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A new electrochemically responsive 2D π -conjugated covalent organic framework as a high performance supercapacitor

Sabuj Kanti Das, Kousik Bhunia, Arijit Mallick, Anirban Pradhan, Debabrata Pradhan and Asim Bhaumik*

We report a novel porous extended network π -conjugated covalent organic framework, which is capable of energy storage up to 379 F g^{-1} at 2 mV s^{-1} scan rate, and offer excellent specific capacitance retention of 75% after 8000 charge discharge cycles.

A new electrochemically responsive 2D π -conjugated covalent organic framework as a high performance supercapacitor

Sabuj Kanti Das,^a Kousik Bhunia,^b Arijit Mallick,^c Anirban Pradhan,^d Debabrata Pradhan^b and Asim Bhaumik^{a*}

^aDepartment of Materials Science, Indian Association for the Cultivation of Science, 2A & B Raja S C Mullick Road, Kolkata-700032, India. Email: msab@iacs.res.in.

^bMaterials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302, India.

^cAdvanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

^dDirector Research Unit, Indian Association for the Cultivation of Science, 2A & B Raja S. C. Mullick Road, Jadavpur, Kolkata 700 032, India.

Keywords: Covalent organic framework; 2D-hexagonal porous structure; supercapacitor; energy storage; electrochemical cells.

Abstract: Covalent organic frameworks (COFs) build via periodic arrangement of organic building blocks are attracting increasing interest in recent times due to the huge scope in their synthesis through a wide range of structural motifs and diversity in their potential applications. Here we report the synthesis of a new porous extended network π -conjugated TFP-NDA-COF via solvothermal Schiff base condensation of 1,3,5-triformylphloroglucinol (TFP) with 1,5-diaminonaphthalene (NDA). The electrochemical study demonstrates that TFP-NDA-COF has the capability of energy storage up to 379 F g⁻¹ at 2 mV s⁻¹ scan rate, 348 F g⁻¹ at 0.5 A g⁻¹ and offer excellent specific capacitance retention of 75% after 8000 charge

discharge cycles. High electrochemical performance could be attributed to the π -electronic conjugation along the polymeric 2D layered network and ion conduction inside the porous channel and permanent porosity of the framework. This indicates that the COF reported herein meets the key requirements like energy storage ability and electrochemical stability needed for developing an efficient energy storage device.

INTRODUCTION

Development of portable electronic device, hybrid powered vehicles, energy storage and conversion devices, and fuel cells are the major energy issues of the progressive era [1-4]. The replacement of non-renewable fossil fuels by an alternative renewable resource of energy is a big challenge to us. Gradually diminishing trend of nonrenewable fossil fuel based energy and rapidly increasing energy demand are the major concerns for the sustainability of human civilization. Supercapacitor is a promising scaffold for power storage and supply to meet the energy demand for the power supplying devices [5-8]. The electric double layer, generated at the electrode/electrolyte surface is the measure of the capacitance of electrode [9]. Electrode material is the key substance for this electrochemically occurring process [10]. The applied voltage depended ion adsorption on the electrode surface is strongly dependent on the chemical environment and textural parameter of the material used for the electrodes. Thus, the development of electrode material with high energy density and high stability is very challenging and promising in the field of sustainable energy. Graphene, nanostructured carbon nanotube, hetero-atom doped graphene etc. are well established as an electrode material to store the high energy density with remarkable stability and outstanding performance [11-14]. Covalent organic framework (COF) [15-18] is a newly emerged class of crystalline organic framework with atomically well-defined pore aperture made from organic molecular assembly. Two-dimensional COFs are more advantageous over three-dimensional COFs because of inherent stacking behavior between two adjacent layers (π - π interaction),

which can provide a nanoscale channel to the stacking direction. Because of the presence of stacking phenomena, the presence of heteroatoms in the 2D structure of COFs can expedite the ion transfer through porous channels. The rigidity of porous architecture of COF materials can be attributed to the periodic covalent linkage between the light elements (C, O, B, N etc.) belongs to the individual building blocks. Boronate ester based COF materials [19, 20] are less popular due to their low hydrolytic stability of boronate linkage but the imine based COFs are very interesting for the practical application due to their considerable chemical stability and high electron density present along the crystalline channel [21].

Low density, permanent porosity, tunable pore engineering of these COFs make them very demanding for the applications like gas storage [22-24], gas separation [25], catalysis [26], photo controlled capture and release of guest molecules [27,28] etc. Extended π -conjugation and donor sites of COFs have been exploited to serve it as a light emitter [29], photocatalyst [30], sensors [31], catalyst [32], electrocatalyst [33] etc. The combination of large surface area, active redox site and extended π -electronic conjugation are essential parameters for their advanced applications as an electrode material [34-36].

In this present work, we adopted a facile method for the synthesis of porous β -ketoenamine-naphthalene based crystalline covalent organic framework for supercapacitive energy storage application. The as synthesized COF, TFP-NDA-COF (Figure. 1A) possesses a 2D hexagonal porous structure [37] having BET surface area of $353 \text{ m}^2 \text{ g}^{-1}$. Figure. 1B and Figure. 1C are representing the star shape porous channel through the crystalline network and 2D layered structure of TFP-NDA-COF. The as-synthesized TFP-NDA-COF showed capacitance with 379 F g^{-1} at 2 mVs^{-1} scan rate. TFP-NDA-COF showed excellent cyclic stability after 8000 cycle with a retention of 75% capacitance.

Experimental Section

Materials

1,5-diaminonaphthalene (MW=158.2) was purchased from Alfa Aesar, phloroglucinol (MW=126.11), hexamine(hexamethylenetetramine), trifluoroacetic acid, 1,4-dioxane, mesitylene were purchased from Spectrochem, India and used without further purification.

Instrumentation

X-Ray diffraction patterns of the powder COFs were obtained by using a X'Pert PRO of PAN analytical diffractometer using Cu K α (= 0.15406 nm) radiation. Volumetric N₂ adsorption/desorption experiment of TFP-NDA-COF has been carried out by using Autosorb 1 (quantachrome, USA) at 77 K to estimate the Brunauer-Emmett-Teller (BET) surface area and porosity. Pore size distribution was estimated by using non local density functional theory (NLDFT). Prior to the measurement, Soxhlate solvent exchange has been performed with the powder sample for 72 hours by using anhydrous MeOH and dried under vacuum at 145 °C. Under high vacuum, the out-gassing temperature was maintained at 405K for 10 h. Percentage of carbon, hydrogen and nitrogen present in TFP-NDA-COF was estimated by using Perkin Elmer 2400 Series II CHN analyzer. Transmission electron microscopic (TEM) images of the microporous covalent organic framework were taken by using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. Scanning electron microscopic (SEM) images were obtained with a JEOL JEM 6700F field-emission scanning electron microscope (FESEM). FTIR spectral data of precursor monomers as well as COF material were collected using a Perkin Elmer Spectrum 100 spectrophotometer. Thermogravimetric (TGA) and differential thermal analysis DTA of the sample were carried out by using a TGA instrument thermal analyzer TA-SDT Q-600. ¹H and ¹³C NMR of synthesized triformylephloroglucinol (TFP) have been done using Bruker AVANCE III- 400 MHz spectrometer at a mass frequency of 8 kHz. The ¹³C cross-polarization magic angle spinning

(CP-MAS) NMR spectrum of TFP-NDA-COF was recorded with 500 MHz Bruker Advance II spectrometer. Cyclic voltammetry experiment was performed in a cyclic voltammeter Biologic SP-150.

Synthetic Procedure

Synthesis of triformylephloroglucinol (TFP)

Triformylephloroglucinol (TFP) was synthesized following a previously reported procedure [38] with little modification. Anhydrous phloroglucinol (6.014g, 49 mmol) and hexamethylenetetramine (15.098 g, 108 mmol) were taken into a pre-dried 250 mL two neck round bottom flask fitted with a magnetic stir bar maintaining inert atmosphere through the whole reaction set up using a condenser and flow of N₂ gas. Under the N₂ atmosphere, 90 mL of trifluoroacetic acid was added to the reaction mixture and stirred for 3 h at 100 °C. Then 150 mL 3M HCl was added into the reaction vessel and the reaction was continued for another 1.5 h under the same condition. After that, the reaction mixture was allowed to cool down to room temperature and filtered through celite. The desired product was extracted from the solution with 380 mL of dichloromethane, dried over anhydrous Na₂SO₄ and filtered. The solvent evaporation of the filtrate using rotary evaporator afforded 1.48 g (7.0 mmol, 14% yield) pure triformylephloroglucinol (TFP). The product was characterized by ¹H and ¹³C NMR (ESI, Figure. S1 and S2). ¹H NMR (400 MHz in CDCl₃) δ 14.117 (s, 3H, -OH), δ 10.153 (s, 3H, -CHO); ¹³C NMR (100 MHz in CDCl₃) δ 192.18 (-CHO), δ 173.71 (C-OH), δ 103.04(C-CHO).

Synthesis of TFP-NDA-COF

TFP-NDA-COF material was synthesized through Schiff-base condensation polymerization method using Pyrex seal tube. The reaction was carried out with TFP (0.063

g, 0.3 mmol) and 1, 5-naphthalenediamine (0.071 g, 0.45 mmol) in 3mL of dioxane and 0.3mL of 6M AcOH (10:1) solvent mixture. The mixture of starting materials was first dispersed in a pyrex tube by sonication for 10 min to form a completely homogeneous mixture. Then the reaction mixture was degassed through the freeze-pump-thaw cycle for three times using liquid N₂ and vacuum pump. After that, the tube was flame sealed and kept in 120 °C oven for 5 days. Finally, the pink coloured material was filtered and washed with 1, 4-dioxane, water, MeOH, THF and acetone, respectively and dried under vacuum at 125 °C for 12 h to obtain the naphthalene based TFP-NDA-COF as an isolated yield of 77 %.

Results and Discussion

Nanostructure analysis

To elucidate the structure of the COFs and to calculate the unit cell parameters, the possible 2D models were optimized using Gaussian-09 and material studio [39]. Several stacking possibilities were considered for reasons reported in the literature. The experimental PXRD patterns are agreeable with the simulated patterns of some near-eclipsed stacking models. Hence we propose this COF structure close to hexagonal space group ($P_{6/m}$) for TFP-NDA-COF by comparing the experimental and simulated PXRD patterns. The unit cell parameters are: $a = b = 22.5660 \text{ \AA}$, $c = 3.4000 \text{ \AA}$. The powder X-ray diffraction (PXRD) pattern revealed the crystalline structure of the COF (Figure 2a). The TFP-NDA-COF exhibited three peaks at 4.58, 7.8, 11.2 and a broad peak at about 26.7, corresponding to the crystal planes 100, 110, 210 and 001 reflections, respectively of a nearly layered 2D-hexagonal COF [40]. The experimental PXRD pattern (Figure 2a, red colored line) matched well with the simulated PXRD pattern (Figure 2a, violet colored line) obtained from the computationally optimized structure and Pawley refinement PXRD pattern (Figure. 2a, blue scattered). The Pawley refinement factor is found to be $R(p) = 3.16\%$. To check the structural

stability of TFP-NDA-COF in acidic condition, we have carried out the PXRD analysis of the COF after treatment with 1M H₂SO₄ solution for one week. The PXRD pattern of the acid treated TFP-NDA-COF remained unaltered (ESI, Figure S3), suggesting high chemical stability of this β -ketoenamine based framework. As shown in Figures 2b and 2c the hexagonal unit and π - π stacking 2D layer distance was 3.4 Å.

Surface area and porosity analysis

To understand the porosity and specific surface area of the activated TFP-NDA-COF, N₂ adsorption-desorption measurement has been carried out at 77 K. Nitrogen adsorption isotherm is of the intermediate of type I and IV adsorption isotherms according to IUPAC nomenclature, which corresponds to porosity within a range of micropores to mesopores (Figure 3) [41]. BET surface area of TFP-NDA-COF was found to be 353 m² g⁻¹. The pore size distribution plot employing NLDFT method suggested the average pore width 1.67 nm (extra-large micropore to small mesopore) in the polymeric network (Figure 3 inset). The porosity has also been estimated for the simulated structure of the TFP-NDA-COF, which suggested the experimental result (ESI, Figure S4). Further, we have carried out the N₂ adsorption-desorption analysis for the TFP-NDA-COF material after 1M H₂SO₄ treatment for 7 days. The nature of the sorption isotherm (ESI, Figure S5) together with the retention of BET surface area (364 m² g⁻¹) and average pore size (1.68 nm) suggested high chemical stability of this covalent organic framework.

Spectroscopic analysis

Solid state ¹³C MAS NMR and XPS analysis

To investigate the chemical environment of various types of carbon atoms present in the covalent organic framework of TFP-NDA-COF the solid state ¹³C MAS NMR analysis has been carried out. The peak positions of ¹³C solid state NMR (Figure. 4d) spectrum

confirmed the formation of TFP-NDA-COF and presence of naphthalene moiety in the organic framework. The presence of the more down fielded resonance signals are at 185 ppm and 147 ppm corresponds to the carbonyl carbon and C-N bond formation in the extended network, respectively [41]. The other signals at 135, 126 and 117 ppm designate the different aromatic carbon atoms of naphthalene ring in the polymeric network. The remaining sharp peak for the same type of sp^2 carbon atom of the phloroglucinol moiety appears at 108 ppm. There is no characteristic peak observed at ~ 192 ppm which indicates no existence of aldehyde group, suggesting the complete condensation reaction of TFP molecule during the Schiff base reaction. The X-ray photoelectron spectroscopic (XPS) study on TFP-NDA-COF suggested the presence of N, C and O atoms along with their respective binding energies are shown in [Figure 4a, 4b and 4c] [42]. Only one type of bonding pattern for N (N_{1s}) is observed with binding energy 398.9 eV, which is the representative of the $>C=C-NH$ moiety. Similarly, in the case of O, a single signal for O_{1s} was observed at binding energy 530.1 eV, which could be attributed to the presence of $>C=O$ (Figure 4b and 4c) [42].

FTIR and Solid state UV-VIS spectrum analysis

To understand the formation of β -ketoenamine linkage in the COF framework the FTIR and UV spectroscopic analyses of TFP-NDA-COF have been carried out. The comparison between FTIR spectra of the monomers and COF sample showed (Figure 5A) the disappearance of N-H stretching of the NH_2 groups at $3100-3300\text{ cm}^{-1}$ vis-à-vis the free diamine present in NDA. In addition disappearance of $-HC=O$ stretching band at 1641 cm^{-1} in free TFP along with appearance of a new $-C-N$ stretching band at 1258 cm^{-1} [43] confirmed the Schiff base condensation reaction. A broad stretching band at 1583 cm^{-1} could be attributed to $>C=C<$ [44]. Another shoulder peak at 1619 cm^{-1} (ESI, Figure S6) confirmed the presence of the $>C=O$ [34, 43, 44] group in the porous network. A broad FTIR band present in polymeric network at about 3415 cm^{-1} indicated the presence of $-NH$ group present

as secondary amine group in the COF material [44]. Further, the FTIR spectrum of the acid treated TFP-NDA-COF material suggested retention of the COF network and bonding (ESI, Figure S6). The band gap of TFP-NDA-COF has been estimated from the solid state UV-VIS diffuse spectrum (Figure 5B and 5C). This spectrum showed the absorption maxima (λ_{max}) at ca. 500 nm with calculated band gap of 2.10 eV. Visible absorption of TFP-NDA-COF together with π -conjugation could be helpful in exploring the conducting properties of this COF material.

Microscopic analysis

The morphology of the synthesized COF can be well investigated by field emission scanning electron microscopic (FE-SEM) and high-resolution transmission electron microscopic (HRTEM) analysis and these are shown in Figure 6. The SEM image (Figure 6a) of the COF showed the nanowire like particle morphology. The HRTEM analysis further confirmed the nanowire-like morphology with hierarchical porous architecture (Figure 6b) with the diameter of the wires of ca. 10 nm.

Thermal stability and elemental analysis.

The thermal stability of TFP-NDA-COF has been investigated by using thermogravimetric analysis at 10 °C per minute ramp under nitrogen atmosphere in the temperature range of 25-800 °C. From the TGA profile diagram of TFP-NDA-COF material (ESI, Figure S7), it is observed that the first weight loss occurred at 98 °C, which could be attributed to the evaporation of surface adsorbed moisture. Second weight loss after 400 °C is attributed to the breakage of the organic framework. Thus, TGA analysis revealed that the TFP-NDA-COF material possesses a good thermal stability. After doing the Soxhlate solvent exchange for 3 days with anhydrous MeOH and drying under vacuum at 165 °C further TGA analysis has been conducted. From the TGA profile diagram, (ESI, Figure S8) we confirmed

this activated TFP-NDA-COF material is free from any guest molecules. We have carried out the electrochemical as well as surface area analysis of this activated sample. CHN elemental analysis also confirmed the composition of the COF material. The experimental CHN analysis showed the presence of C, H and N are 69.97 %, 4.08 % and 9.93 %, respectively. This also confirmed the formation of imine bond formation as well as the presence of N atom in the polymeric framework. The experimental CHN analysis data agreed well with the theoretical CHN values (C, H and N are 73.27 %, 3.84 % and 10.68 %).

Electrochemical study

The electrochemical energy storage performance of activated sample of TFP-NDA-COF material was investigated on a Biologic SP-150 by performing cyclic voltammetry (CV) study with conventional three electrode system in 1(M) H_2SO_4 as electrolyte within a potential window of 0 to 1 V. Activated sample of the COF was used to analyze the electrochemical performance because no interference of surface or pore contain moisture or guest molecule was desired. The working electrode was prepared by the drop casting the ink prepared with the sample over 1 cm^2 graphite sheet. Pt wire was used as counter electrode and saturated calomel electrode (SCE) as a reference electrode.

The CV curve of the TFP-NDA-COF at different scan rates 2-100 mV/s exhibit similar quasi-rectangular shaped as presented in the Figure 7a. The electrolyte (aqueous H_2SO_4) solution contain the solvated cation (H_3O^+) and anion (SO_4^{2-}) having ion sizes of 0.42 nm and 0.53 nm respectively [45-47]. These ions can easily diffuse through the materials having micropore size more than 1 nm. Here the COF material has been used as electrode material contains pore size 1.67 nm which is quite favorable for ion transfer. The current plateau of CV over the increasing scan rate increased, suggesting fast accessible ions electrolyte through the porous channel of TFP-NDA-COF. Even at high scan rate the CV curve remain undistorted implies low contact resistance of TFP-NDA-COF. Two symmetric

redox type peaks appeared at low scan rate. The anodic peaks appeared at 0.5 V (vs. SCE) during forwards scan and cathodic peak appeared at 0.4 V (vs. SCE) during the reverse scan at slow scan rate 2-10 mV/s which disappeared upon further increase in the scan rate as presented in the Figure 7b. The anodic peak and cathodic peak which appeared at slow scan 2mV/s is presented individually in the ESI, Figure S9. The appearance of these types of weak redox peaks in CV plot can be well explained by the proton transfer as well as intercalation/deintercalation by the COF material. Due to the presence of porous channel along with N atom containing higher conjugated proton transferable crystalline polymer network this type CV plots were obtained. If negative potential is applied proton can be transferred from the electrolyte solution to the working electrode, got adsorbed and take part in the reaction. At the slow scan rates, H^+ / H_3O^+ ions have sufficient time to arrive at the surface of TFP-NDA-COF, can be able to penetrate through the pore of the crystalline material and react favorably [48]. The redox peak slowly disappeared with the increase of scan rate probably the restriction of ion insertion through the porous channel and slow redox kinetics during the fast scan rate [49]. The redox activity of the material is quite similar to the previous reports [34,36,43,50]. In this present work we observed the rectangular shape of CV plot along with redox peak at the slow scan rate, which suggested that the charge is stored through the electrochemical double layer as well as surface-bound Faradaic processes. The adsorption/desorption of protons on the TFP-NDA-COF which is likely dominant for the energy storage ability of TFP-NDA-COF electrode on the other hand, the intercalation/deintercalation of protons, which is accompanied by the faradic reaction as we have explained earlier. The probable Faradic ion transfer mechanistic pathway with TFP-NDA-COF electrode material has been shown in ESI, Figure S10 [34,36,50,51].

The specific capacitance of TFP-NDA-COF was estimated from CV over different scan rate using equation (I) [52].

$$C_{sp} = \int (IdV)/vmV \quad (I)$$

Where I is response current, V is potential window, v is potential scan rate, and m is mass of the active materials, respectively. The estimated specific capacitance of the COF material was found to be 379 F g^{-1} at 2 mV s^{-1} scan rate (ESI, Figure S11a). With the increase of the scan rate the specific capacitance was gradually decreased down. This may be possible due to the restriction of ion insertion in to the pores and weak redox kinetics of materials at fast scan rates [49]. The gradual decrease in the capacitance over increasing the scan rate is quite similar to many reports [53, 54]. The presented capacitance value of TFP-NDA-COF is comparable to recently reported carbon base electrode materials as discussed later. We have also estimated the specific capacitance over different current density as presented in the ESI, Figure S11b. The details charge storage ability of the COF material was further evaluated from the galvanostatic charge-discharge (GCD) at various load current densities as presented in the Figure 7c. The specific capacitance (C_{sp}) was derived from the GCD curve using the equation (II) [52].

$$C_{sp} = \frac{(I \times \Delta t)}{(\Delta V \times m)} \quad (II)$$

Where I is the applied current density, Δt is the discharge time, ΔV is the potential window and m is the weight of the electrode materials. The GCD charge-discharge of the TFP-NDA-COF appeared as equilateral triangle shapes, implied EDLC behavior and ideal charge storage activity with a good reversibility of the electrode material through the charge-discharge process. The nonlinearity of the charge-discharge curve verifies the pseudo capacitance behavior of TFP-NDA-COF due to faradic reaction occur at the electrode surface. With increasing the load current density, the specific capacitance of the electrode material tends to decrease. The highest specific capacitance was estimated 348 F g^{-1} at 0.5 A g^{-1} load current density. The high specific capacitance value of TFP-NDA-COF is attributed

to better utilization of porous surface, presence of heteroatom (nitrogen), which could provide numerous active sites for facile ion transfer and the π electronic conjugation along the polymeric 2D layered network. The nanoscale porosity in the polymeric chain together with porous channel acts as ion reservoir to facilitate fast electrolyte permeation into the polymer matrix by shortening the H^+ ion diffusion distance to the active redox site. Therefore, the TFP-NDA-COF showed excellent capacitive behavior. The estimated specific capacitance is comparable with current state of the art metal oxide nanostructure and carbon base materials. Some recently reported materials are metal oxide and carbon base material such as biomass derived nitrogen doped porous carbons (239 F g^{-1} @ 0.5 A g^{-1}) [55], three-dimensional NiO/ultrathin derived graphene hybrid (425 F g^{-1} @ 2 A g^{-1}) [56], mesoporous Carbon/ iron oxide nanoparticle composites (326 F g^{-1} @ 0.5 A g^{-1}) [57], ZnO/reduced graphene oxide nanocomposite (308 F g^{-1} @ 1 A g^{-1}) [58], curved graphene nanosheets (256 F g^{-1} @ 0.3 A g^{-1}) [59], microwave assisted reduced graphene oxide (191 F g^{-1} @ 0.15 A g^{-1}) [60], hydrothermally reduced graphene oxide (367 F g^{-1} @ 1 A g^{-1}) [61], nitrogen doped porous carbon (281 F g^{-1} @ 0.05 A g^{-1}) [62], porous carbon nanosheets (296.2 F g^{-1} at 0.05 A g^{-1} in 6 M KOH) [63] showed comparable performance with TFP-NDA-COF.

Furthermore, chemical stability of the as-synthesized COF material was investigated by employing charge-discharge cycle at load current density of 5 A g^{-1} as presented in the Figure 7d. The as-synthesized TFP-NDA-COF retains 75% capacitance after 8000 charge-discharge cycles. The excellent electrochemical stability can be manifested due to the N-rich π -conjugated porous structures of the covalent organic framework. The energy density and power density are the two key factors for evaluating energy storage materials. The excellent energy storage ability of a good material can be defined from the ability to provide high energy density at high charge discharge rate. We have also estimated the energy density 48.3

W h kg⁻¹ (power density 247 W kg⁻¹) and 28.4 W h kg⁻¹ (power density 2434 W kg⁻¹) at current density 0.5 A g⁻¹ and 5 A g⁻¹ respectively (Supporting information: Section 1). The energy density and power density was found to be similar trend with previous reports.[64] To know more about the electrode-electrolyte interface kinetics we have studied electrochemical impedance study. The Nyquist plot of TFP-NDA-COF was presented in Figure. 8. The impedance spectra consisted with an arc at a higher frequency region and a vertical line at a lower frequency region. At very high frequencies, the intercept at real part (Z_{real}), which is a combination of ionic resistance of the electrolyte, intrinsic resistance of the substrate, and contact resistance at the active material/current collector interface. The major significance of the impedance spectra relies on the high-frequency range. High-frequency region corresponds to the charge transfer resistance (R_{ct}) which is determined by the diameter of the semicircle. Smaller the semicircle of the as-synthesized TFP-NDA-COF implies fast charge transfer at the electrode-electrolyte interfaces. Furthermore, after the cyclic stability test of the electrode material, the semicircle nature of the Nyquist plot has been retained (Figure 8). The observed results attributed to the extended porous network which allows the H⁺ ions diffusion hence decreases R_{ct} [65]. Hence, it increased the energy storage ability of the as-synthesized TFP-NDA-COF.

Conclusions

In summary, we have successfully developed a new β -ketoenamine linked naphthalene based porous covalent organic framework TFP-NDA-COF through simple Schiff base condensation polymerization reaction between 1,5-naphthalenediamine (NDA) and triformylphloroglucinol (TFP) using 1,4-dioxane solvent in the presence of acetic acid as catalyst. Further, we have used this material as an electrode for supercapacitor application. The electrochemical measurement of the material showed very good supercapacitive

behavior. Its excellent energy storage ability with high retention of chemical stability (75%) even after 8000 cycles could be attributed to the presence of naphthalene moiety for facile π conjugation, N as a hetero atom for redox activity, high specific surface area and permanent porosity in the channel-like polymer network. From our experimental results, we can conclude that exploration of this type of imine based π -conjugated COF materials for supercapacitor electrode will be very promising in the field of developing portable power storage devices.

AUTHOR INFORMATION

Corresponding Author

* E-mail: msab@iacs.res.in

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Figure Captions:

- Figure 1.** The synthetic scheme (A) and extended structural view (B, C) of TFP-NDA-COF.
- Figure 2.** a) PXRD pattern of TFP-NDA-COF, b) Single hexagonal unit of the COF, c) π - π stacking of 2D layer with distance.
- Figure 3.** N₂ adsorption-desorption and pore size distribution diagram (inset) of TFP-NDA-COF.
- Figure 4.** XPS plot of TFP-NDA-COF: full range scan (a), short range scan for C1s (b), N1s (c) and ¹³C solid state NMR spectrum (d).
- Figure 5.** A) FTIR plot of TFP-NDA-COF, B) UV-VIS spectrum of the COF, C) Binding energy diagram.
- Figure 6.** A) FESEM image and B) HRTEM image of TFP-NDA-COF.
- Figure 7.** a) CV curve of TFP-NDA-COF at different scan rate, b) CV curve with redox peaks at 2-20 mV s⁻¹ scan rate, c) galvanic charge-discharge diagram d) plot for the cyclic performance test of TFP-NDA-COF.
- Figure 8.** Nyquist plot of TFP-NDA-COF.

Figure 1

Figure 1. The synthetic scheme (A) and extended structural view (B, C) of TFP-NDA-COF.

Figure 2

Figure 2. a) PXRD pattern of TFP-NDA-COF, b) Single hexagonal unit of the COF, c) π - π stacking of 2D layer with distance.

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Figure 4

Figure 4. XPS plot of TFP-NDA-COF: full range scan (a), short range scan for O1s (b), N1s (c) and ^{13}C solid state NMR spectrum (d).

Figure 5

Figure 5. A) FTIR plot of TFP-NDA-COF, B) UV-VIS spectrum and C) binding energy plot of the TFP-NDA-COF.

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Figure 6. A) FESEM image and B) HRTEM image of TFP-NDA-COF.

Figure 7

Figure 7. a) CV curve of TFP-NDA-COF at different scan rate, b) CV curve with redox peaks at 2-20 mV s⁻¹ scan rate, c) galvanic charge-discharge diagram d) plot for the cyclic performance test of TFP-NDA-COF.

Figure 8

Figure 8. Nyquist plot of TFP-NDA-COF

Research Highlights

- A new porous crystalline extended network π -conjugated covalent organic framework have been designed.
- Solvothermal Schiff base condensation of 1,3,5-triformylphloroglucinol (TFP) with 1,5-diaminonaphthalene (NDA) resulted this new COF.
- The electrochemical study suggested the capability of energy storage up to 379 F g^{-1} at 2 mV s^{-1} scan rate by this COF.
- TFP-NDA-COF displayed excellent specific capacitance retention of 75% after 8000 charge discharge cycles.
- π -conjugation along 2D layered network, ion conduction inside the porous channels and permanent porosity is responsible for the efficient energy storage of this COF.