Supporting Information for

Tuning the Electronic Energy Level of Covalent Organic Framework for Crafting High-rate Na-ion Battery Anode

Sattwick Haldar,^{ab} Dhananjayan Kaleeswaran,^a Deepak Rase,^{ab} Kingshuk Roy,^{ac} Satishchandra Ogale^{bcd} and Ramanathan Vaidhyanathan^{ab*}

1. General information

General remarks:

Phloroglucinol, 4-aminobenzonitrile, 6-amino-3-pyridinecarbonitrile, terphenyl diamine were purchased from Sigma Aldrich; hexamine and trifluroacetic acid (TFA) were purchased from Avra Synthesis Pvt Ltd. All other reagents were of analytical grade. All chemicals were used without any further purification.

Powder X-ray diffraction:

Powder XRDs were carried out using a full-fledged Bruker D8 Advance and Rigaku Miniflex instruments. The data analysis was performed using the Reflex module of the Materials Studio V6.0.

Thermo-gravimetric analysis:

Thermo-gravimetric analysis was carried out on NETSZCH TGA-DSC system. The TGAs were done under N₂ gas flow (20ml/min) (purge + protective) and samples were heated from RT to 600 $^{\circ}$ C at 5 K/min.

¹³C Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy:

High-resolution solid-state NMR spectrum was recorded at ambient pressure on a Bruker AVANCE III spectrometer using a standard CP-TOSS pulse sequence (cross polarization with total suppression of sidebands) probe with 4 mm (outside diameter) zirconia rotors. Cross-polarization with TOSS was used to acquire ¹³C data at 100.37 MHz. The ¹³C ninety-degree pulse widths were 4 μ s. The decoupling frequency corresponded to 72 kHz. The TOSS sample-spinning rate was 5 kHz. Recycle delays was 2s.

Infra-Red Spectroscopy:

IR spectra were obtained using a Nicolet ID5 attenuated total reflectance IR spectrometer operating at ambient temperature. The solid state IR spectra were recorded using KBr pellets as background.

Field Emission-Scanning Electron Microscopy (FE-SEM):

Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford X-max instruments 80mm₂. (Carl Zeiss NTS, Gmbh), Imaging conditions: 2 kV, WD= 2 mm, 200 kX, Inlens detector. For SEM images, as an initial preparation, the samples were ground thoroughly,

soaked in ethanol for 30 min. and were sonicated for 2 hrs. These well-dispersed suspensions were drop casted on silicon wafer and dried under vacuum for at least 12 hrs.

High resolution Transmission Electron Microscopy (HR-TEM):

Transmission electron microscopy (TEM) was performed using JEM 2200FS TEM microscope operating at an accelerating voltage of 200 kV). The diffractograms were recorded at a scanning rate of 1° min⁻¹ between 20° and 80°.

Adsorption study

Adsorption studies were carried out using a Micromeritics 3-FLEX pore and surface area analyser.

Electrochemical Measurements:

The constant current charge-discharge measurements were performed using AMETEK Battery analyser using VERSA STUDIO (Version 2.61 beta) software. The cyclic voltammetry and potentiostatic electrochemical impedance studies were performed in PARSTAT Multichannel electrochemical workstation.

Impedance data fitting was done using Z- view software (version 3.4).

2. Materials and methods for monomer synthesis:

Synthesis of 2, 4, 6-triformylphloroglucinol:

About 90 mL trifluoroacetic acid was added to dried phloroglucinol (6.014 g) and stirred for 15 mins to obtain a white suspension. Then hexamine (15.098 g) was added to the suspension. The resulting

solution was heated at 100 °C for 2.5 h under N_2 atmosphere and the color of the suspension changed to dark brownish. To hydrolyse the compound 150 mL 3N HCl was added with heating at 100 °C for 1 h. The color of the dark turbid solution became clear. After cooling at room temperature, the compound was filtered



through a celite flash column. The resulting filtrate was extracted using 350 mL dichloromethane and dried over magnesium-sulfate and then filtered. The solvent was evaporated by rotary evaporation, giving an off-white (yield 1.7 g) powder. The compound was recrystallized in hot DMF and characterization was done using ¹H and ¹³C NMR (Figure S1), and IR studies (Figure S10).





Synthesis of s-tetrazine diamine:

In a typical synthesis, about 8 g of 4 amino-benzonitrile was dissolved in 20 ml of ethanol. 15 ml of

hydrazine hydrate (con.90%) and 4 g of sulphur powder was then added to it. The solution was kept for stirring at 90 °C for 8 hrs until a bright golden yellow colored thick suspension was observed. The suspension was filtered and washed with ethanol and acetone multiple times and kept for vacuum drying overnight. The bright yellow powder was dispersed in dry DMSO by stirring and was subjected to an overnight O_2 purge. To this oxidized compound, 150 ml of distilled water was added to precipitate out a bright-red product. The filtered and dried red powder was dispersed in 5% H₂O₂ solution to oxidize fully. The bright



red coloured product was isolated by centrifugation and dried in vacuum for 12 hrs. The product was washed with acetone and characterised by ¹H and ¹³C NMR (Figure S2) and IR studies (Figure S3).



Figure S2: The room temperature ¹H-NMR and ¹³C-NMR of s-tetrazine diamine were recorded in deuterated chloroform and in dimethyl sulfoxide (DMSO- d_6), respectively.



Figure S3: IR spectra of 4-aminobenzonitrile and s-tetrazinediamine.

 Table S1:
 Comparison of characteritics IR frequencies.

	NH ₂ primary amine (cm ⁻¹)	C≡N Nitrile (cm ⁻¹)	N-H bend Primary amine (cm ⁻¹)	C=C bond (cm ⁻¹)	C-N bond (cm ⁻¹)	
4-aminobenzonitrile	3422, 3335,	2205	1605	1501	1298	
	3149					
s-tetrazine diamine	3422, 3335,	absent	1617	1421	1302	
	3149					

Note: Absence of IR frequencies of nitrile groups in s-tetrazine diamine confirms the formation of tetrazine ring.

Synthesis of bispyridine-s-tetrazine diamine:

In a typical synthesis, about 8 g of 6 amino-3-pyridinecarbonitrile was dissolved in 20 ml of ethanol. 20 ml of hydrazine hydrate (con.90%) and 4 g of sulphur powder were added to it. The solution was

kept for stirring at 90 °C for 8 hrs until a bright golden yellow colored thick suspension was observed. This suspension was filtered and washed with ethanol and acetone multiple times and kept for an overnight vacuum drying. The yellowish-orange powder was dispersed in dry DMSO by stirring and O_2 was purged into the dispersion overnight to oxidize the product. 150 ml of distilled water was added to it to precipitate out the red product. The filtered and dried red powder was dispersed in 5% H_2O_2 solution to oxidize fully. The dark red colored product (with yield of 70%) was isolated by centrifugation and dried in



vacuum for 12 hrs. The product was washed with dimethyl-formamide and characterised by ¹H and ¹³C NMR (Figure S4), IR studies (Figure S5) and HRMS (Figure S6).



Figure S4 (A): ¹H-NMR and ¹³C-NMR of bispyridine-s-tetrazine diamine recorded in dimethyl sulfoxide (DMSO- d_{δ}) at room temperature.

Note: The solubility of bispyridine-s-tetrazine diamine is very less in any organic solvent. But with the increase of temperature it solubilizes in (DMSO- d_6). So that, ¹H NMR data has also been taken in 373 K (Figure S4 (B)).



Figure S4 (B): ¹H-NMR and ¹³C-NMR of bispyridine-s-tetrazine diamine recorded in dimethyl sulfoxide (DMSO- d_6) at 373 K.

Note: Two different isomeric peaks were observed with systematic shifts. The ratio of the intensities of two sets of isomeric peaks (a,b,c,d) and (a_1, b_1, c_1, d_1) is 3:1. So the isomers coexists as a mixture with a 3:1 concentration ratio. The probability of the presence of any unreacted product was discarded as HRMS data showed a single molecular weight.



Figure S5: IR spectra of 6-amino-3-pyridinecarbonitrile and bis-pyridine-s-tetrazine diamine.

Table S2: (Comparison	of characteritic IR	frequencies.
-------------	------------	---------------------	--------------

	NH2 primary amine (cm ⁻¹)	C≡N Nitrile (cm ⁻¹)	N-H bend Primary amine (cm ⁻¹)	C=C bond (cm⁻¹)	C-N bond (cm⁻¹)
6-amino-3-	3422, 3335,	2205	1614	1414	1279
pyridinecarbonitrile	3149				
bispyridine s-	3422, 3335,	absent	1621	1401	1300
tetrazine diamine	3149				

Note: Absence of IR frequencies of nitrile groups in bispyridine-s-tetrazine diamine confirms the formation of tetrazine ring.



Figure S6: HRMS data of bispyridine-s-tetrazine diamine shows only a single intense peak of $[M+H]^+$: 265.19. The exact molecular mass of bispyridine-s-tetrazine diamine ($C_{12}H_{10}N_8$) is 266.10.

3. Materials and methods for the COF syntheses:



Scheme S1: Formation of COFs from corresponding monomers. Inset shows the photograph of the COF powders.

Synthesis of IISERP-COF16 (labelled as COF-16 throughout this supporting information):

2,4,6-triformyl-phloroglucinol (65 mg, 0.3 mmol) and terphenyl-diamine (116 mg, 0.45 mmol) were weighed into a Pyrex tube and were dissolved in dioxane (6.0 mL) and mesitylene (3.0 mL) and stirred until a homogeneous yellow colour was observed. To this mixture, 1.0 mL of 0.6 M acetic acid was added. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 135°C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded about 140 mg of bright yellow coloured solid which was washed with hot DMF, dioxane, MeOH, acetone and THF (85%, isolated yield). This product was also subjected to a Soxhlet extraction using hot DMF/methanol/THF as solvent and filtered solid was characterized by ¹³C solid state NMR (Figure S7) and IR (Figure S10).



Figure S7: CP MAS ¹³C-NMR spectra of the COF16 measured at 500 MHz. a, b, c, d, e, f, g and h are the corresponding peaks positions obtained from the NMR data. (*) denotes the presence of side bands.

Synthesis of IISERP-COF17 (labelled as COF-17 throughout this supporting information):

2,4,6-triformyl-phloroglucinol (65 mg, 0.3 mmol) and s-tetrazine-diamine (118 mg, 0.45 mmol) were weighed into a Pyrex tube and were dissolved in dioxane (6.0 mL) and mesitylene (3.0 mL) and stirred until a homogeneous red colour was observed. To this mixture, 1.0 mL of 0.6 M acetic acid was added. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 135 °C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded about 130 mg of bright yellow coloured solid which was washed with hot DMF, dioxane, MeOH, acetone and THF (70%, isolated yield). This product was also subjected to a Soxhlet extraction using hot DMF/methanol as solvent and filtered solid was characterized by ¹³C solid state NMR (Figure S8) and IR (Figure S10).



Figure S8: CP MAS ¹³C-NMR spectra of the COF17 measured at 500 MHz. a, b, c, d, e, f, g and h are the corresponding peaks positions obtained from the NMR data. (*) denotes the presence of side bands.

Synthesis of IISERP-COF18 (labelled as COF-18 throughout this supporting information):

2,4,6-triformyl-phloroglucinol (65 mg, 0.3 mmol) and bispyridine-s-tetrazine-diamine (120 mg, 0.45 mmol) were weighed into a Pyrex tube and were dissolved in dioxane (5.0 mL) and mesitylene (3.0 mL) and stirred until a red colour was observed. To this mixture, 1.0 mL of 0.8 M acetic acid was added. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 135 °C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded about 175 mg of bright yellow coloured solid which was washed with hot DMF, dioxane, MeOH, acetone and THF (90%, isolated yield). This product was also subjected to a Soxhlet extraction using hot DMF/methanol as solvent and filtered solid was characterized by ¹³C solid state NMR (Figure S9) and IR (Figure S10).



Figure S9: CP MAS ¹³C-NMR spectra of the COF18 measured at 500 MHz. a, b, c, d, e, f, g, h and i are the corresponding peaks positions obtained from the NMR data. (*) denotes the presence of side bands.



Figure S10: Comparison of the IR spectra of the COFs.

Table S3: IR data analysis of COFs

COF-Name	Enolic OH (cm ⁻¹)	carbonyl (C=O) (cm ⁻¹)	C=C bond (cm ⁻¹)	C-N bond (cm ⁻¹)
COF16	absent	1590	1441	1280
COF17	3420	1609	1412	1271
COF18	3411	1620	1410	1245

Note: The enolic hydroxyl groups present in COF17 and COF18 are rapidly interconvertible to *β*-ketoenamine form.

4. <u>Structure modeling of the COFs:</u>



Figure S11: A (i), B (i) and C (i) Unit cells and columnar view COFs, obtained from DFTB geometryoptimized structures. **A (ii), B (ii)** and **C (ii)** Polymeric propagation of the COFs['] represented by $(4 \times 4 \times 8)$ supercells.

5. Adsorption data analysis of the COFs:



Figure S12: (A) N_2 adsorption-desorption isotherm of COF16 at 77 K (B) A BET fit obtained using the low pressure region data of the N_2 adsorption isotherm. (C) A Langmuir fit obtained using the N_2 adsorption isotherm. (D) A plot of the pore width *vs.* incremental pore area of COF16.



Figure S13: (A) N_2 adsorption-desorption isotherm of COF17 at 77 K. (B) A BET fit obtained using the low pressure region data of the N_2 adsorption isotherm. (C) A Langmuir fit obtained using the N_2 adsorption isotherm. (D) A plot of the pore width *vs.* incremental pore area of COF17.



Figure S14: (A) N_2 adsorption-desorption isotherm of COF18 at 77 K. (B) A BET fit obtained using the low pressure region data of the N_2 adsorption isotherm. (C) A Langmuir fit obtained using the N_2 adsorption isotherm. (D) A plot of the pore width *vs.* incremental pore area of COF18.

COFs	BET SA (m²/g)	Langmuir SA (m ² /g)	Modeled SA (m ² /g)
COF16	452	920	2601
COF17	656	1452	2684
COF18	757	1745	2479

 Table S4: Comparison of experimental surface area (SA) with modeled surface area.

Note: The calculated values are much higher than the surface area values estimated from BET or Langmuir fits. We agree that in the ideal case, the surface area estimated from the fits should agree with the surface area calculated using the DFT-optimized model. In our experience, we have seen that this work quite well when it comes to ultra and microporous COFs. However, for mesoporous materials, different methods such as BET, Langmuir and NLDFT used to fit the experimental isotherms all yield a much lower surface area than what is expected from the modeled structure.

This makes the accurate estimation of the surface area of mesoporous material difficult. However, the lowering of surface area for COFs could certainly have contributions from the layer slipping or defects in the polymeric structure and a relatively lower degree of crystallinity as compared to other materials such as MOFs. 6. Thermal and chemical stability studies of the COFs:



Figure S15: Thermogravimetric analysis of COFs under N₂ flow with a heating rate of 5K/min. COF16 is stable up to 420 $^{\circ}$ C. But COF17 and COF18 are lesser stable, degrades near 280 $^{\circ}$ C.



Figure S16: (A), (B), (C) PXRD patterns of COF16, COF17 and COF18 recorded after boiled in DMF, soaked in acid and soaked in base.

7. FE-SEM images of the COFs:



Figure S17: FE-SEM images of (A) COF16, (B) COF17 and (C) COF18 at different resolutions.

Note: At lower resolution, a fluffy cotton-like morphology can be seen. In closer view the presence of aggregated-flakes can be seen.

8. HR-TEM images of the COFs:



Figure S18: HR-TEM images of the **(A)** COF16, **(B)** COF17 and **(C)** COF18 under different magnifications showing the aggregates formed by stacking of many sheets. Darker regions are from such multi-flake stacking. While at 10 nm resolution the uniform micropores all along the surface of the COF can be seen.

9. SAED pattern of the COFs:



Figure S19: A (i) and **(ii)** HR-TEM images of the COF16 under higher magnifications showing the lattice fringes present in the COF. **(iii)** FFT pattern of the fringes area shows the d-spacing values. **(iv)** SAED pattern of COF16 shows the diameters of reciprocal circles.

Note: These lattice fringes could be observed across samples from different preparations and also in many regions of the drop-casted samples. The SAED pattern confirms the high degree of crystallinity in the selected flakes of the COF. Many such crystalline flakes were observed. However, the thin flakes burn under the exposure to e- beam of the HRTEM.



Figure S20: A (i) and **(ii)** HR-TEM images of the COF17 under higher magnifications showing the lattice fringes present in the COF. **(iii)** FFT pattern of the fringes area shows the d-spacing values. (iv) SAED pattern of COF17 shows the diameters of reciprocal lattice.



Figure S21: A (i) and **(ii)** HR-TEM images of the COF18 under higher magnifications showing the lattice fringes present in the COF. **(iii)** FFT pattern of the fringes area shows the d-spacing values. (iv)SAED pattern of COF18 shows the dimeters of reciprocal lattice.

Note: d-spacing value calculated from the diameter (R) of the reciprocal lattice (d=2/2R) matches well with lattice fringes observed in FFT pattern.

Table S5: The diameter of the reciprocal circles in SAED pattern and calculated inter-planar spacing.

COFs	Diameter of the reciprocal circle: 2R (1/nm)	Interplanar spacing: d (nm)
COE16	6.49	0.31
COLIE	7.07	0.29
CO[17	7.59	0.26
COFI	8.18	0.25
COE18	5.80	0.35
COFIS	7.25	0.28
	8.54	0.23



Figure S22: HR-TEM images at higher contrast level showing the porous nature of the COFs at the edges of each COF flakes. The brighter region is the carbon coated Cu grid surfaces.

10. Cyclic voltammetry of the monomers:

Electrodes were fabricated by coating an ethanolic dispersion of the monomers on carbon paper. Coating was maintained over a 1×1 cm² area. Then it was dried in vacuum for 24 hrs. The electrodes were used for the CV measurements carried out in a non-aqueous electrolyte system (*t*-butyl ammonium hexaflurophospahte dissolved in acetonitrile, ^tBuNH₄PF₆/ACN). A non-aqueous Ag/Ag⁺ reference electrode and platinum flag counter electrodes were used. CV measurements were carried in 50 mV/s scan rate from –ve to +ve potential window.



Figure S23: Cyclic voltammograms of **(A)** terphenyl amine **(B)** s-tetrazine diamine **(C)** bispyridne-stetrazine diamine **(D)** triformylphloroglucinol @50 mV/s using 0.5 (M) solution of ^tBuNH₄PF₆/ACN (non-aqueous electrolyte system). **(E)** Position of lowest reduction potential region of the monomers.

Observation: The oxidation and reduction potential of the monomers are distinctly different in comparison with their respective COFs. A gradual shift of the lowest reduction peak is observed in the –ve quadrant as we move from terphenyl diamine to tetrazine diamine to bis-pyridine-s-tetrazine diamine. Thus the monomer itself indicates the favourability of using the bis-pyridine-tetrazine units.

11. Cyclic voltammetry of the COF and the bandgap calculations:

Electrodes were fabricated by coating an ethanolic dispersion of the COFs on carbon paper. Coating was maintained over a 1×1 cm² area. Then it was dried in vacuum for 24 hrs. The electrodes were subjected to CV measurements in a non-aqueous electrolyte system (*t*-butyl ammonium hexaflurophospahte dissolved in acetonitrile, ^tBuNH₄PF₆/ACN) under argon atmosphere. A non-aqueous Ag/Ag⁺ reference electrode and platinum flag counter electrodes were used. CV measurements were carried in 50 mV/s scan rate from -1.8 V to 2.2 potential window. Following theconvention, the highest oxidation potential has been taken to evaluate the position of the HOMO and lowest reduction potential to evaluate the position of the LUMO.



Figure S24: **(Left)** Cyclic voltammetry measurements of COFs @50 mV/s using 0.5 (M) solution of ${}^{t}BuNH_{4}PF_{6}/ACN$ (non-aqueous electrolyte system). **(Right)** Position of oxidation and reduction potential (vs. NHE) of COFs with respect to Na/Na⁺.

Note: Na can be easily oxidized to Na⁺ and during this oxidation process reduction of the COFs happens. The reduction affinity of COFs increases with the increase of the reduction potential of the COFs. COF18 possess highest reduction potential among other three COFs.

COFs	E _{Ox} vs SCE	E _{Ox} vs. NHE	E _{HOMO} (eV)	E _{Red} vs. SCE	E _{Red} vs. NHE	E _{LUMO} (eV)	E _g from CV (eV)	Optical E _g from DRS
COF16	1.75 V	2.44 V	-6.66 eV	-1.18 V	-0.49 V	-3.75 eV	2.93 eV	2.75
COF17	1.72 V	2.41 V	-6.63 eV	-0.889 V	-0.19 V	-4.10 eV	2.51 eV	2.51
COF18	1.80 V	2.49 V	-6.68 eV	-0.554 V	0.150 V	-4.31 eV	2.32 eV	2.20
$\begin{split} E_{HOMO} &= - \left[E_{OX} - E_{(Fc/Fc}^{+}) + 4.8 \right] eV \\ E_{LUMO} &= - \left[E_{Red} - E_{(Fc/Fc}^{+}) + 4.8 \right] eV \\ E_{Ag/Ag}^{+}_{(non-aqueous)} \text{ vs. NHE: } 0.696 \text{ V and } E_{(Fc/Fc}^{+}) \text{ : } 0.58 \text{ V} \\ \end{split}$ $\begin{split} Where, \text{ NHE: Normal Hydrogen Electrode} \\ \text{ SCE: Saturated Calomel Electrode} \\ \text{ Fc/Fc}^{+} \text{ : Ferrocene/Ferrocenium ion couple} \end{split}$								

Table S6: Bandgap calculations using electrochemical data.

12: Plausible interactions of sodium with the COFs:



Figure S25: A (i), B (i) and C (i) Shown are the CVs of the three COFs subjected to 10 CV cycles at 0.5 mV/s. The highlighted region shows potential window responsible for the sodiation of the COFs. A (ii), B (ii) and C (ii) The potential vs. capacity plot of COFs at 100 mA/g current density provides the total discharging capacity and no of sodium inserts into the framework.

Calculation: 1 mAh = $3.6 C = 2.2 \times 10^{19}$ number of electron or Na⁺.

Here, for the COF based coin-cells if we observed a specific capacity of 'A' mAh/g in the potential region of 0.05 - 1 V, this would yield the number of Na⁺ ion = A × 2.2 × 10¹⁹.

Thus, the specific capacity of 'A' mAh/g is realized from $A \times 2.2 \times 10^{19}$ no of Na⁺ (assuming they are the sole charge carriers).

If the calculated molecular weight of the COFs is 'B' g/mol. The weight for unit cell of the COF is $B / (6.023 \times 10^{23})$ g.

Considering that for 1g of the COF, the number of Na⁺ ion calculated is $A \times 2.2 \times 10^{19} =>$ number of Na⁺ per unit cell = ($A \times 2.2 \times 10^{19} \times B$) / (6.023×10²³).

Table S7: Calculated number of Na⁺ inserted into the framework.

COFs	Molecular weight	No of Na ⁺ inserted
COF16	1081 g/mol	3
COF17	1086 g/mol	8
COF18	1093 g/mol	15



Scheme S2: A probable mechanism showing the Na⁺ insertion into the functional sites of COF18 under the applied potential. The presence of pyridine nitrogen next to the β -ketoenamine unit provides the suitable chelation sites for inserted Na⁺.

13. Diffusive vs. capacitive type of charge storage in the COFs:

CVs were measured in the potential window of 0.05 - 3.0 V at different scan rates (0.1 - 2.5 mV/S), to evaluate the sp. capacity obtained due to the interaction of Na⁺ with the highly redox active functional groups. If the Sodiation happens via the redox functional groups' participation, the surface active capacitive behaviour predominates over diffusive mechanism. We used the power law i = av^b (where, v represents the scan rate and a and b are alterable parameters) to verify the capacitive behaviour. In general, when b = 0.5, it means that the electrode reaction is diffusion controlled and satisfies the Cottrell's equation: i = av^{0.5}. While the chemical interactions between the functional groups and the Na⁺ occur as a surface process giving rise to values for 'b' being close to 1. The parameter 'b' (slope) was determined from a plot of log (i) versus log (v).



Figure S26: A (i), B (i) and C (i) Cyclic voltammogram plots of COFs derived coin-cell (fresh cell) measured at different scan rates. A (ii), B (ii) and C (ii) Log. of peak current intensity (anodic) vs. log. of scan rate at different potentials extracted from the CV plots.



Note: the linear increment of the peak current with the increase of current density.

Figure S27: A bar plot shows the percentage of sp. capacity of COFs comes in capacitive and in diffusion controlled way.

Note: By using the power law, we see that most of the Na⁺ insertion into the COF16 happens via a diffusion-controlled mechanism, whereas for COF17 and COF18 the surface controlled capacitive Na⁺

storage predominates. So, the introduction of electron deficient tetrazine ring definitely increases the surface redox activity of the COFs.

14. Stabilization of the coulombic efficiency:

We carried out the OCV studies using the COF-derived coin-cells. The OCV gradually decreases with time (Figure S27). This indicates the self-discharge process of the battery without the influence of an external potential. This could also be contributing to the initial drop in columbic efficiency along with the SEI layer formation. The first cycle coulombic efficiency appears only ~50% for these COFs due to stable Solid Electrolyte Interphase (SEI) formation on the COF derived electrode surface. A lot of sodium consumption happens irreversibly at the first discharge itself as the electrolytes decompose on the highly functionalized porous surface of the COFs. After a few cycles, the reversibility achieved in the sodiation-desodiation process. That stabilizes the sp. capacities with ~98% coulombic efficiency (Figure S28, Table S8). The steadiness of columbic efficiency well after the initial cycles indicates the stability of the COF-derived electrodes over multiple cycles of charge-discharge at high current densities.



Figure S28: Self discharge process of the COF-derived half-cells as a function of time.



Figure S29. A (i), (ii) and **(iii):** Galvanostatic charge-discharge measurements for 1st, 2nd, 3rd and 100th cycles at the applied current density of 100 mA/g showing the sodiation-desodation of the COFs.

COFs	Discharge sp. capacity (mAh/g) @100 mA/g	Charge sp. capacity (mAh/g) @100 mA/g	Coulombic Efficiency (%)
COF16	210	120	57.0
COF17	590	310	53.2
COF18	1220	605	49.6

Table S8: First cycle coulombic efficiency of COF derived anodes estimated from galvanostatic chargedischarge at 100 mA/ current density.

15. Comparison of the anodic performance:



Figure S30: (A) Sp. capacity of the COF-derived anode material for sodium ion battery @100 mA/g. **(B)** Decrease of sp. capacity of COF-derived anode material with increase of current density.

Table S9: Comparison table showing the electrode performance of different materials in SIB:

	Electrode materials for SIB	Sp. capacity (@0.1 A/g)	Sp. capacity (@higher current densities)
	IISERP-COF18 ^{this work}	410 mAh/g	174 mAh/g @10 A/g, 128 mAh/g @15 A/g
COF and COF	TFPB-TAPT COF ^{S1}	180 mAh/g	145 mAh/g @0.2 mA/g
derived materials	DAAQ-COF4 ⁵²	420 mAh/g	198 mAh/g @5 A/g
	TQBQ-COF ⁵³	328 mAh/g	135 mAh/g @10 A/g
	NPC-2 ⁵⁴	229 mAh/g	127 mAh/g @2.5 A/g
	CON16 ^{S5}	230 mAh/g	124 mAh/g @1 A/g
Polymeric	ALP (Azo linked Polymer) ^{s6}	170 mAh/g (@84 mA/g)	42 mAh/g @11.5 A/g
material	PI-1 (NTCDA-triazine) ⁵⁷	331 mAh/g	103 mAh/g @5 A/g
	PI-2 (PMDA-triazine) ⁵⁷	210 mAh/g	70 mAh/g @5 A/g
	O-PDA-2 ^{s8}	433 mAh/g	122 mAh/g @3.2 A/g
	CNS ⁵⁹	305 mAh/g	133 mAh/g @10
Carbonaceous			A/g, 112 mAh/g @20 A/g
material	RNSC-800 ⁵¹⁰ (N and S co- doped)	575 mAh/g	236 mAh/g @10 A/g
	NSC-2 ^{S11} (N and S doped)	250 mAh/g	102 mAh/g @10 A/g
	NC/RGO ⁵¹²	395 mAh/g	211 mAh/g @10 A/g

<u>A comparative discussion</u>: The very first report of COF derived anode for SIB (TFPB-TAPT COF)^{S1} shows the probability of sodium insertion in-between the interlayer space of p-stacked COF. In this COF, mainly mild redox-active Schiff base interacts with Na⁺. Following this, an acid delaminated COF (DAAQ-COF4)^{S2} with exposed β-ketoenamine units undergoes sodiation under potential via α-radical formation. Easy accessibility of redox-active groups in delaminated COF helped to improve the sp. capacity. And a high-performance SIB has been fabricated with a carbonyl rich framework (TQBQ-COF),^{S3} wherein the functional groups are arranged proximally inside the Nano-channel. The rate performance was also improved significantly by the fast movement of Na+ ions inside the highly functionalized Nano-channel. In another approach, COF's (NPC-2)^{S4} conductivity was improved by pyrolyzing it at high temperature, and it enhanced the rate performance. Again better diffusion of Na+ inside thin layer COFs was well investigated in thiophene-rich covalent organic nanosheets (CON-16).^{S5}

Following the insights from these different studies, in our designer approach, we have optimized all the necessary factors such as the proximity of the redox-active functional groups, easy accessibility via the porous nanochannelled structure, and appreciable conductivity during sodium insertion to improve the performance. The essential electronic demand for the sodiation process of the COF has been taken into account by introducing the tetrazine units. And its impact has been vindicated by a range of and modeling studies. A systematic investigation of this electronically driven enhancement of anodic property is established.

Our bispyridine-tetrazine-tfp COF (IISERP-COF18) shows superiority over the so far reported COF materials and organic polymeric materialsS6-S8 in terms of delivering high sp. capacity and ultra-high rate performance (128 mAh/g @15A/g). Its performance is comparable to the heteroatom doped carbonaceous material, which is known to have much higher electronic conductivity.⁵⁹⁻⁵¹² In comparison, the molecular-level tuning of the COF material through design to develop a high-performance anode for SIB is undoubtedly a superior approach to deriving carbonaceous material via pyrolysis of expensive COF/MOF materials.



16: Impedance spectra analysis of the COFs:

Figure S31: Fitted Nyquist plot of the COFs.

Note: The Nyquist plots of AC-impedance measurements under applied DC voltage of 0.1 V shows the decreased charge transfer resistance of the COFs.

Table S10: Fitting parameters of Nyquist plots using Z view software (All the parameters have the units in ohms)

COF16	R1	CPE1-T	CPE1-P	R2	R3	Wo1-R	Wo1-T	Wo1-P
Z _{real}	1.20E+01	1.61E-05	0.83002	530	2	399	27.15	0.368
Z _{im}	1.11E-04	8.03E-01	90	5	50	3.8	0.2981	

COF17	R1	CPE1-T	CPE1-P	R2	R3	Wo1-R	Wo1-T	Wo1-P
Z _{real}	5	3.21E-05	0.85502	420	2	340	98	0.38999
Z _{im}	0.000111	0.80276	90	5	50	3.8	0.2981	

COF18	R1	CPE1-T	CPE1-P	R2	Wo1-R	Wo1-T	Wo1-P
Z _{real}	4.2	1.01E-05	0.88002	80	150	3.2	0.29
Zim	0.000111	0.80276	90	5	50	3.8	0.2981

17. Modeling and computational details

All modelling and simulations were carried out using the Aterials Studio V.6 (Accelrys).

The COF structures were solved following the procedure mentioned in the main text. The Na⁺-COF interactions were modelled only for the IISERP-COF18, which showed the highest experimental anodic performance. The number of Na⁺ ions per unit cell was estimated from the electrochemical data to be 15 for the IISERP-COF18. Into the anionic framework of IISERP-COF18, the Na⁺ ions were introduced using Grand canonical Monte Carlo (GCMC) algorithm.^{(S13-} ^{\$15)} All parameters including the unit cell as well as the coordinates were relaxed. The minimization yielded a structure of the COF with Na⁺ in the pores. A 3 x 3 x 3 supercell was constructed from this structure and was subjected to a rigorous dispersion corrected DFT optimization using the CASTEP routine embedded in the Materials Studio.^(S16, S17) A Generalized Gradient Approximation-Perdew--Burke--Ernzerhof (GGA-PBE) functional was used for the exchange and correlation energy of electrons.^(S18) SMART finite basis set correction was applied with a plane wave basis set cut-off of 370 eV. Electronic minimizations were done using the Density Mixing Scheme. The valence electrons were treated using the Ultrasoft pseudopotentials. The SCF tolerance was set to 1 x 10⁻⁶ eV/atom. The calculations were repeated two times to eliminate any bias from the initial configuration. Excellent convergence was achieved both the times with total energies having negligible differences (in the third decimal of the kcal/mol units).

References:

S1. B. C. Patra, S. K. Das, A. Ghosh, P. Moitra, M. Addicoat, S. Mitra, A. Bhaumik, S. Bhattacharya and A. Pradhan, *J. Mater. Chem. A*, 2018, **6**, 16655-16663.

S2. S. Gu, S. Wu, L. Cao, M. Li, N. Qin, J. Zhu, Z. Wang, Y. Li, Z. Li and J. Chen, *J. Am. Chem. Soc.*, 2019, **141**, 9623-9628.

S3. R. Shi, L. Liu, Y. Lu, C. Wang, Y. Li, L. Li, Z. Yan and J. Chen, *Nat. Commun.*, 2020, **11**, 1-10.

S4. X. Zhang , G. Zhu, M. Wang, J. Li, T. Lu, L. Pan, Carbon, 2017, 116, 686-694.

S5. M.-S. Kim, W.-J. Lee, S.-M. Paek and J. K. Park, *ACS Appl. Mater. Interfaces*, 2018, **10**, 32102-32111.

S6. K. S. Weeraratne, A. A. Alzharani, and H. M. El-Kaderi, *ACS Appl. Mater. Interfaces*, 2019, **11**, 23520–23526.

S7. Z. Li , J. Zhou, R. Xu, S. Liu, Y. Wang, P. Li, W. Wu, M. Wu, *Chemical Engineering Journal*, 2016, **287**, 516-522.

S8. T. Sun, Z.-j. Li, H.-J. Wang, D. Bao, F.-L. Meng, and X.-B. Zhang, *Angew. Chem. Int. Ed.*, 2016, **55**, 1-6.

S9. Y. Chen, L. Shi, S. Guo, Q. Yuan, X. Chen, J. Zhou and H. Song, *J. Mater. Chem. A*, 2017, *5*, 19866-19874.

S10. W. Song, J. Kan, H. Wang, X. Zhao, Y. Zheng, H. Zhang, L. Tao, M. Huang, W. Liu and J. Shi, *ACS Appl. Nano Mater.*, 2019, **2**, 5643-5654.

S11. Q. Jin, K. Wang, P. Feng, Z. Zhang, S. Cheng and K. Jiang, *Energy Storage Mater.*, 2020, **27**, 43-50. **S12.** R. Dan, W. Chen, Z. Xiao, P. Li, M. Liu, Z. Chen and F. Yu, *Energy Fuels*, 2020, **34**, 3923-3930.

S13. F-. X. Coudert, A. H. Fuchs, Coordination Chemistry Reviews, 2016, 15, 211-236.

S14. C. Abrioux, B. Coasne, G. Maurin, F. Henn, A. Boutin, A. Di Lella, C. Nieto-Draghi and A. H. Fuchs, *Adsorption*, 2008, **14**, 743–754.

\$15. S. Buttefey, A. Boutin, C. Mellot-Draznieks, A. Fuchs, J. Phys. Chem. B, 2001, **105**, 9569-9575.

S16. First principles methods using CASTEP, S. J. Clark et al., Z. Kristallogr., 2005, **220**, 567-570.

S17. L. Ascherl, T. Sick, J. T. Margra, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M.

Döblinger, T. Clark, K. W. Chapman, F. Auras and T. Bein, Nature Chemistry, 2016, 8, 310-316.

S18. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.