SUPPORTING INFORMATION

Supporting Information

2D Organic nanosheets of self-assembled guanidinium derivative for efficient single sodium-ion conduction: rationalizing morphology editing and ion conduction

Anik Kumar Dey,[a,b] Sam Sankar Selvasundarasekar,[c] Subrata Kundu,[c]* Amal Kumar Mandal, [a, b]*, Amitava Das[d]* and Sumit Kumar Pramanik[a, b]*

a. Analytical and Environmental Science Division and Centralized Instrument Facility, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat-364002, India.

b. Academy of Scientific and Innovative Research (AcSIR), CSIR- Human Resource Development Centre, (CSIR-HRDC) Campus, Sector 19, Kamla Nehru Nagar, Ghaziabad, Uttar Pradesh-201 002, India.

c. Electrochemical Process Engineering (EPE) Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu, 630003, India. Email:

d. Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur: 741 246, West Bengal, India.

*Corresponding Author Email: sumitpramanik@csmcri.res.in;
akmandal@csmcri.res.in;
kundu.subrata@gmail.com;
amitava@iiserkol.ac.in

SUPPORTING INFORMATION

No	Contents	Page No
1	Materials and Characterization	3
2	Synthesis routes and methodology of GUA & AD-1	3-4
3	^{1}H NMR spectrum of GUA	5
4	^{13}C NMR spectrum of GUA	7
5	ESI-MS spectrum of GUA	8
6	FT-IR spectrum of GUA	10
7	^{1}H NMR spectrum of AD-1	11
8	^{13}C NMR spectrum of AD-1	13
9	FT-IR spectrum of AD-1	13
10	XPS survey plot of AD-1	14
11	High-resolution XPS spectra of AD-1	14
12	TEM and HRTEM image of nanosheet morphology	14
13	SAED images of nanosheet and nanotube morphology	15
14	Temperature-dependent UV-vis study of Marigold, Sunflower, Nanorod morphology	10
15	Value of kiso, ΔH and ΔS of the self-assembly process in all water/IPA proportions (67:33, 50:50, 33:67)	10
16	PXRD pattern of all morphology	11
17	FT-IR spectra of all morphology	11
18	TGA profile of all morphology	12
19	DSC plot of all morphology	12
20	Value of exothermic and endothermic peak for all morphologies	13
21	The upper and lower temperatures for the loss of solvents recorded from the TGA profiles for the respective morphologies. Corresponding DSC data for loss of solvents	13
22	Methods of sample preparation for FE-SEM, TEM	13
23	Comparable chart for sodium-ion conductivity values and transference number with reported materials	14
24	Determination of the degree of aggregation (α_{agg})	15
25	Experimental details of conductivity measurement	15
26	Sample preparation for Na-ion conductivity	16
27	Conductivity value for nanosheet morphology at different temperatures	16
28	Impedance plot for nanosheet morphology at different temperatures and the Arrhenius plot	16
29	Experimental details of Na$^+$ transference number measurement	17
30	Experimental details of electrochemical stability	17

1. Materials and Characterization

1.1 Materials: The chemicals like Disodium-4-formylbenzene-1,3-disulfonate, Guanidium hydrochloride, Hydrazine hydrate used for synthesis were purchased from

commercial suppliers and used directly without further purification. Solvents such as isopropanol (IPA), methanol, were purchased from Spectrochem Chemical company. A Barnstead System, U.S., was employed to get high purity nanopure water for making all the aqueous solutions.

1.2 Characterization: ^{1}H NMR and ^{13}C NMR were recorded using Geol resonance ECZ600R spectrometer at 25 °C. TMS was used as an internal reference during NMR spectroscopic study. Parkin Elmer 883 spectrometer was used to record the FT-IR data using the KBr pellet. UV-Vis absorption spectra were recorded using Shimadzu corp 80109 UV-Vis spectrophotometer. Using a Zetasizer Nano-ZS90 (Malvern) instrument with a 632.8 nm He-Ne laser DLS, experiments were carried out at 298 K. Transmission electron microscopy images were collected using a JEOL JEM-2100 electron microscope working at 200 kV accelerating voltage. The samples were prepared on the surface of lacey-carbon-supported copper TEM grids. JEOL JSM-7100F instrument working at 18 kV accelerating voltage was used to record the FE-SEM data. Before taking the FE-SEM images, the thin coating of Au (~ 4 nm) was coated using a vacuum evaporator. Using a Q-of-micro quadrupole mass spectrophotometer (Micromass), ESI-MS was done. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a Philips X'pert X-ray powder diffractometer using Cu-Ka radiation (λ=1.5418 A) in the 2θ range of 5–50º. XPS analysis was carried out using a Thermo Scientific ESCALAB 250 Xi photoelectron spectrometer (XPS) using a monochromatic Al Kα X-ray as an excitation source. Thermo-gravimetric analysis (TGA) was conducted using an Auto TGA 2950 apparatus under a nitrogen flow of 100 mL min^{-1} while heating from room temperature. DSC measurements were carried out in a Netzsch DSC 204 F1 Phoenix instrument. The conductivity study has been done using the electrochemical work station (VSP Biologic, France).

2. Synthesis scheme of AD-1:

Compound AD-1 was synthesized following a two-step reaction.

2.1 Synthesis procedure of GUA:

0.0209 mol (2 g) Guanidium Hydrochloride was dissolved in 15 mL isopropanol. Then 3.1 mL Hydrazine Hydrate was added dropwise using a syringe. The whole solution was placed for reflux at 85°C overnight. After some time, a white precipitate was observed. This white precipitate was filtered and the residue was washed with isopropanol. This residue was further dried in a desiccator. Yield 2.43 g (83%). ^{1}H NMR (500 MHz, DMSO-d$_6$, δ ppm): 8.61 (3H, s), 4.51 (6H, s). ^{13}C NMR (125 MHz, DMSO-d$_6$, δ ppm): 159.0. m/z value, [M-Cl]$^+$: 105.09
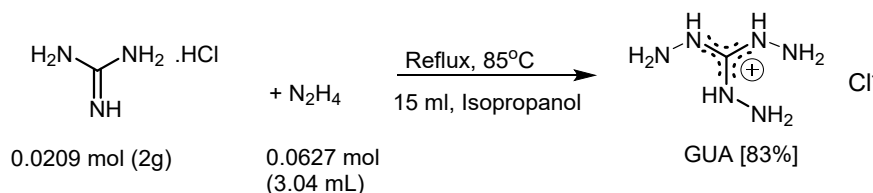
Figure S1: Synthesis scheme of GUA

2.2 Synthesis procedure of AD-1:

Initially, 1 mmol (140.58 mg) Tri-ammonium guanidium hydrochloride was taken and dissolved in 2.5 mL Milli-Q water. Then 3.1 mmol (961.62 mg) Disodium-4-formyl-1,3-disulfonate was taken in 5 mL Methanol. Then this aldehyde solution was added to the amine solution and the reaction mixture was refluxed at 70°C overnight. Then yellow-colored precipitate was obtained. Then the yellow precipitate was filtered and dried in a desiccator. Yield 773 mg (76%). ^{1}H NMR (500 MHz, DMSO-d6, δ ppm): 12.49 (3H,s), 9.57 (3H,s), 8.35 (3H, d, J=10), 8.148 (3H, d, J=2), 7.685 (3H, d, J=5). ^{13}C NMR (125 MHz, DMSO-d6, δ ppm): 149.85, 149.06, 148.3, 146.1, 129.38, 126.26, 125.01, 123.80.
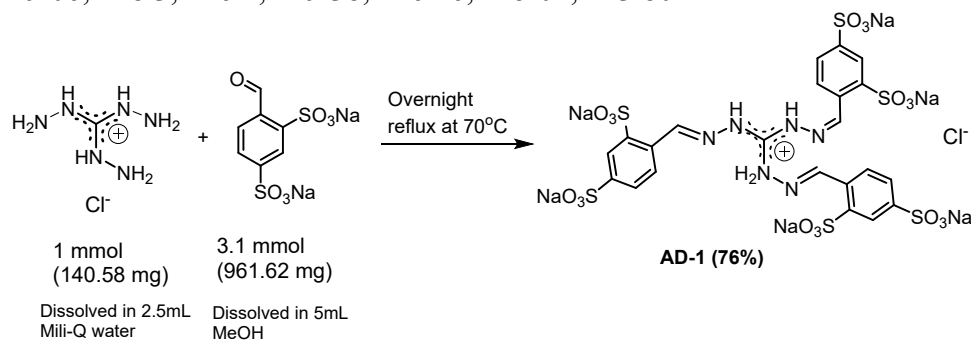

Figure S2: Synthesis scheme of AD-1
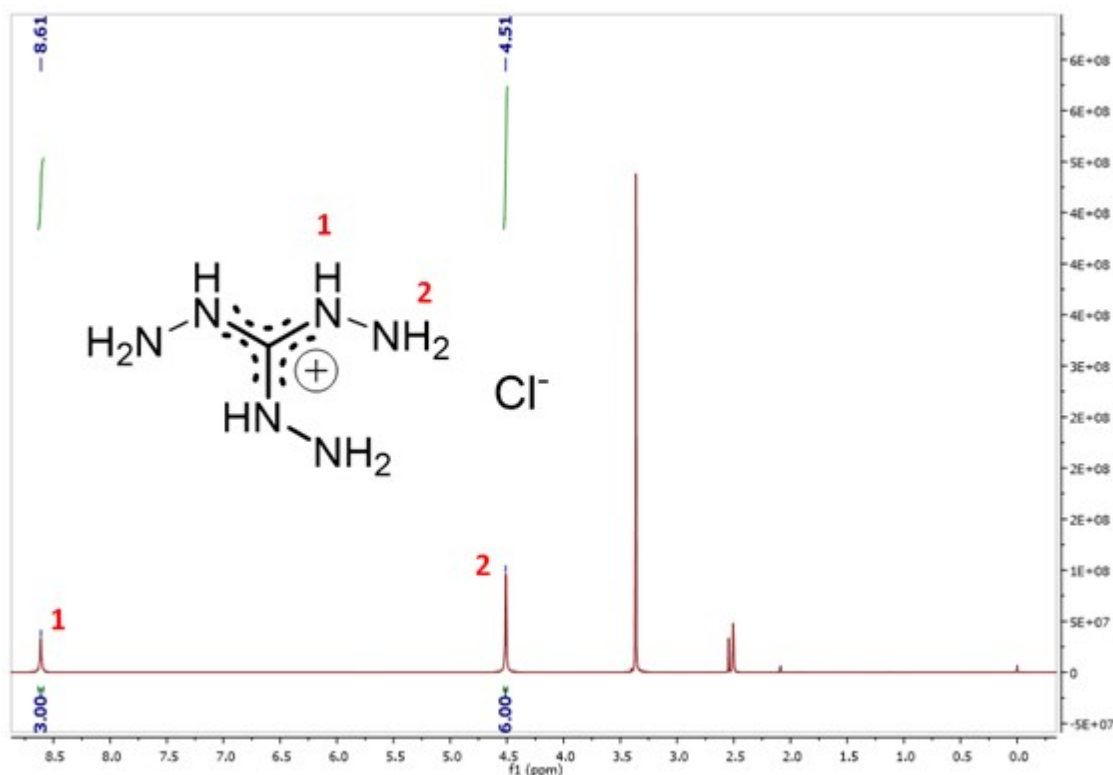
3. ^{1}H NMR spectra of GUA:

Figure S3: ^{1}H NMR spectrum of GUA recorded in DMSO-*d6*
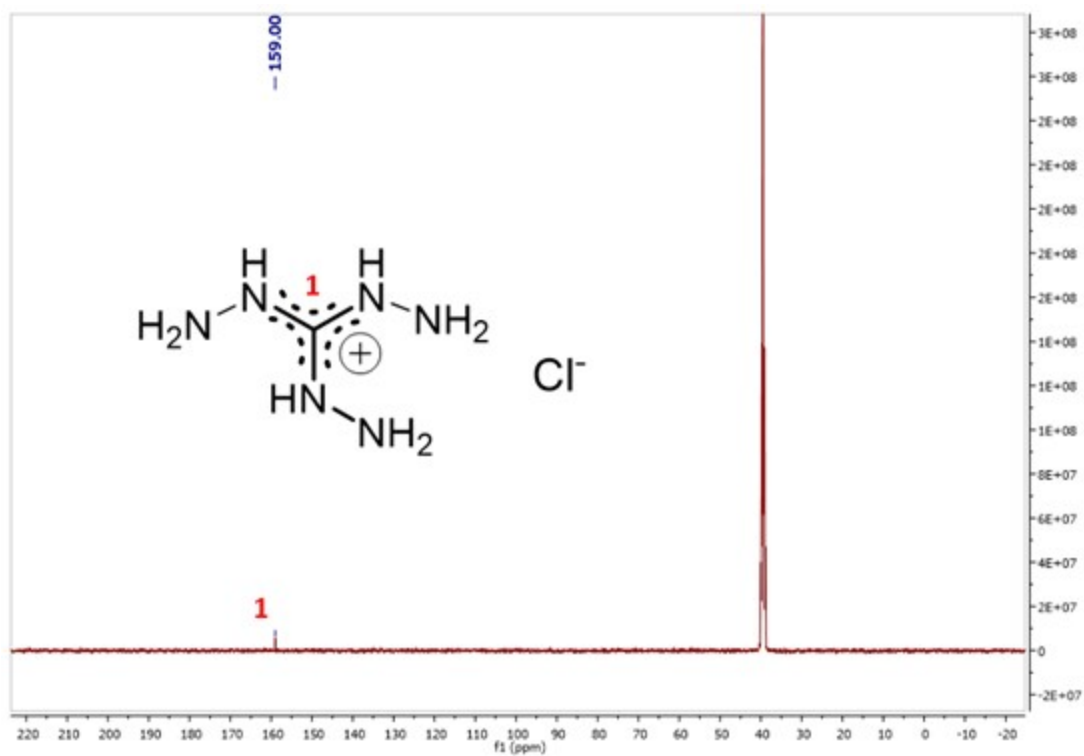
4

4. ^{13}C NMR spectra of GUA:

Figure S4: ^{13}C NMR spectrum of GUA recorded in DMSO-*d6*

5. ESI-MS spectrum of GUA:

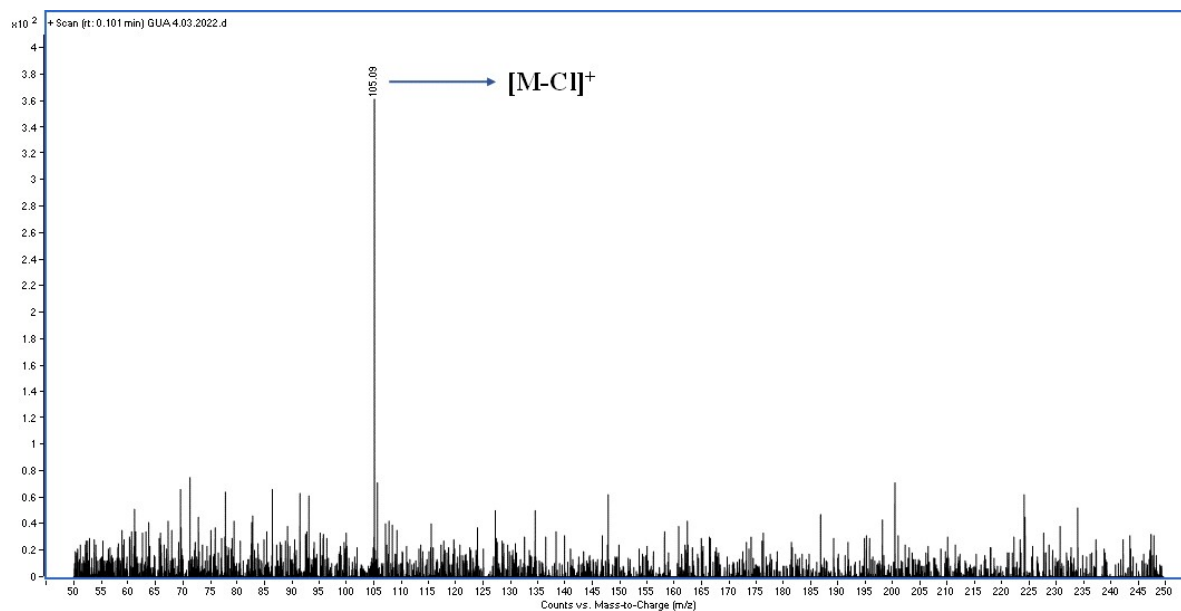**Figure S5:** ESI-MS spectrum of GUA recorded in Methanol

6. FT-IR spectrum of GUA:
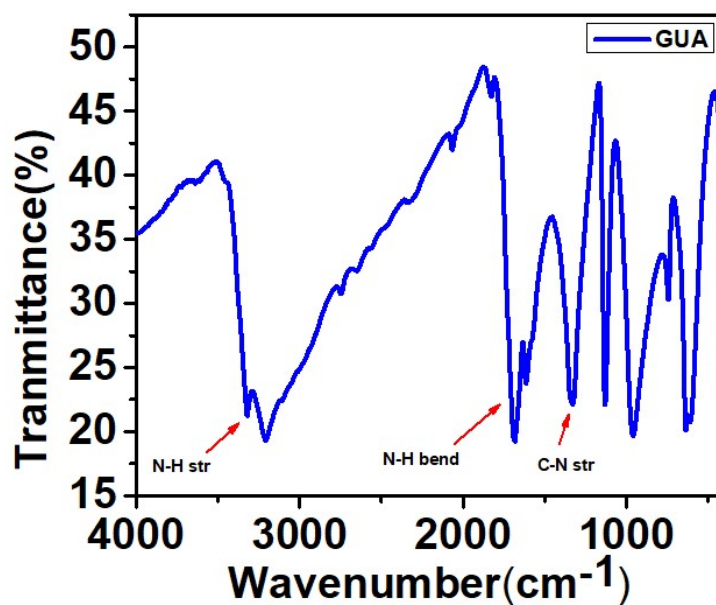
Figure S6: FT-IR spectrum of GUA

7. ^{1}H NMR spectra of AD-1:
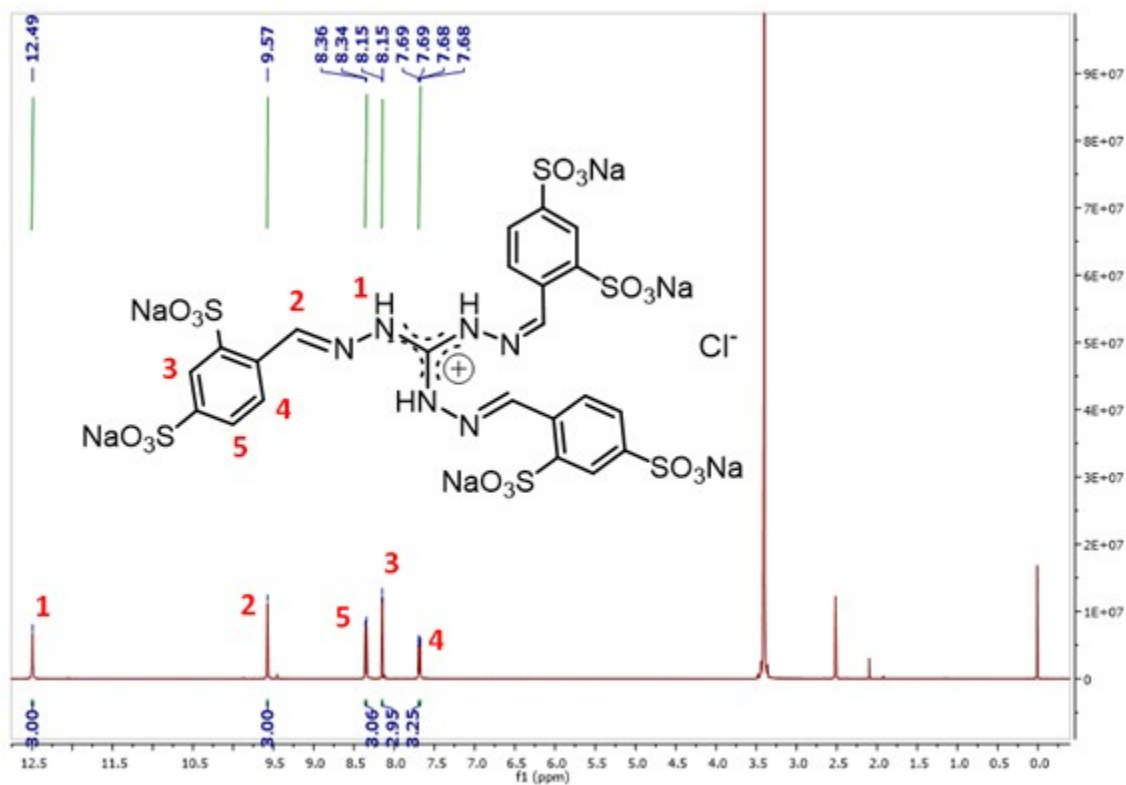
Figure S7: ^{1}H NMR spectrum of AD-1 recorded in DMSO-*d6*

8. ^{13}**C NMR spectra of AD-1:**

Figure S8: ^{13}C NMR spectrum of AD-1 recorded in DMSO-*d6*

9. FT-IR spectrum of AD-1:
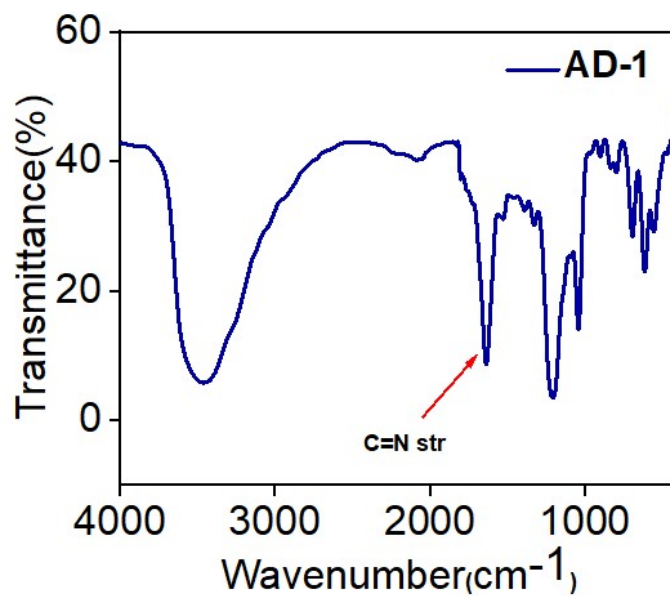
Figure S9: FT-IR spectrum of AD-1

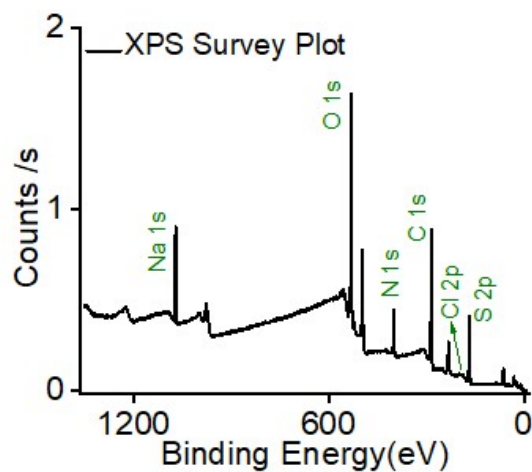**10. XPS Survey Plot of AD-1:**

Figure S10: XPS Survey Plot of AD-1

11. High Resolution XPS Spectra of AD-1:
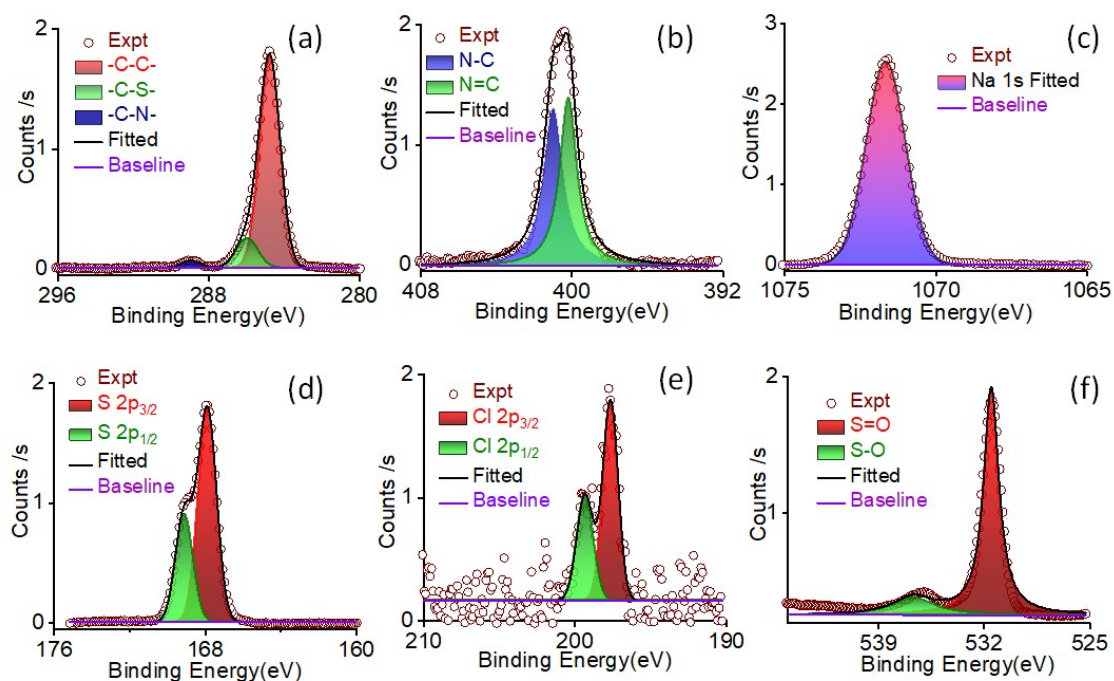
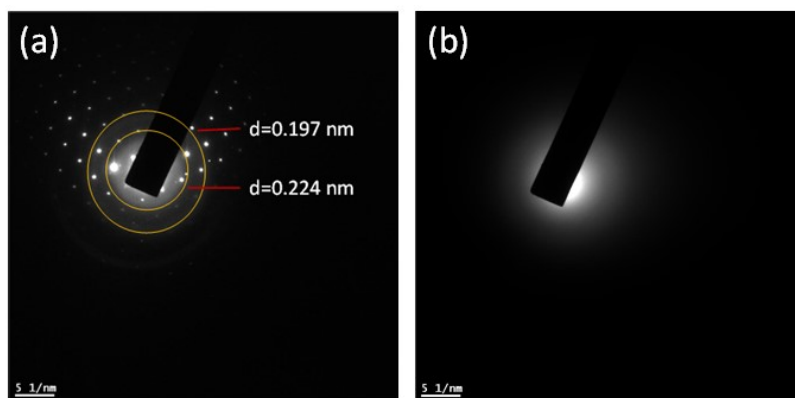**Figure S11:** XPS spectra of AD-1; (a) C 1s; (b) N 1s; (c) Na 1s; (d) S 2p; (e) Cl 2p; (f) O 1s.

8

12. TEM and HRTEM images of Nanosheet morphology:
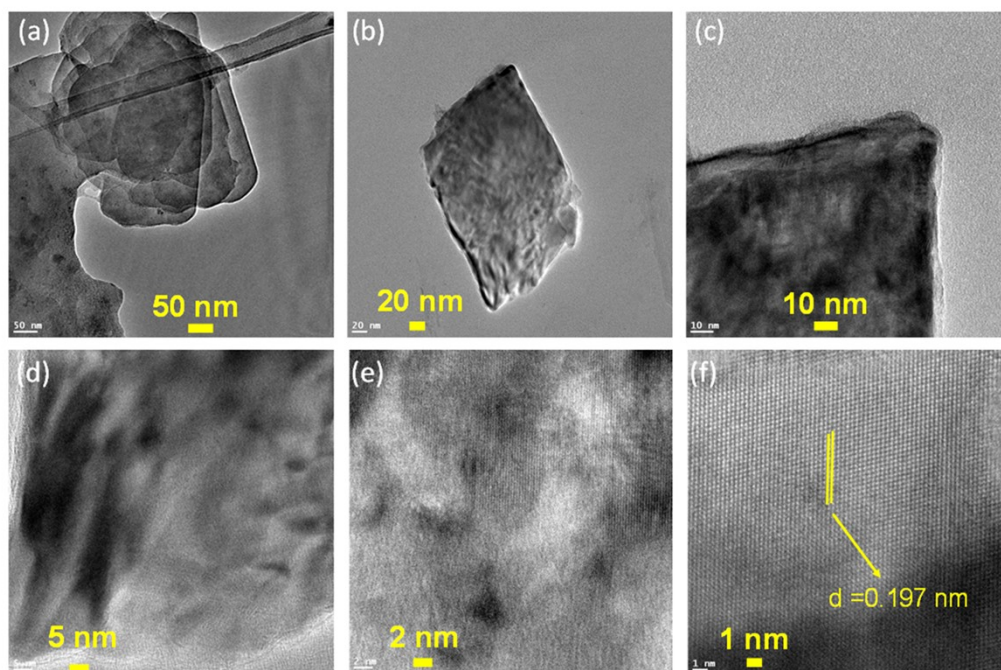
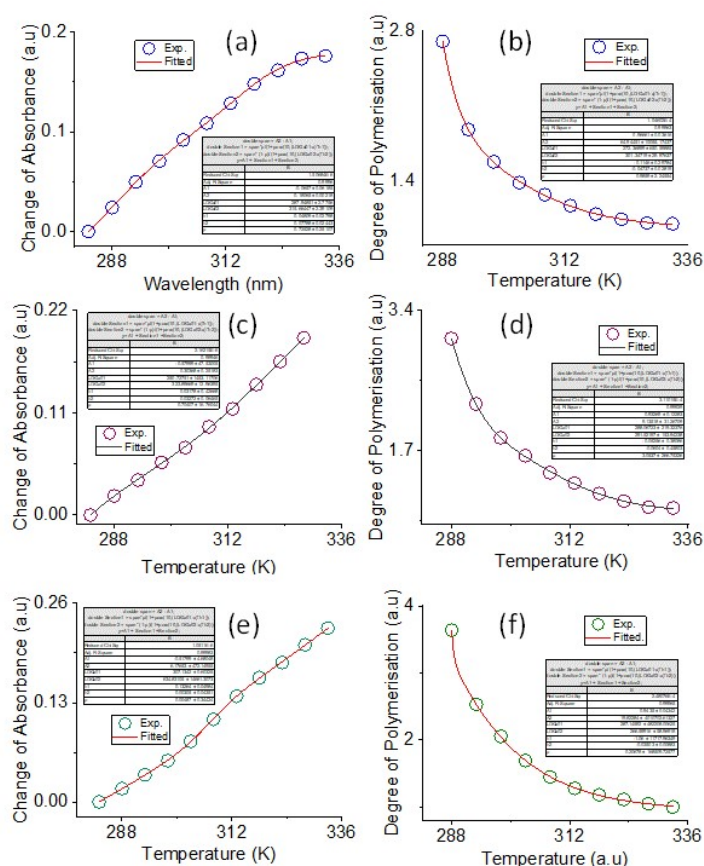**Figure S12:** (a-d) TEM images of nanosheet morphology; (e-f) HRTEM images of nanosheet morphology.

13. SAED images of Nanosheet and Nanotube morphology:

Figure S13: (a) SAED image of nanosheet morphology; (b) SAED image of nanotube morphology.

14. Temperature-dependent UV-vis study of Marigold, Sunflower, Nanorod morphology:

Figure S14: (a) Corresponding plot of change of absorbance at 374 nm with temperature for Marigold morphology; (b) Corresponding plot of the degree of polymerization, DP_N, as a function of temperature; (c) Corresponding plot of change of absorbance at 374 nm with temperature for Sunflower morphology; (d) Corresponding plot of the degree of polymerization, DP_N, as a function of temperature; (e) Corresponding plot of change of absorbance at 374 nm with temperature for Nanorod morphology; (f) Corresponding plot of the degree of polymerization, DP_N, as a function of temperature.

15. Value of k_{iso}, ΔH and ΔS (Table S1) of the self-assembly process in varying water/IPA proportions (67:33, 50:50, 33:67)

Solvent ratio of the self-assembly process (Water: IPA)	k_{iso} (M^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
67:33	5.4×10^4	-95.98	-231.1
50:50	3.9×10^4	-84.62	-195
33:67	2.2×10^4	-74.51	-167.2

16. PXRD pattern of all morphology:
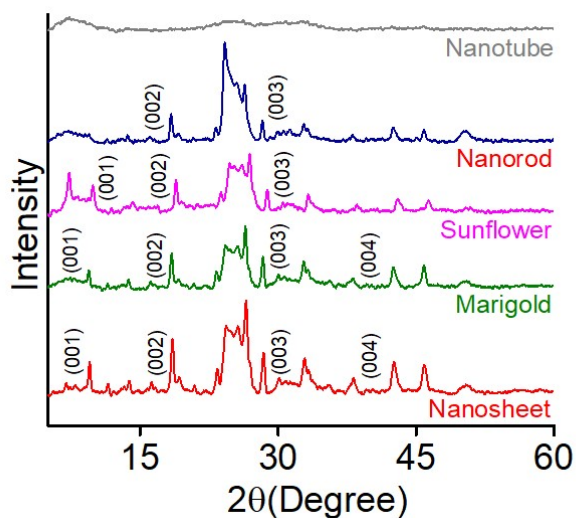
Figure S15: PXRD pattern of all morphology

17. FT-IR spectra of all morphology:
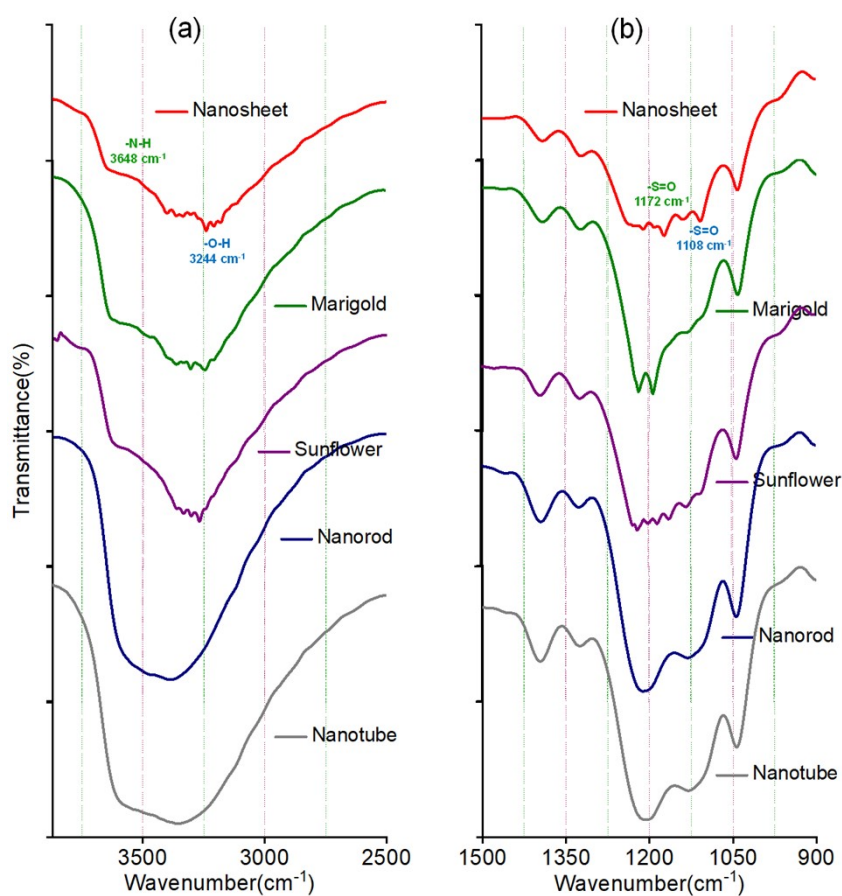
Figure 16: Partial FT-IR spectra of the respective morphologies focusing on (a) –N-H and –O-H stretching vibration and (b) –S=O stretching vibration, respectively.

11

18. TGA profile of all morphology:
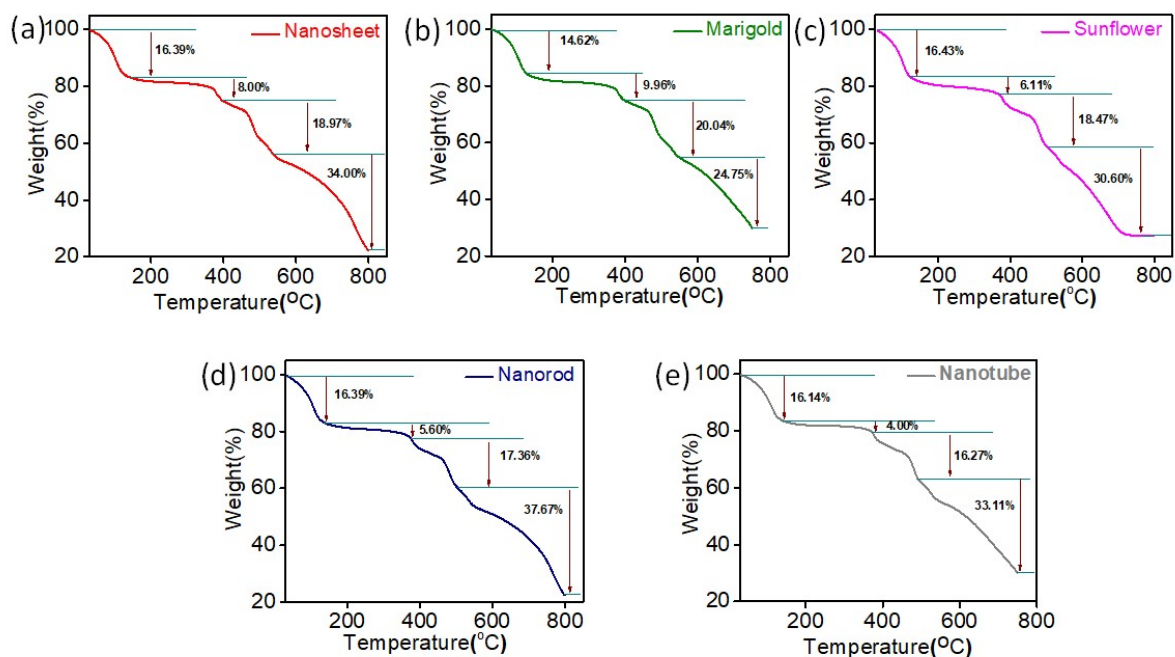
Figure S17: Thermogravimetric analysis (TGA) curves of (a) nanosheet, (b) marigold, (c) sunflower, (d) nanorod, (e) nanotube morphology.

19. DSC plot of all morphology:
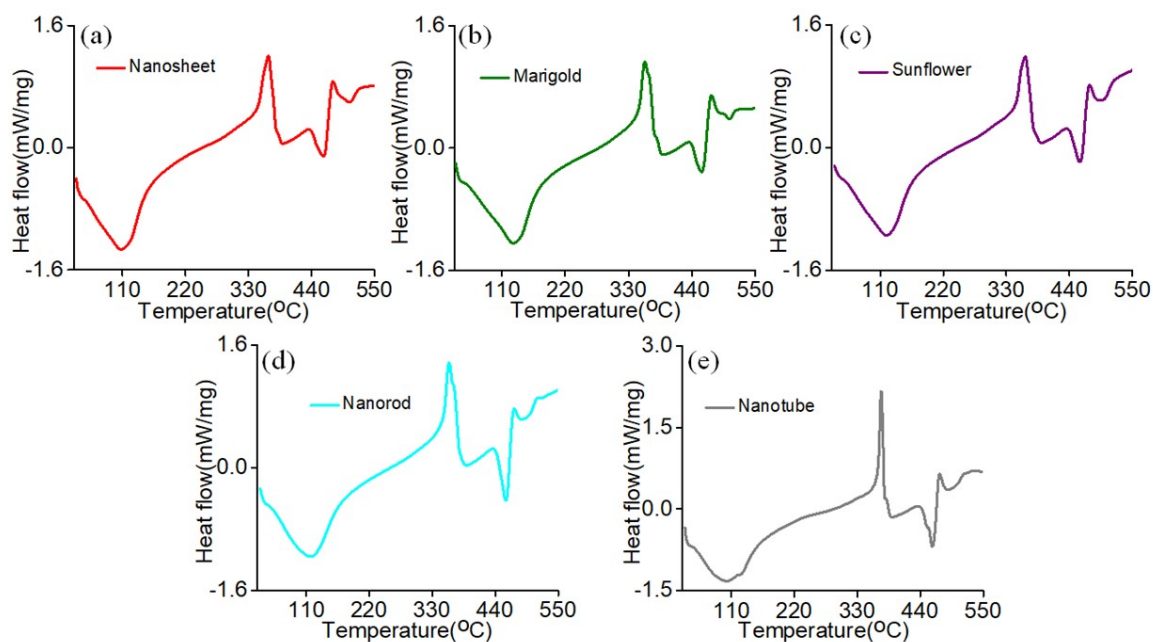
Figure S18: DSC plot for (a) nanosheets, (b) marigold, (c) sunflower, (d) nanorod, and (e) nanotube morphology, respectively.

12

20. Value of exothermic and endothermic peak (Table S2) for all morphologies:

Morphology	Solvent ratio (Water : IPA)	Endothermic peak for solvent dissociation	Exothermic peak	Endothermic peak for melting
Nanosheet	100:0	107.7 °C	364.7 °C	466 °C
Marigold	67:33	129.7 °C	358.7 °C	467 °C
Sunflower	50:50	120.7 °C	362.7 °C	467 °C
Nanorod	33:67	117.7 °C	359.7 °C	467 °C
Nanotube	0:100	102.0 °C	371.1 °C	467 °C

21. The upper and lower temperatures for the loss of solvents recorded from the TGA profiles (Table S3) for the respective morphologies. Corresponding DSC data for loss of solvents.

Nanostructured Morphology	Starting point in TGA profile(°C)	Ending point in TGA profile(°C)	Solvent degradation temperature in DSC plot(°C)
Nanosheet	RT	119.9	107.7
Marigold	RT	135.1	129.7
Sunflower	RT	132.0	120.7
Nanorod	RT	136.5	117.7
Nanotube	RT	135.8	102.0

22.   Methods of sample preparation for FE-SEM, TEM:

Sample preparation for Nanosheet and Nanotube morphology: To get the exfoliated nano sheet, water was used as a solvent. 1 mg/mL (total volume 5mL) water suspension of the compound AD-1 was initially sonicated for 10 minutes. Then allow for 30 minutes to assemble the molecule. Then the solution is half diluted and sonicated for 10 min. Then again allow for 30 minutes to get the final morphology. From that solution, 20 μL was drop cast on Si (100) wafer, and we observed the nanosheet-like morphology. From that aliquot, 20 μL was drop cast on a TEM grid and Si (100) wafer, and we observed the nanosheet morphology. After drop-casting, all the samples were dried under a desiccator. Before taking the FE-SEM images, the ultrathin gold layer was coated on all the samples.
The same procedure was done by using isopropanol to get nanotube morphology.

Sample preparation for Marigold, Sunflower and Nanorod morphology: First 2 mg of AD-1 was dissolved in 1 mL of IPA. Then, this solution was exposed to 1 mL of water to maintain a solvent ratio of 1:1 IPA/water (v/v). The solution was sonicated for 10 minutes and then was allowed to assemble for 30 minutes. Then, the solution was half-diluted maintaining the volume ratio of solvents. The solution was further sonicated for 10 minutes and was allowed for 30 minutes to get the final morphology. From that solution, 20 μL was drop cast on Si (100) wafer, and we observed the nanoflower-like morphology. From that aliquot, 20 μL was drop cast on a TEM grid and Si (100) wafer, and we observed the nanoflower morphology. After drop-casting, all the samples were dried under a desiccator. Before taking the FE-SEM images, the ultrathin gold layer was coated on all the samples.
The same procedure was followed for 1:2 (v/v) and 2:1 (v/v) IPA/water solvent combination.

23. Comparable chart (Table S4) for Sodium-ion conductivity values and transference number with reported materials:

Sample	Conductivity value/ S cm^{-1} & t_{Na}	Temperature	Description	Reference
AD-1	3.724×10^{-4} t_{Na} 0.83	Room temperature	SONs	Present study
$Na_3Zr_2Si_2PO_{12}$	3.6×10^{-4} t_{Na} 0.92	Room temperature	NASICON	*Energy Environ. Sci.* **2015**, 8, 3589-3596
TPDBD-Can	1.3×10^{-4} t_{Na} 0.9	At 25 °C	COF	*Nat. Commun.* **2023**, 14, 3066
EO10-PFPE	1×10^{-4} t_{Na} 0.46	At 80 °C	Solid Polymer Electrolytes	*Nat. Mater.* **2022**, 21, 1057–1065
$Na_{2.9}PS_{3.95}Se_{0.05}$	1.21×10^{-4} t_{Na} 0.9997	Room temperature	Solid-state ion conductor	*ACS Nano* **2018**, 12, 2809−2817
PFSA-Na with EC-PC	2.8×10^{-4} t_{Na} 0.85	Room temperature	Solid polymer electrolytes	*Adv. Sci.* **2017**, 4, 1700072
PVC/CPE	1.2×10^{-4} t_{Na} 0.60	At 25 °C	Solid polymer electrolytes	*ACS Appl. Mater. Interfaces* **2019**, 11, 43056
$(Na[(FSO_2)(n-C_4F_9SO_2)N]$, NaFNFSI)/PEO	3.36×10^{-4} t_{Na} 0.24	At 80 °C	Solid polymer electrolytes	*J. Mater. Chem. A* **2017**, 5, 7738
PEO/CQDs-Na	7.17×10^{-5} t_{Na} 0.48	Room temperature	Solid polymer electrolytes	*Adv. Sci.* **2018**, 5, 1700996
PEO-SN-NaClO$_4$/PAN-Na$_3$Zr$_2$Si$_2$PO$_{12}$-NaClO$_4$	1.36×10^{-4} t_{Na} 0.42	Room temperature	Solid polymer electrolytes	*Adv. Funct. Mater.* **2021**, 31, 2002144
40% SPA−SPP Single Na-ion conductor	10^{-4} t_{Na} 0.97	Room temperature	Solid Polymer Electrolytes	*Energy Fuels* **2022**, 36, 6459-6467

24. Determination of the degree of aggregation (α_{agg}):

The degree of aggregation (α_{agg}) was calculated from the temperature-dependent UV-Vis spectral data by using equation (1) as mentioned below.

$$\alpha(T) = \frac{\varepsilon(T) - \varepsilon_M}{\varepsilon_A - \varepsilon_M} \quad\text{...............(1)}$$

Where $\varepsilon(T)$ is the measured extinction coefficient at temperature T; ε_M and ε_A are the extinction coefficients of the monomer and fully aggregated state, respectively. The latter two values were determined from the spectral data at high and low temperatures, respectively.

The experimentally determined degree of aggregation was fitted temperature-dependent isodesmic self-assembly model accordingly with equation (2) as mentioned below, to obtain the enthalpy value ΔH.

$$\alpha(T) = \frac{1}{1 + \exp\left[-0\cdot908\Delta H\dfrac{T - T_m}{RT_m^2}\right]} \quad\text{...........(2)}$$

Where α is the degree of aggregation, and Tm is the melting temperature defined as the temperature at $\alpha = 0.5$ at $T = T_m$. R is the Boltzmann constant.

From the experimentally determined degree of aggregation, the number-averaged degree of polymerization, DP_N, calculated temperature-dependent isodesmic self-assembly model accordingly with equation (3), as mentioned below.

$$DP_N(T) = \frac{1}{\sqrt{1 - \alpha(T)}} \quad\text{..............(3)}$$

From the number-averaged degree of polymerization, DP_N, and the known concentration of molecules, C_T, the equilibrium constant K_e was determined as a function of temperature using equation (4), as mentioned below.

$$DP_N(T) = \frac{1}{2} + \frac{1}{2}\sqrt{4k_e(T)C_T + 1} \quad\text{...........(4)}$$

25. Experimental details of conductivity measurement:

The ionic conductivity measurements were carried out using stainless steel (SS) electrodes, unlike the comb-shaped Au electrodes, as used by Wu *et al.* to prepare their samples for ionic conductivity measurements. The use of SS electrodes is a more reliable and fast method to measure ionic conductivity compared to the Au electrodes. We have used the Whatman filter membrane separator, which had more permeability, and the thickness was 0.026 cm, which is calculated using the screw cage method. The radius of the SS electrode surface was 7 mm, and the calculated area was 1.5386 cm^2. Once the sample solution was ready, we drop-casted four drops over the separator, which became wet, and kept it for drying in the oven at 50⁰ C for 2 hours. The sample was prepared under room temperature. After drying, the impedance study was carried out under room temperature in order to know the resistance values and subsequently, we calculate the related conductivity values using the standard equation

$$\sigma = \frac{d}{RA}$$

Where d = Thickness (cm), R = Resistance (ohm) and A = Area (cm^2).

26.   Sample preparation for Na-ion conductivity:

26.1. Methods of sample preparation for nanosheet and nanotube morphology:

To obtain exfoliated nanosheets, water was used as a solvent. A 1 mg/mL (total volume 5 mL) water suspension of the compound AD-1 was initially sonicated for 10 minutes and then allowed to assemble for 30 minutes. The solution was then diluted by half, sonicated for another 10 minutes, and allowed to assemble for 30 minutes. An aliquot of this homogeneously dispersed solution of nanostructures was drop-cast onto the surface of a Whatman filter membrane separator. The sample was dried at 50°C for 2 hours to remove free water. Subsequently, the sample was sandwiched between SS electrodes. The entire sample preparation was conducted at room temperature.Same procedure was done by using isopropanol to get nanotube morphology.

26.2. Methods of sample preparation for Marigold, Sunflower and Nanorod morphology:

2 mg of AD-1 was dissolved in 1 mL of IPA. This solution was then mixed with 1 mL of water to maintain a 1:1 IPA/water (v/v) solvent ratio. The resultant solution was sonicated for 10 minutes and allowed to assemble for 30 minutes. Subsequently, the solution was diluted by half while maintaining the solvent ratio. The diluted solution was sonicated for another 10 minutes and allowed to assemble for 30 minutes. An aliquot of this homogeneously dispersed solution of the nanostructures was drop-cast onto the surface of a Whatman filter membrane separator. To remove residual free water, the prepared samples were dried at 50°C for 2 hours and then sandwiched between SS electrodes.

The same procedure was followed for 1:2 (v/v) and 2:1 (v/v) IPA/water.

**27.   Conductivity value of nanosheet morphology at different temperatures:**

Table S5. The observed value of conductivity of nanosheet morphology in different temperatures.

Temperature (K)	Conductivity (S cm^{-1})
303	1.977×10^{-4}
313	2.962×10^{-4}
323	4.251×10^{-4}
333	4.639×10^{-4}
343	6.754×10^{-4}
353	9.001×10^{-4}
363	1.007×10^{-3}

Impedance plot of nanosheet morphology at different temperatures and the Arrhenius plot:
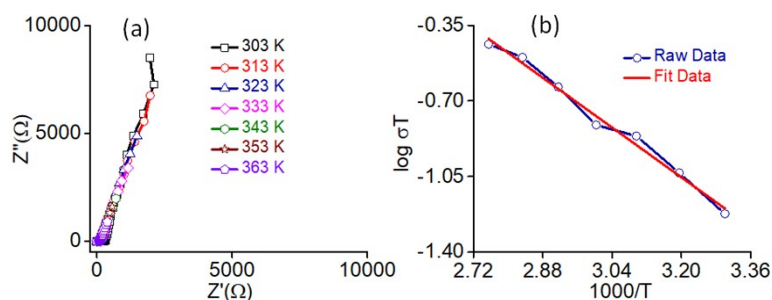
Figure S19: (a) Impedance plot of nanosheet morphology at different tempeartures; (b) Corresponding Arrehnius plot.

28. Experimental details of Na⁺ transference number measurement:

For the calculation of the Na^+ transference number, we utilized the well-known Bruce-Vincent method, wherein a symmetric cell (Na/Nanosheets/Na) was constructed, and a DC current was allowed to flow through the cell. To ensure accurate measurements, all the water in the channels needed to be coordinated. In our experiments, we ensured that all water in the channels was bound through the weight loss method. We drop-casted our sonicated nanosheets onto Whatman filter paper and kept them in an oven at 50°C for 2 hours to evaporate any excess free water from our sample. The Na/Nanosheets/Na symmetric cell was assembled inside an Ar-glove box. Therefore, according to our experimental protocol, we are confident that there was no involvement of free water during the experiment. The steady-state current obtained through potentiostatic polarization study and the related spectral curve was given as Fig. 4d for Na/nanosheet-Na/Na. The measured impedance curves are given as Fig. 4e corresponding to Na/nanosheet-Na/Na. The required values needed for the calculation of the transference number (t_{Na^+}) were tabulated.

Table S6. The observed values for t_{Na^+} calculation were measured through the potentiostatic polarization method.

Material	I_{SS} (mA)	ΔV (mV)	I_0 (mA)	R_0 (Ω)	R_{SS} (Ω)	t_{Na^+}
Na/nanosheet/Na	0.179	0.05	0.471	913.5	1093.6	0.83

The Na-ion transference number is calculated by the following equation:

$t_{Na^+} = (\Delta V - I_0 R_0)/I_0(\Delta V - I_{SS}R_{SS})$

where, I_{SS} is the steady state current, ΔV is the applied potential, I_0 is the initial current, R_0 and R_{SS} are the interfacial resistance before and after potentiostatic polarization studies, respectively.

29. Details of electrochemical stability:

The electrochemical stability study was carried out using a Na/nanosheet/Ti asymmetric cell setup to realistically simulate actual operating conditions. The sonicated nanosheets were drop-cast onto Whatman filter paper. To remove residual water from the sample, the drop-cast separator was dried in an oven at 50°C for 2 hours. The cell was then assembled inside an Ar-filled glove box. The polarization study was conducted at a sweep rate of 0.01 mV s⁻¹ within a fixed voltage window (0.9 V to 3 V vs. Na/Na⁺) at room temperature.