

# Supplementary Information

## Electrochemical Energy Storage Enhanced by intermediate Layer Stacking of Heteroatom-Enriched Covalent Organic Polymers in Exfoliated Graphene

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## **General Information**

**1.1. Chemicals:** Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), Nafion, Isopropyl alcohol (IPA), Resorcinol were purchased from Spectrochem India. 1,3,4-Thiadiazole-2,5-diamine was purchased from BLD pharm. All the chemical reagents were analytical grade and used directly without further purification. All the aqueous solutions were made using Deionized (DI) water.

## **1.2. Material characterization**

**Infrared Spectroscopy:** COP, exfoliated graphene (EGR), and RTh-COP-EGR nanohybrid were characterized using the FTIR BRUKER VERTEX 70 Sr. 2236 FTIR instrument at room temperature.

**<sup>13</sup>C solid-state NMR spectroscopy** To confirm structural analysis, Bruker NMR400 instrument was used.

**Powder X-ray diffraction:** To analyze the crystallinity of covalent organic polymers, Powder X-ray diffraction (PXRD) analysis was conducted using a Bruker D8 Advanced instrument, which employs Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The analysis was performed over a  $2\theta$  range of  $5^\circ$  to  $60^\circ$ , with an acceleration voltage of 40 kV.

**X-ray photoelectron spectroscopy:** X-ray photoelectron spectroscopy (XPS) was conducted to determine the bonding configuration and surface elemental composition using a K-Alpha 1063 spectrometer in an ultrahigh vacuum chamber at  $7 \times 10^{-9}$  torr.

**Field Emission Scanning electron microscopy (FESEM)** The Field Emission Scanning Electron Microscope (SEM) Jeol JSMIT300 was utilized to characterize the detailed surface morphology further.

**Transmission electron microscope (TEM)** was conducted using the JEM 2100 instrument

## **1.3. Electrochemical characterizations**

All cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted using the Biologic VSP-128 system electrochemical workstation. The measurements utilized a three-electrode assembly, consisting of a glassy carbon electrode (GCE) with a surface area of 0.071 cm<sup>2</sup> as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (3.5 M KCl) reference electrode, all in a 1 M H<sub>2</sub>SO<sub>4</sub> solution.

#### 1.4. Electrode fabrication

The glassy carbon electrode (GCE) was selected for the supercapacitor study. Before drop-casting, the surface of the GCE was cleaned with 0.05 μm alumina, followed by ultrasonic treatment in deionized water (DI) and isopropyl alcohol (IPA), then purged with inert argon gas to eliminate any surface impurities. The COP-EGR ink was prepared by mixing a quantitative amount of COP-EGR nanohybrid in a 1:1 (v/v) ratio of water and IPA, with 5% Nafion added to a total volume of 1 mL. The GCE was coated with a loading of 0.6 mg cm<sup>-2</sup>.

#### 1.5. Crystallite site determination

(a) Crystallite sizes were determined using Debye-Scherrer formula

$$\text{Crystallite size } D = \frac{K \lambda}{\beta \cos \theta}$$

Where, K denotes Scherrer constant, λ: wavelength of wavelength, β: full width half maxima and θ: diffraction angle.

(b) The general expression that gives the crystallite size ( $L_a$ ) from the integrated intensity ratio  $I_G/I_D$  by using any laser line in the visible range is given by the equation.

$$L_a(nm) = (2.4 \times 10^{-10})(\lambda_l^4) \left[ \frac{I_G}{I_D} \right]$$

Where  $\lambda_l$  is laser line wavelength (532 nm) and  $[I_D/I_G]$  is ratio of D- and G- band intensities.

## 1.6. Specific Capacitance Calculations

The areal-specific capacitance  $C_{sp}$  (mF cm<sup>-2</sup>) can be calculated from cyclic voltammetry (CV) from the following equation

$$C_{sp} = \frac{I(V)}{2 \cdot A \cdot v \cdot V} \quad (i)$$

where  $A$  (in cm<sup>2</sup>) is the geometric area,  $v$  is the voltage scan rate (V s<sup>-1</sup>),  $V$  (in V) is the potential window of the CV curves, and  $I(V)$  is current at different potentials.

Alternatively, the specific capacitance for the electrodes can be obtained from GCD data using the following equation.

$$C_{sp} = \frac{I}{A \frac{dV}{dt}} \quad (ii)$$

Where  $C_{sp}$  is the specific capacitance (mF cm<sup>-2</sup>),  $I$  is current (A),  $dV/dt$  is the discharge slope after the  $IR$  drop, and  $A$  is the geometrical area of the single electrode.

The area normalized energy density  $E_A$  and power density  $P_A$  were calculated from galvanostatic GCD curves by the following equations

$$E_A = \frac{1}{2} \cdot \frac{C_{sp} \cdot \Delta V^2}{3.6} \quad (iii)$$

$$P_A = \frac{E}{\Delta t} \cdot 3.6 \quad (iv)$$

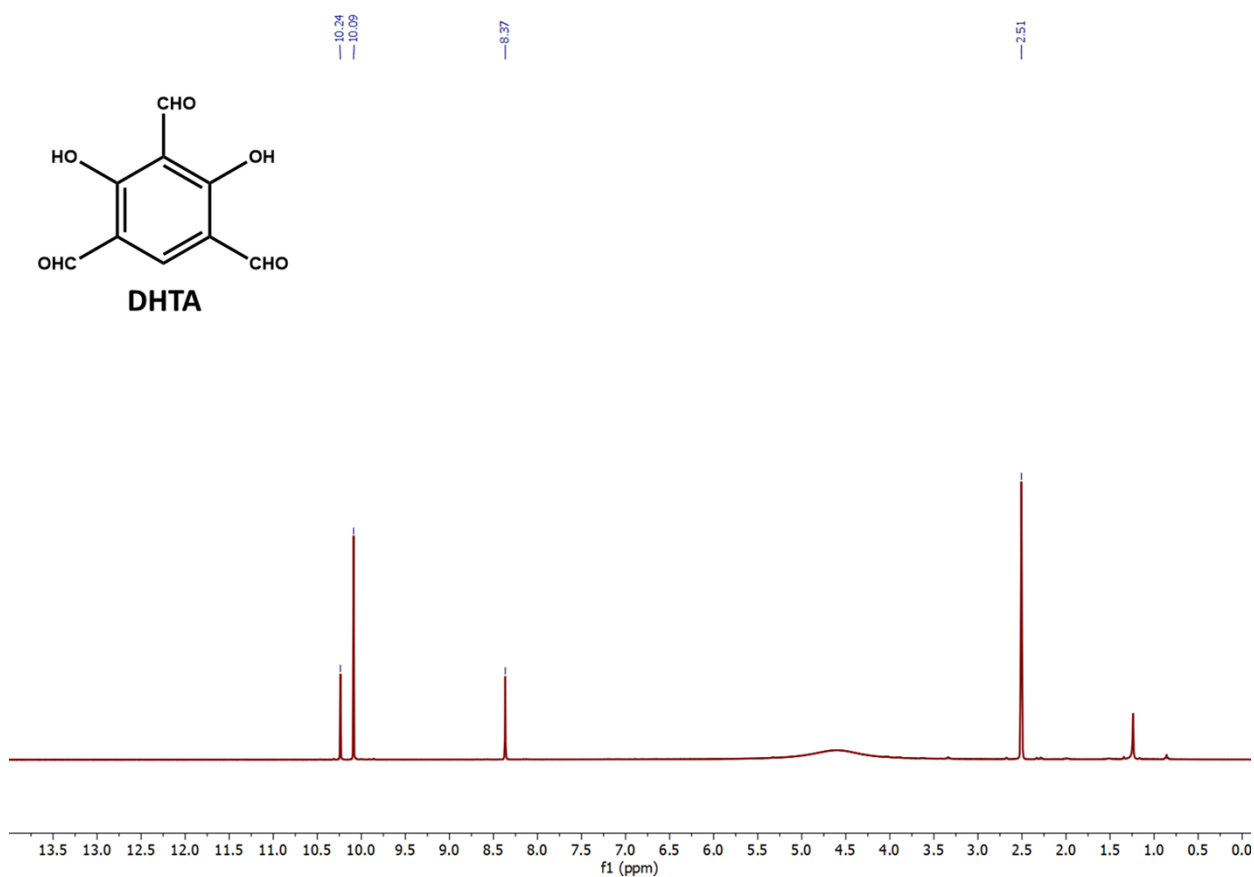
where  $E_A$  is the energy density (m Wh cm<sup>-2</sup>),  $P_A$  is the power density (kW cm<sup>-2</sup>),  $C_{sp}$  is the specific capacitance,  $\Delta V$  is the potential window ( $\Delta V = V_{max} - V_{drop}$ ),  $\Delta t$  is the discharge time (s).

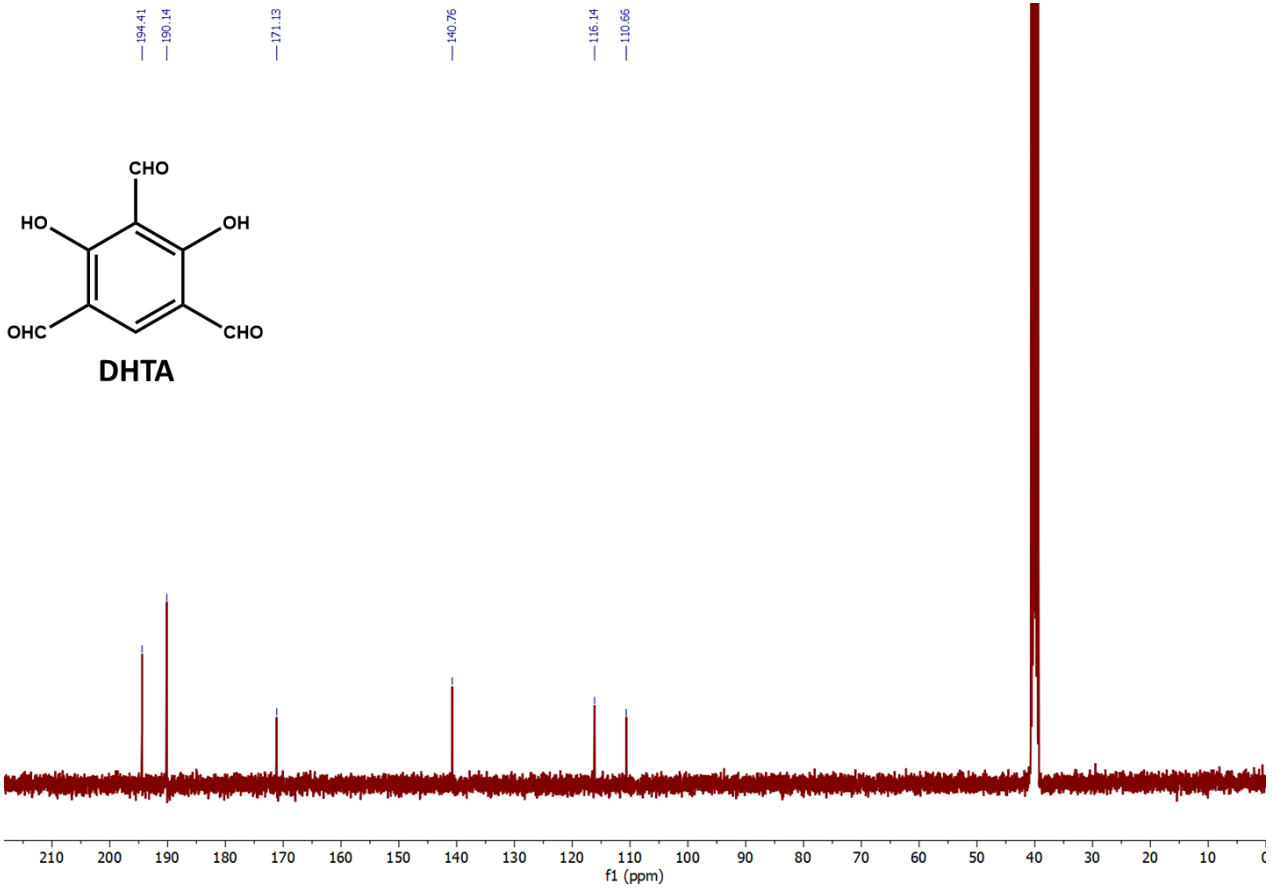
## 1.7. Experimental section:

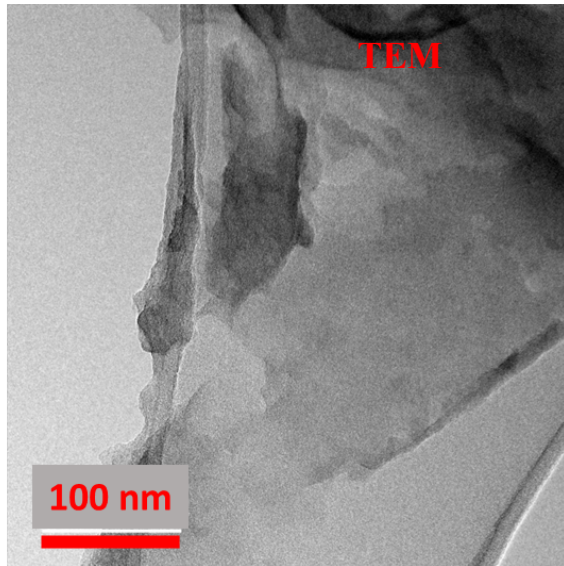
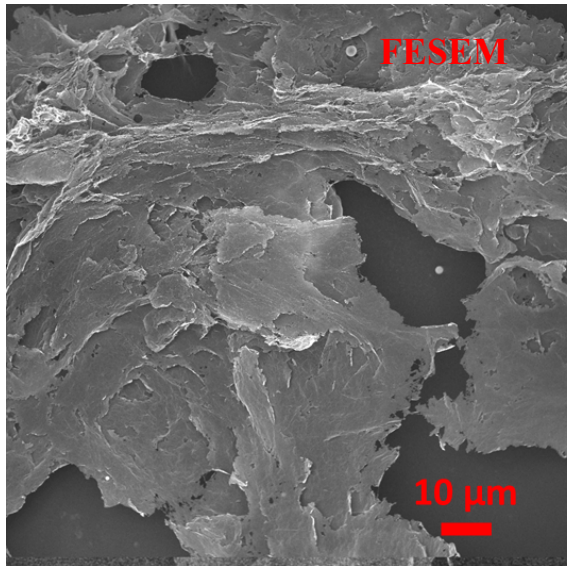
### Synthesis of 2,4-dihydroxy-1,3,5-triformylcarbaldehyde (DHTA):

This molecule was synthesized following the reported procedure.<sup>1</sup> 2.75 g (25 mmol, 1 eq.) of resorcinol and hexamethylenetetramine 7.7 g (55 mmol, 1.1 eq.) was charged into an oven dried 100 mL round bottom flask. Then 50 mL trichloroacetic acid was gradually added into the flask at 0 ° C under argon atmosphere. Then, the mixture was heated to 130 ° C for 16 h followed by heating at 150 ° C at 3 h. Then the solution was cooled to 100 ° followed by the addition of 40 mL 3M HCl and again heated to 105 ° C for another 30 min. Obtained yellow precipitate was filtered, washed with ethanol thoroughly and dried under vacuum.

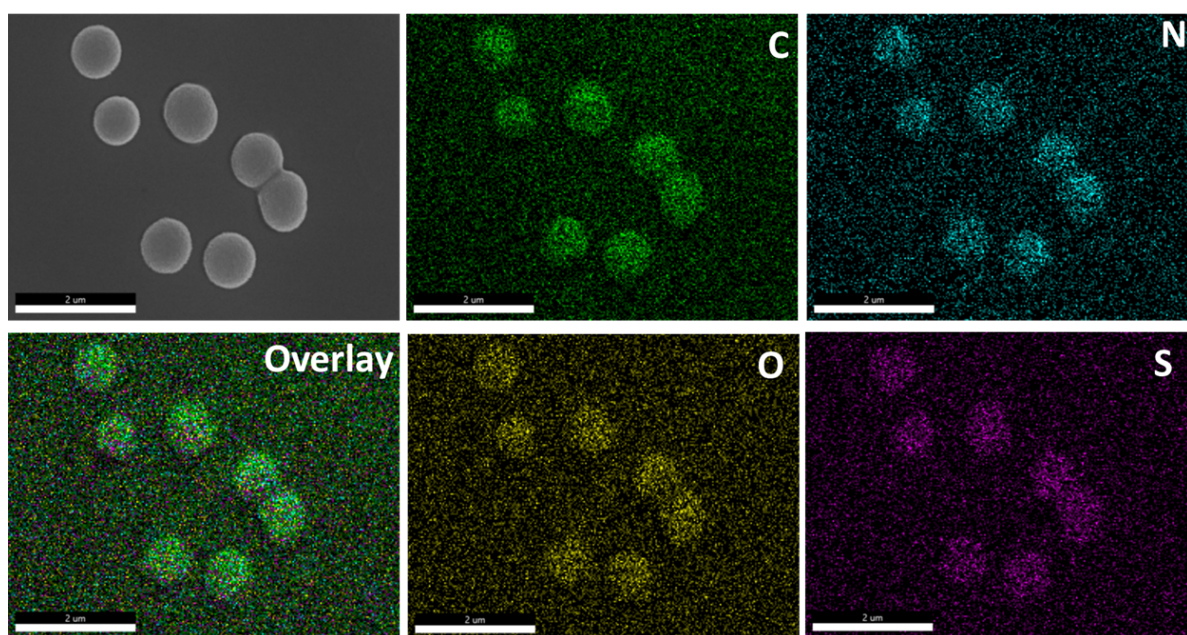
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ= 10.24 (s, 1H), 10.09 (s, 2H), 8.37 (s, 1H). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>): δ= 194.41, 190.14, 171.13, 140.76, 116.14, 110.66.





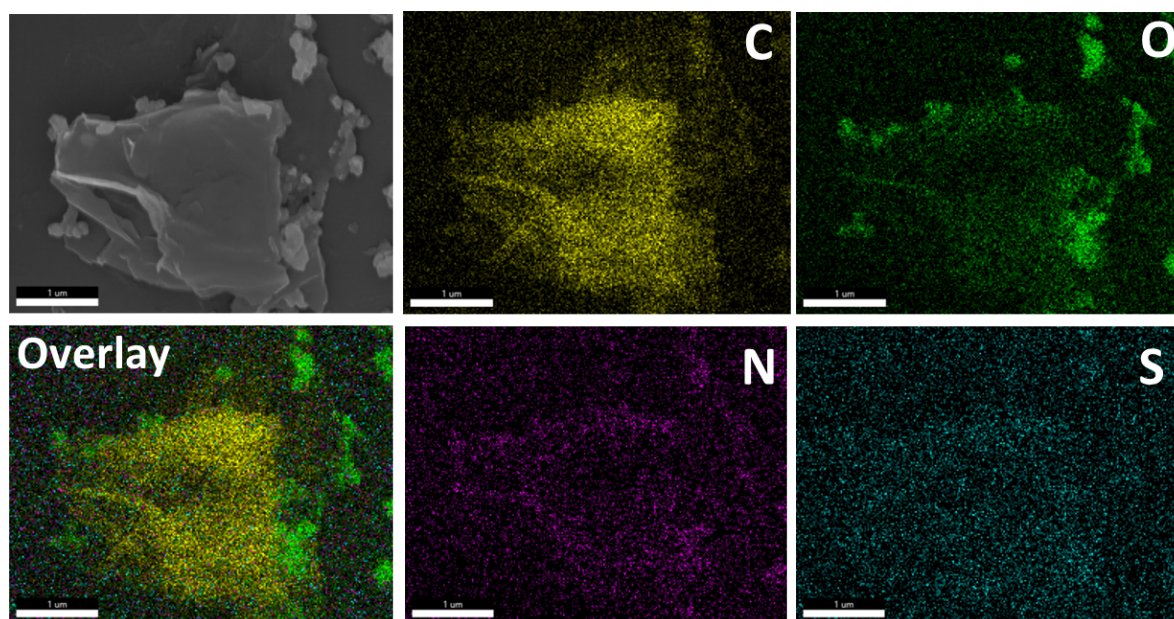


**Fig. S1** FESEM and TEM image of Graphene



**Fig. S2** Elemental mapping of RTh-COP confirming uniform distribution of constituent C, N, S, O elements.





**Fig. S3** Elemental mapping of RTh-COP-EGR confirming uniform distribution of constituent C, N, S, O elements denoting successful incorporation of RTh-COP material within graphene layers.

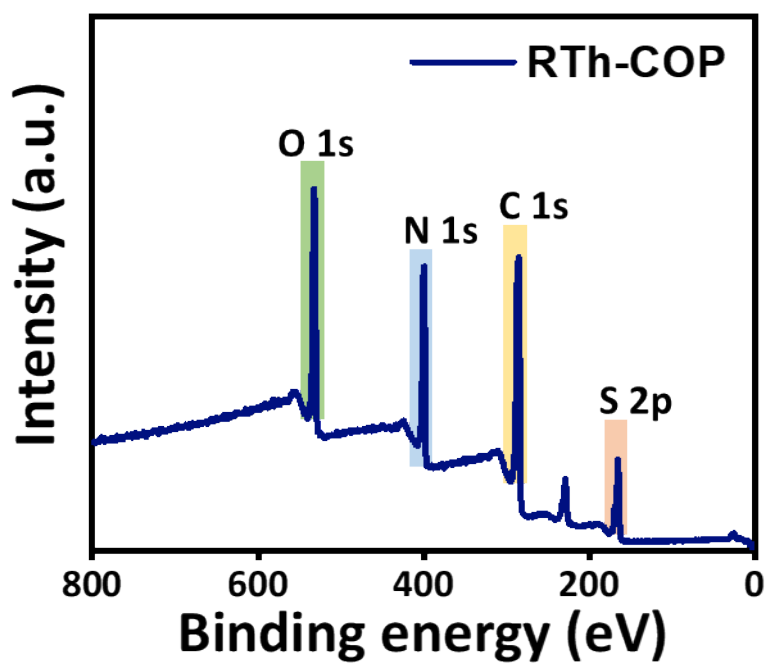


Fig. S4 XPS survey spectra of RTh-COP

| Elements | Atomic % |
|----------|----------|
| S 2p     | 7.28     |
| C 1s     | 54.11    |
| N 1s     | 20.74    |
| O 1s     | 17.87    |

**Table S1** Elemental composition of RTh-COP obtained from XPS survey.

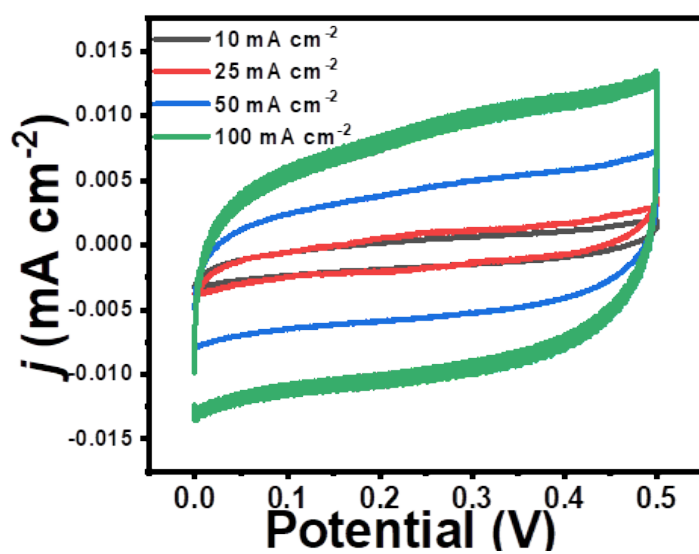


Fig. S5 CV plot at different scans of RTh-COP

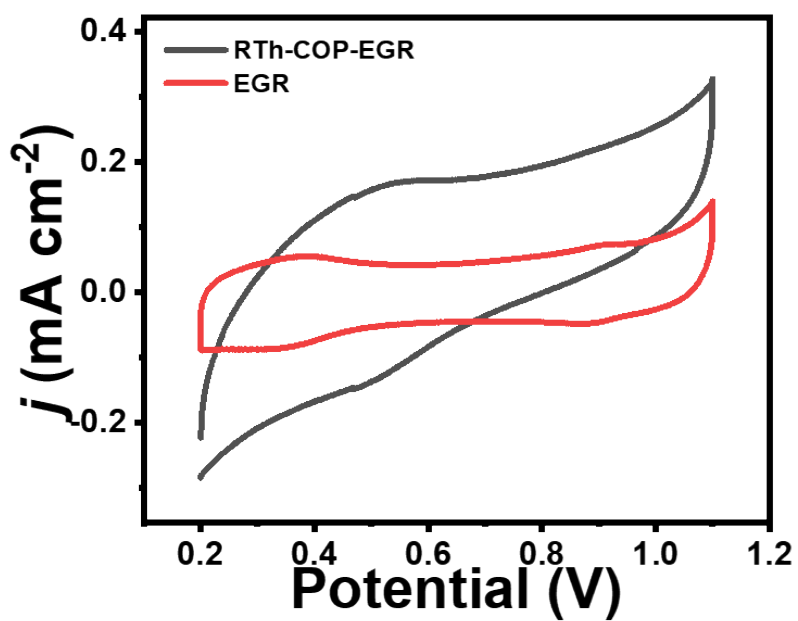


Fig. S6 CV plot @  $50 \text{ mV s}^{-1}$  of RTh-COP-EGR and EGR

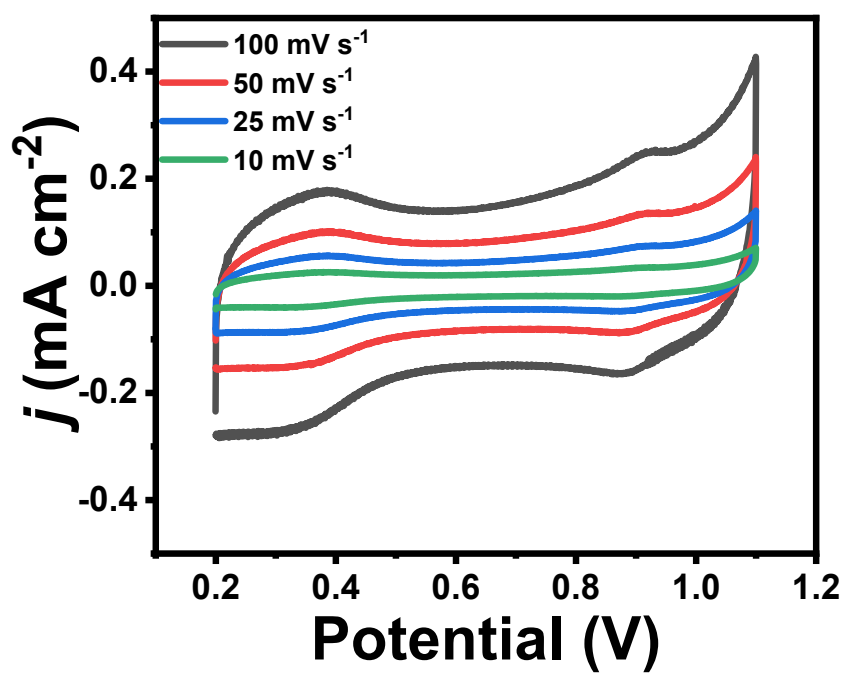


Fig. S7 CV plot for EGR at different scan rate

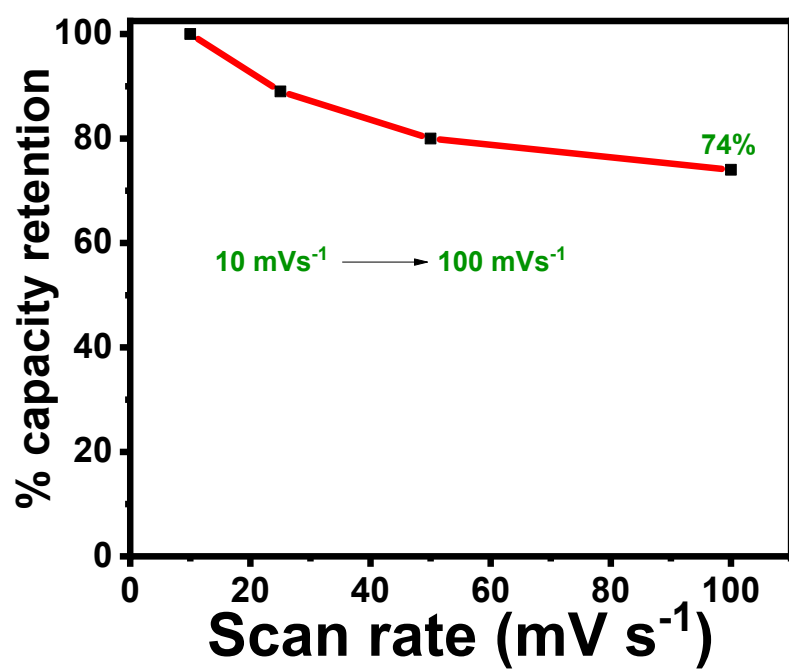


Fig. S8 Rate capability plot for RTh-COP-EGR

| S.No. | Material                          | Capacitance                | Cycle Number/Capacity retention | Energy density              | Power density            | Reference        |
|-------|-----------------------------------|----------------------------|---------------------------------|-----------------------------|--------------------------|------------------|
| 1.    | Large area porphyrin-COF nanofilm | 0.99 mF cm <sup>-2</sup>   | 5000/91%                        | 67.2 mWh cm <sup>-3</sup>   | 3.46 W cm <sup>-3</sup>  | <sup>2</sup>     |
| 2.    | Alpha-Co(OH) <sub>2</sub> /rGO    | 273.86 mF cm <sup>-2</sup> | 2000/99.35%                     | 20 mWh cm <sup>-2</sup>     | 56 mW cm <sup>-2</sup>   | <sup>3</sup>     |
| 3.    | COF-nanofilm                      |                            | 5000/77%                        | 318 mWhcm <sup>-2</sup>     | 6 W cm <sup>-2</sup>     | <sup>4</sup>     |
| 4.    | Polypyrrole-Polyimide COF         | 358 mF cm <sup>-2</sup>    | 3000/83%                        | 145 μWhcm <sup>-2</sup>     | 4509 μW cm <sup>-2</sup> | <sup>5</sup>     |
| 5.    | TpOMe-DAQ COF film                | 1600 mF cm <sup>-2</sup>   | 50000/65%                       | 2.9 μWh cm <sup>-2</sup>    | 61.8 μW cm <sup>-2</sup> | <sup>6</sup>     |
| 6.    | Ketoenamine COF                   | 88 mF cm <sup>-2</sup>     | 10000/200%                      | 148 μWh cm <sup>-2</sup>    | 7100 μW cm <sup>-2</sup> | <sup>7</sup>     |
| 7.    | Thiadiazole-COP/Graphene          | 4.2 mF cm <sup>-2</sup>    | 10,000/82%                      | 0.4725 mWh cm <sup>-2</sup> | 314.4 W cm <sup>-2</sup> | <b>This work</b> |

**Table S2:** Comparison of RTh-COP-EGR with other supercapacitor material.



## References

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