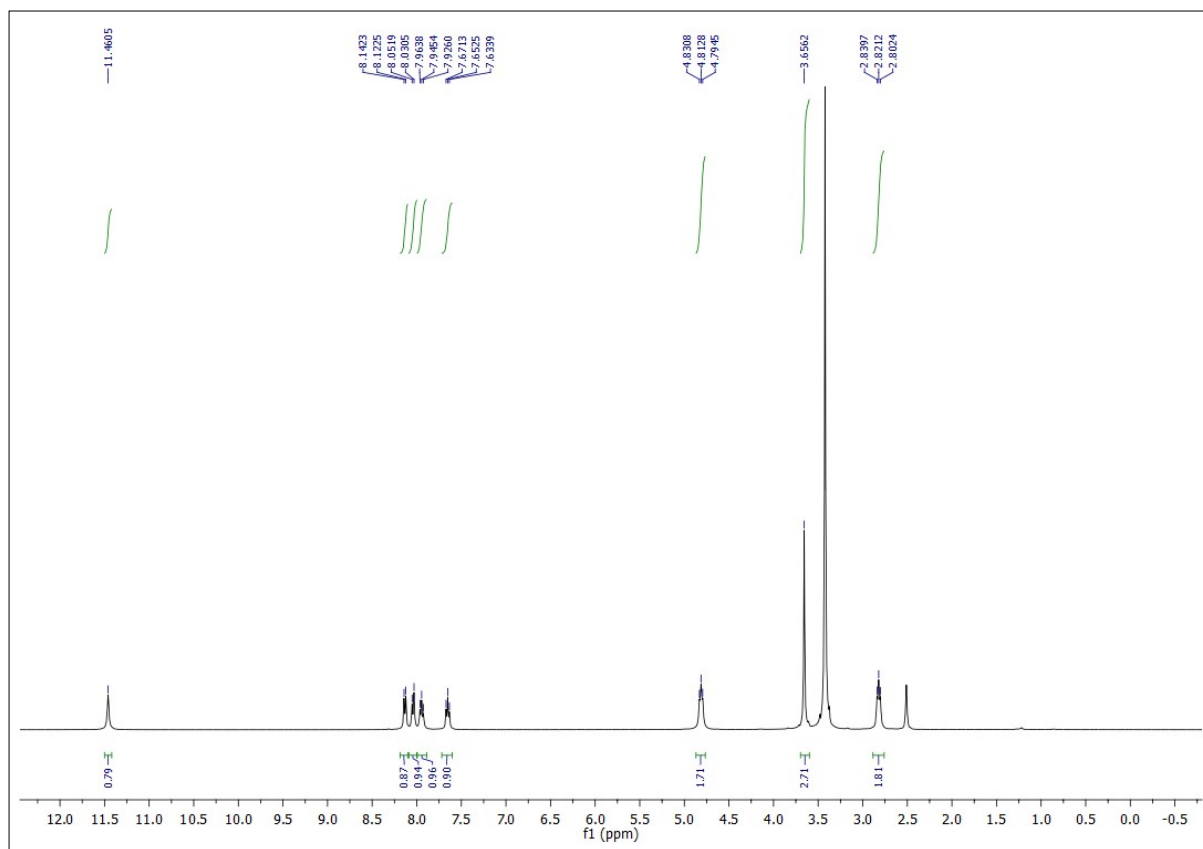


Figure S2. ^1H NMR of **5** in $\text{DMSO-}d_6$

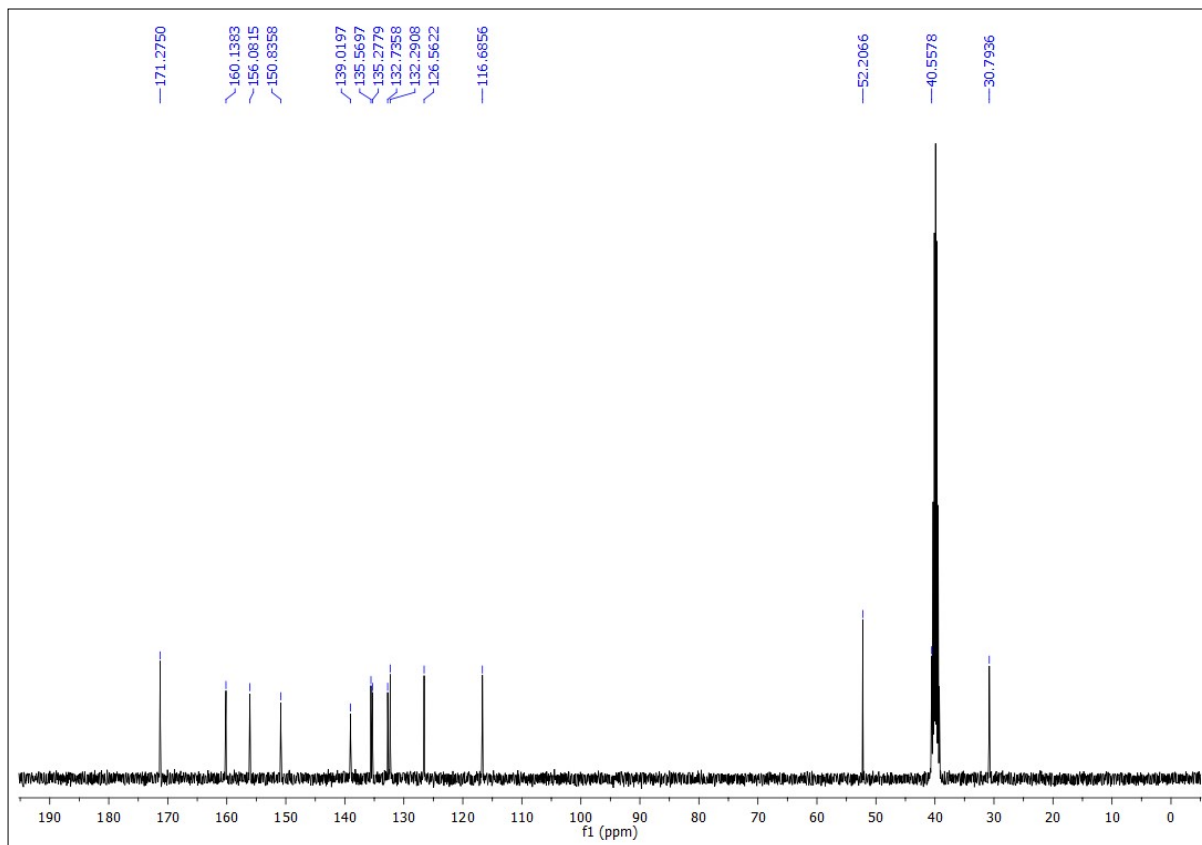


Figure S3. ^{13}C NMR of **5** in $\text{DMSO-}d_6$

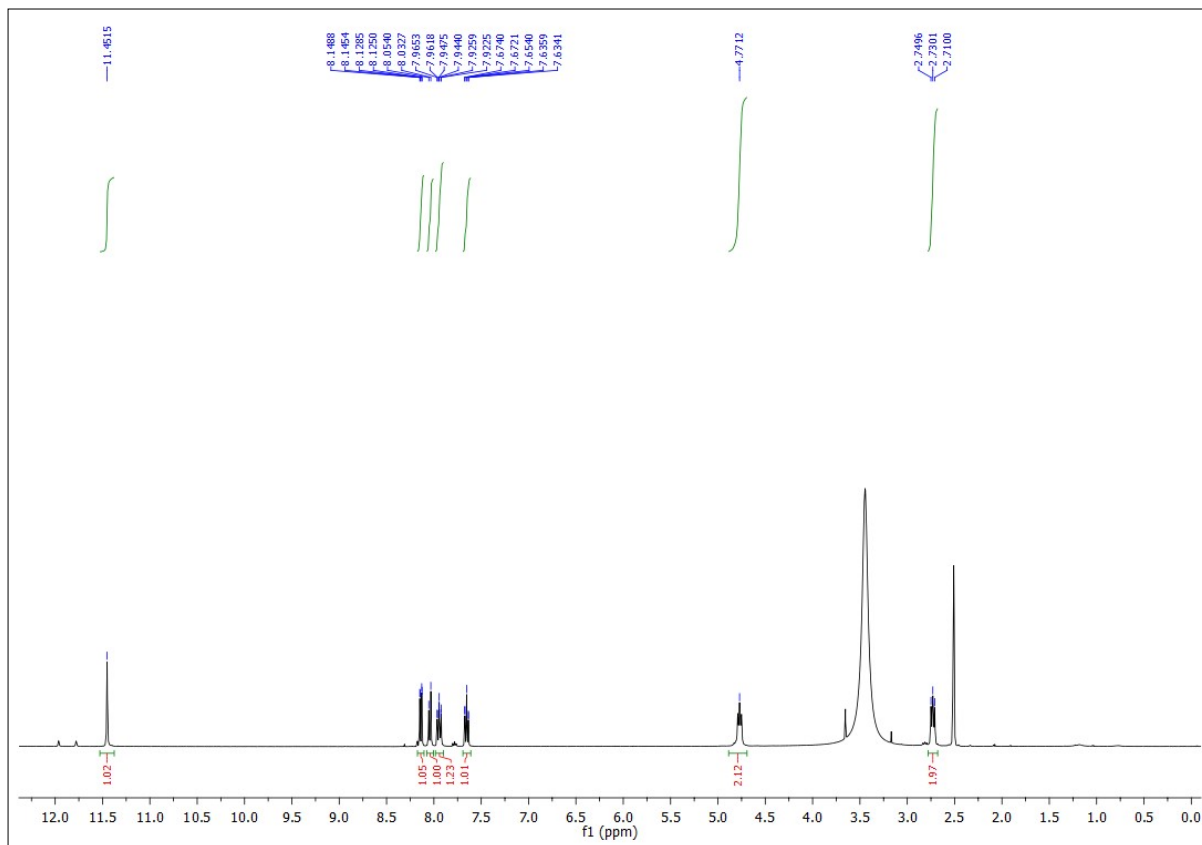


Figure S4. ^1H NMR of *cFl* in $\text{DMSO-}d_6$

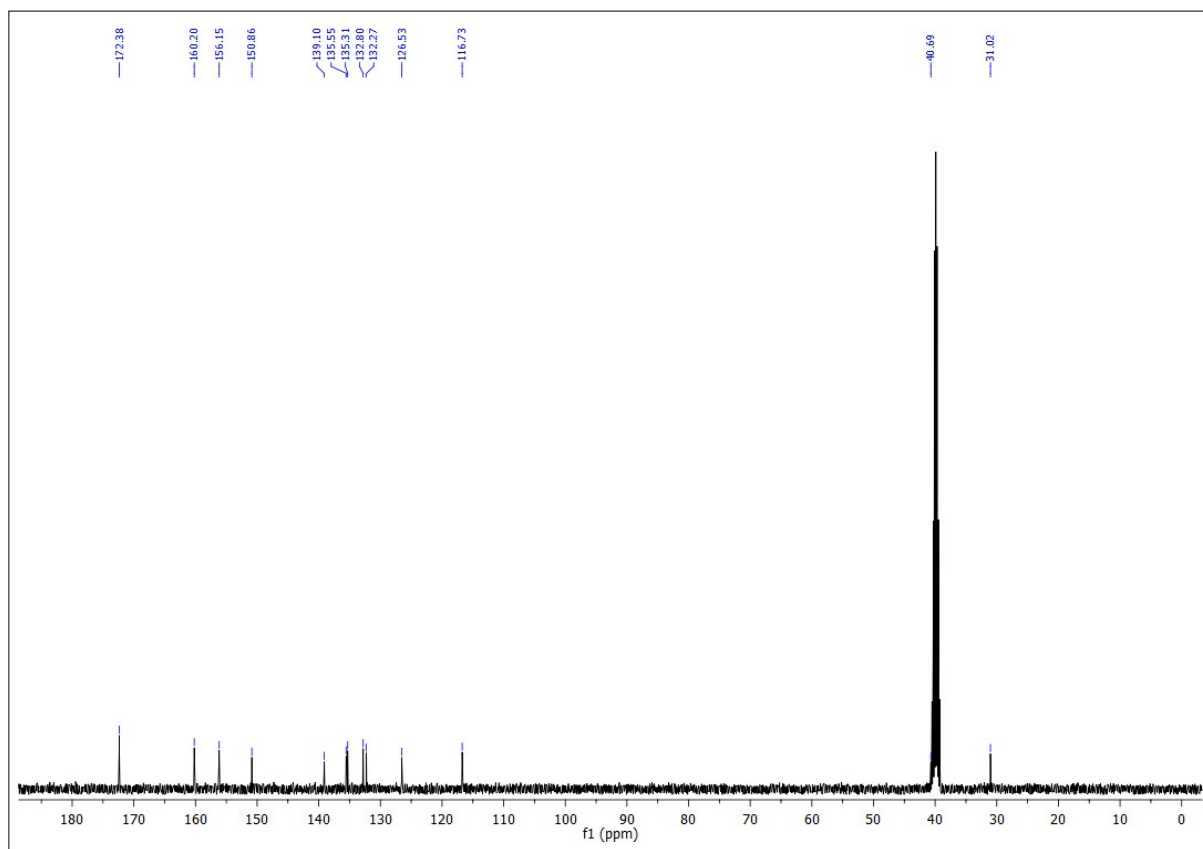


Figure S5. ^{13}C NMR of *cFl* in $\text{DMSO-}d_6$

List of HRMS spectra

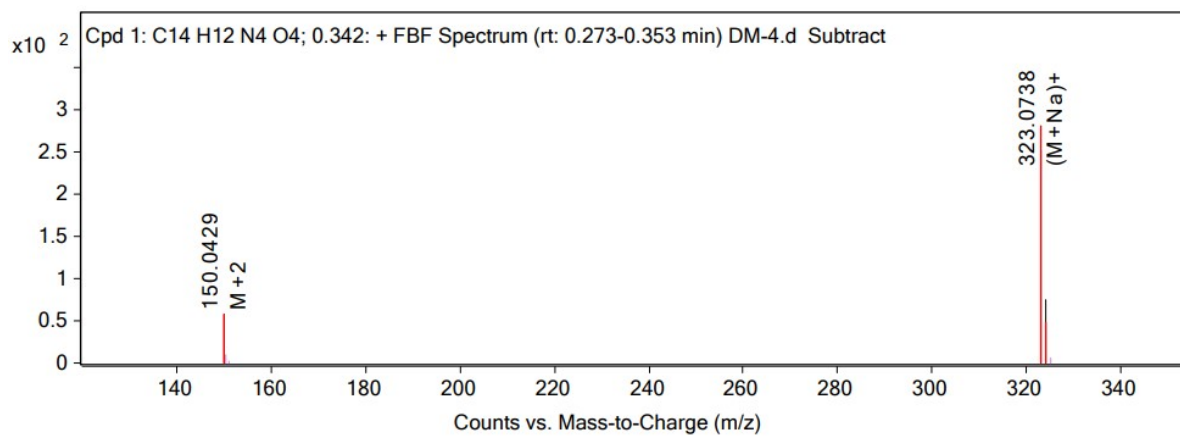


Figure S6. HRMS of **5**

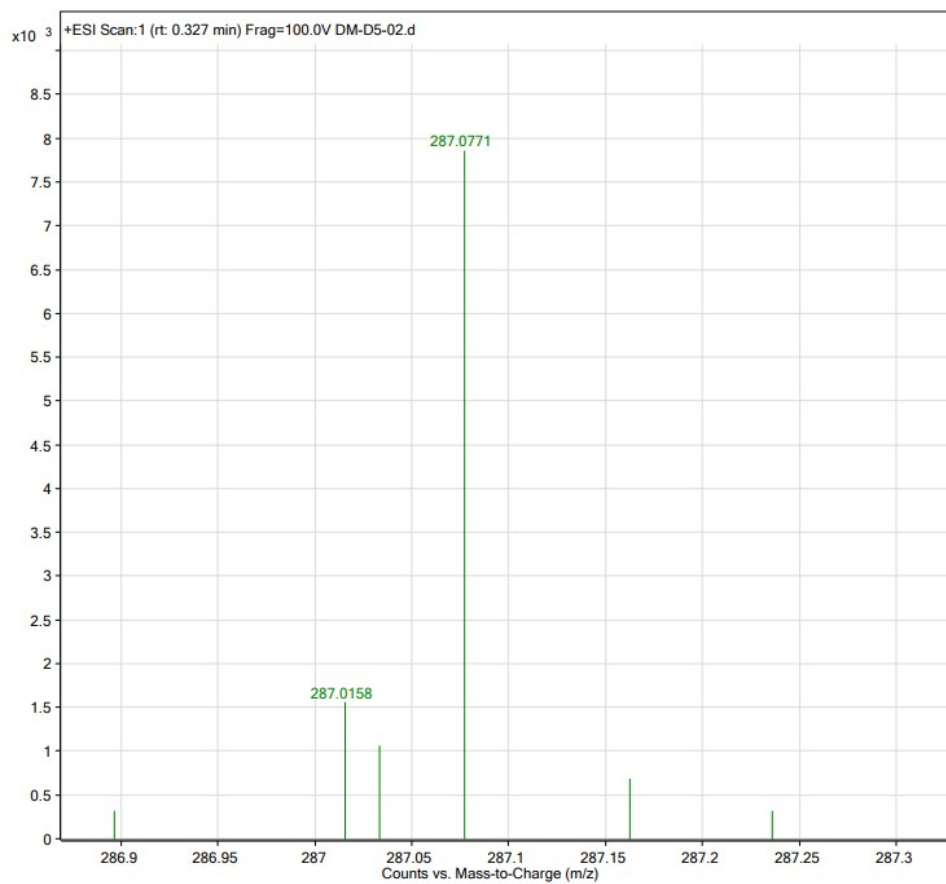


Figure S7. HRMS of *cFl*

FE-SEM images of *c*Fl and Fl

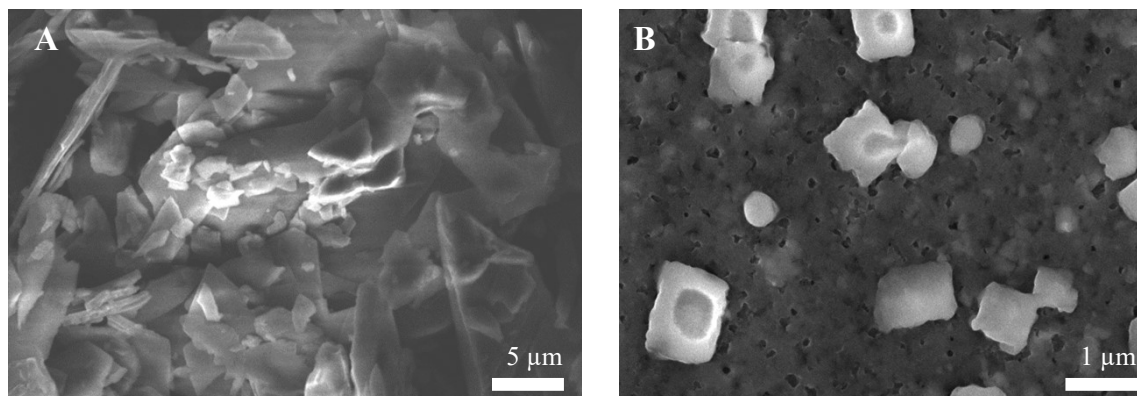


Figure S8. FE-SEM images of (A) *c*Fl and (B) Fl (conc of flavins = 0.5 mM)

N₂ adsorption/desorption isotherms (BET study)

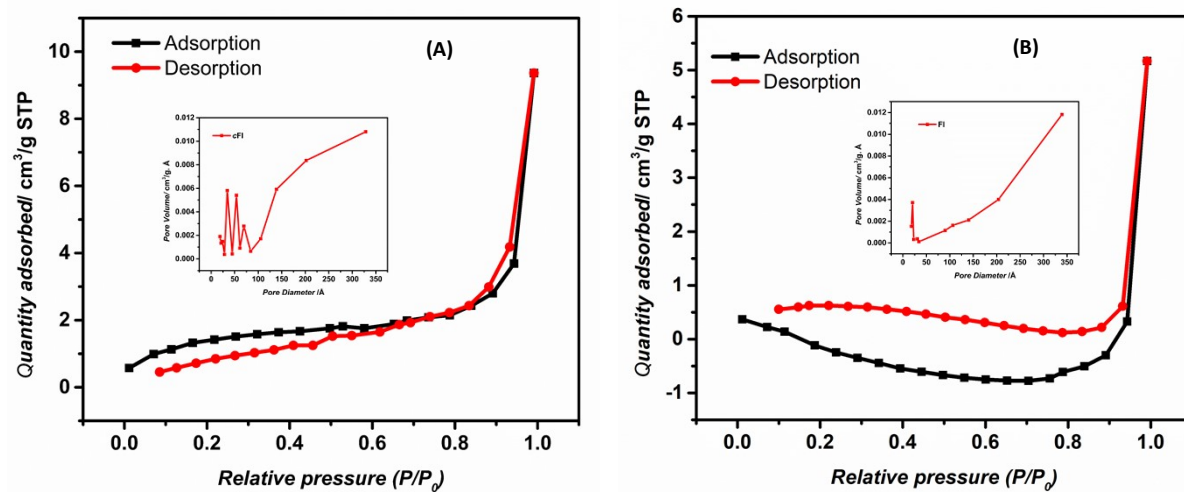


Figure S9. BET plot of (A) cFl and (B) Fl, inset shows the BJH plot

Electrochemical cycling performance

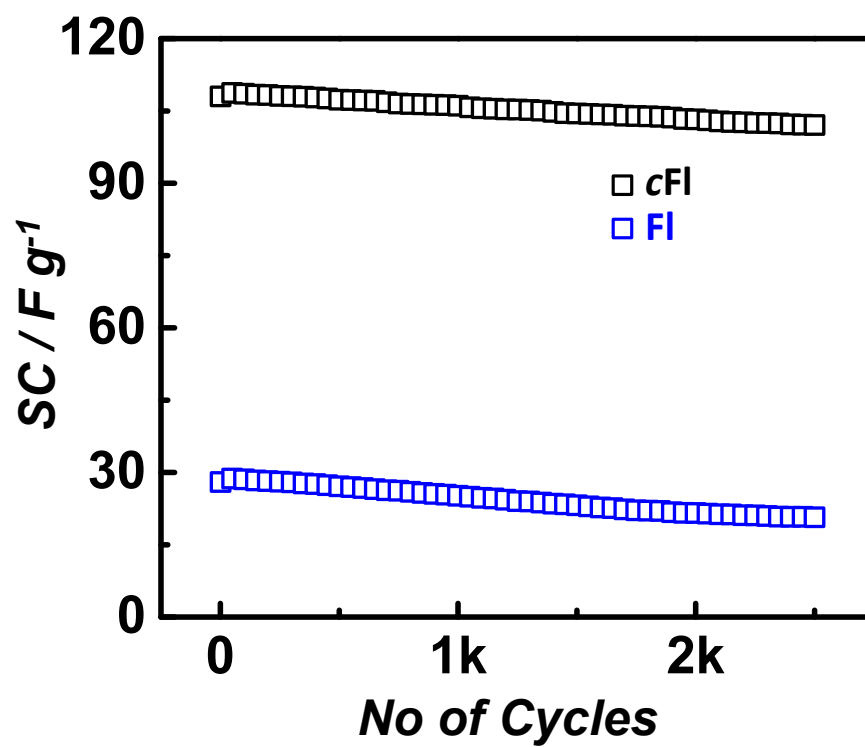


Figure S10. Electrochemical cycling performance of cFl//AC and Fl//AC ASCs over 2500 cycles at a current density of $4 A g^{-1}$

Photophysical property of *c*Fl and Fl

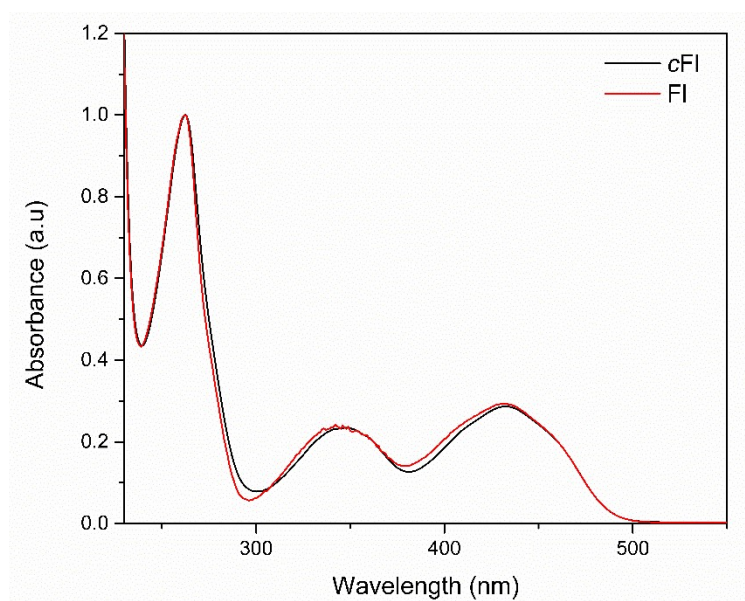


Figure S11. Normalized UV-Vis absorption spectra of *c*Fl and Fl (solvent = methanol, concentration of flavins = 30 μ M, room temp)

Photophysical property of cFl and Fl

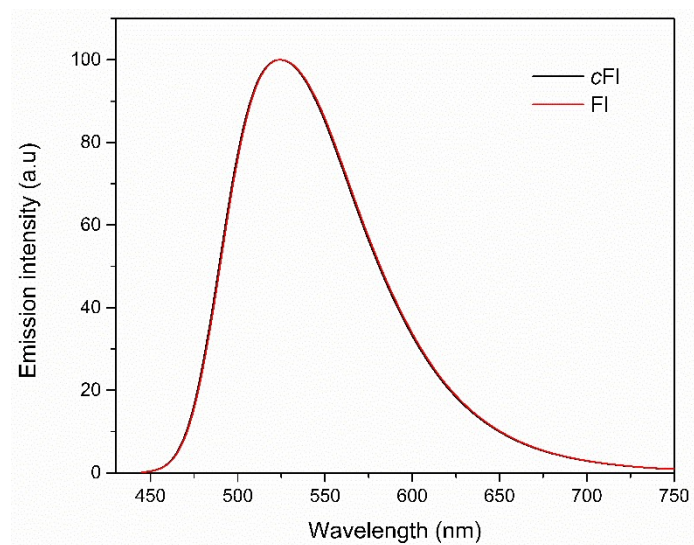


Figure S12. Normalized emission spectra of **cFl** and **Fl** (Excitation wavelength = 433nm, solvent = methanol, concentration of flavins = 30 μ M, room temp)

Cyclic voltammetry of cFl and Fl in aqueous medium

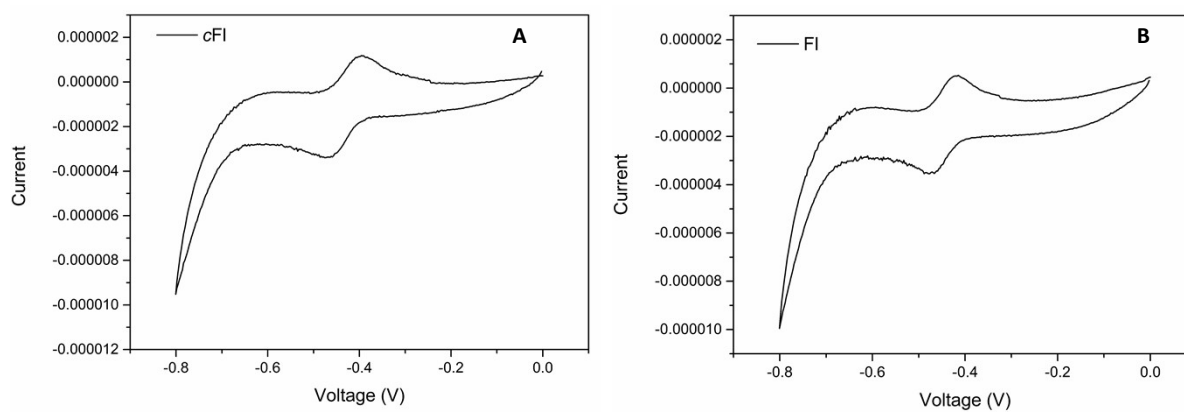


Figure S13. Cyclic voltammetry of (A) cFl and (B) Fl in Tris buffer (supporting electrolyte = KCl, Reference electrode = Ag/AgCl, Counter electrode = Pt; conc of flavins = 1 mM, conc of KCl = 1M).

Table S1. Comparison of energy density of **cFI//AC** with reported organic supercapacitor based electrodes.

S. no	Materials	Energy density (Wh kg⁻¹)	References
1	Poly-peryene-3,4,9,10-tetracarboxydiimide-anthraquinone modified on reduced graphene oxide	19.8	46
2	4,5-trihydroxybenzamide and graphene oxide system	14	47
3	Poly(4-amino-diphenylamine) (P(4-ADPA))	24.4	48
4	Naphthalene diimide derivative (NDI) modified on reduced graphene oxide	26.3	49
5	3,4,9,10-perylenetetracarboxylic acid (PTCA) immobilized on reduced graphene oxide (rGO ₁)	14	50
6	Riboflavin-functionalized activated carbon	58.6	51
7	Quinone-amine co-doped on porous carbon nanospheres (PCNs)	65.8	52
8	cFI//AC	38	Our paper