Supporting Information

High-Voltage Non-Aqueous Hybrid Supercapacitor Based on N2200 Polymer Supported Over Multiwalled Carbon Nanotube

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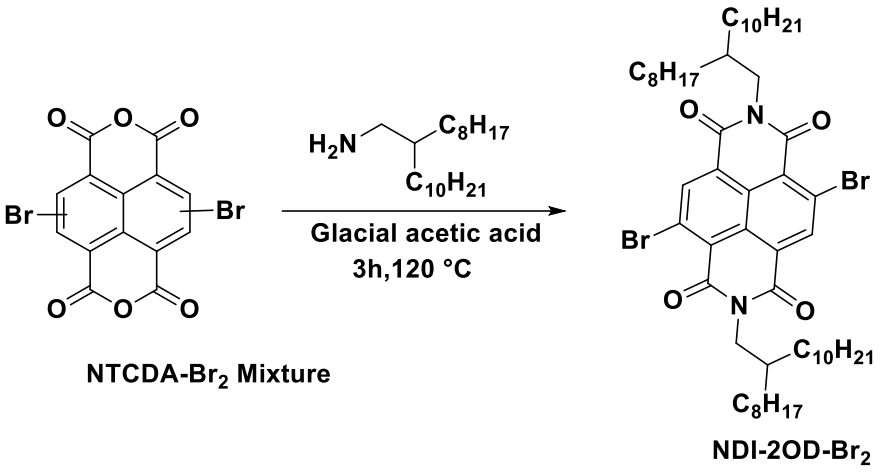
Section S1

1. **Synthesis of NDI-2OD-Br2.**



NTCDA-Br_2 Mixture

NDI-2OD-Br_2

Synthesis of N, N'-Bis (2-octyldodecyl)-2,6-dibromo-1,4,5,8-naphthalenediimide (NDI-2OD-Br2): Synthesis of NDI-2OD-Br_2 was done using the same procedure as reported in earlier literature from our group.[1] 2,6 dibromo-1,4,5,8-naphthalenetetracarboxylic acid dianhydride (NTCDA-Br_2) (4.0 g, 9.389 mmole) was taken in a two neck round bottom flask to which 106 mL of glacial acetic acid was added under N_2 atmosphere and stirred at 60-70 °C for a short period of time to get a homogeneous dispersion which was followed by addition of 2-octyldodecyl amine (11.17 g, 37.55 mmol). The reaction mixture was stirred and refluxed at 120 °C to complete dissolution for 3 hours, after which it was cooled to room temperature. The excess glacial acetic acid was evaporated and reaction mixture was concentrated under reduced pressure by rotary evaporator. Then the reaction mixture was washed with methanol to yield reddish brown powder that was filtered and dried under vacuum. The crude product was purified by column chromatography using pet ether and ethyl acetate as eluent followed by re-crystallization from acetone to get yellow powder of pure compound. Product was dried in vacuum oven at 60 °C. Yield: 1.97 g (21 %, by considering 2, 6 isomer). Melting point (85-86 °C); ^{1}H NMR (200 MHz, CDCl3) δ ppm: 8.93 (s, 2H, aromatic), 4.15 (d, 4H), 1.92 (m, 2H), 1.16, (m, 64 H), 0.80 (m, 12H).

Figure S1. ^{1}H NMR spectrum of monomer NDI-2OD-Br_2

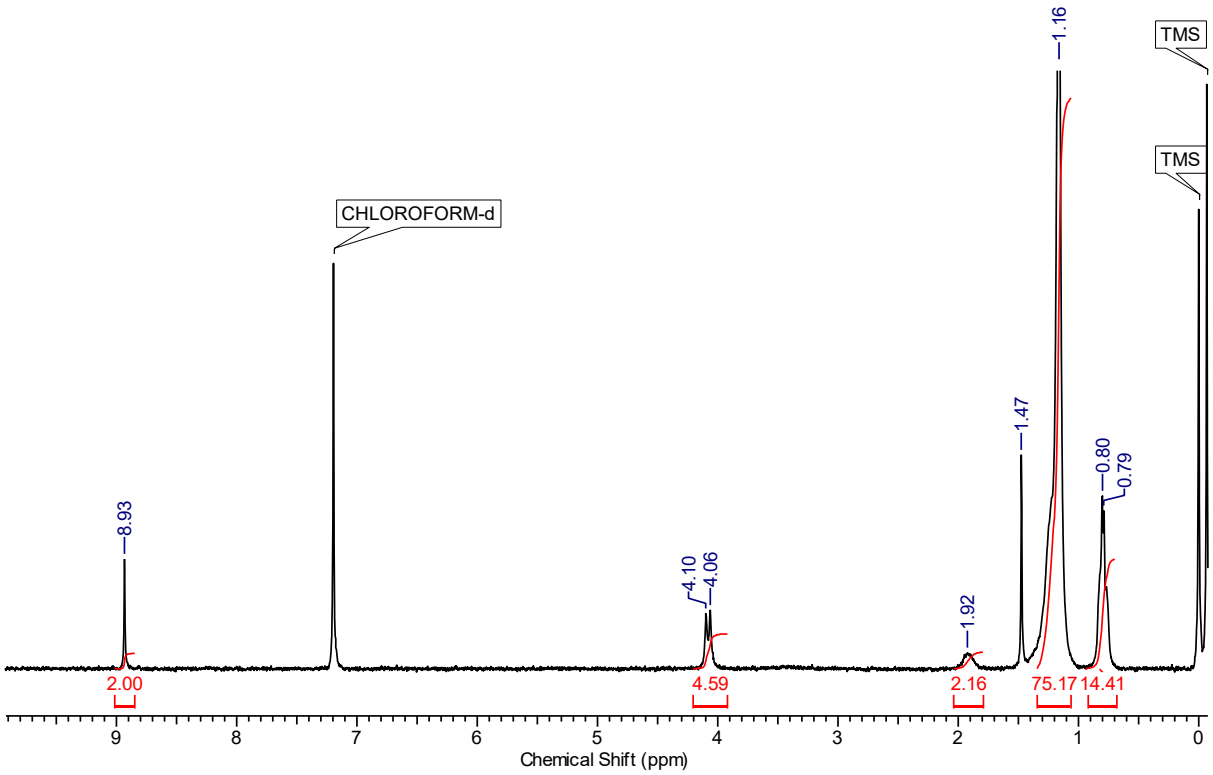


Figure S2. ^{1}H NMR spectrum of P(NDI2OD-T2) (P-0) Polymer.

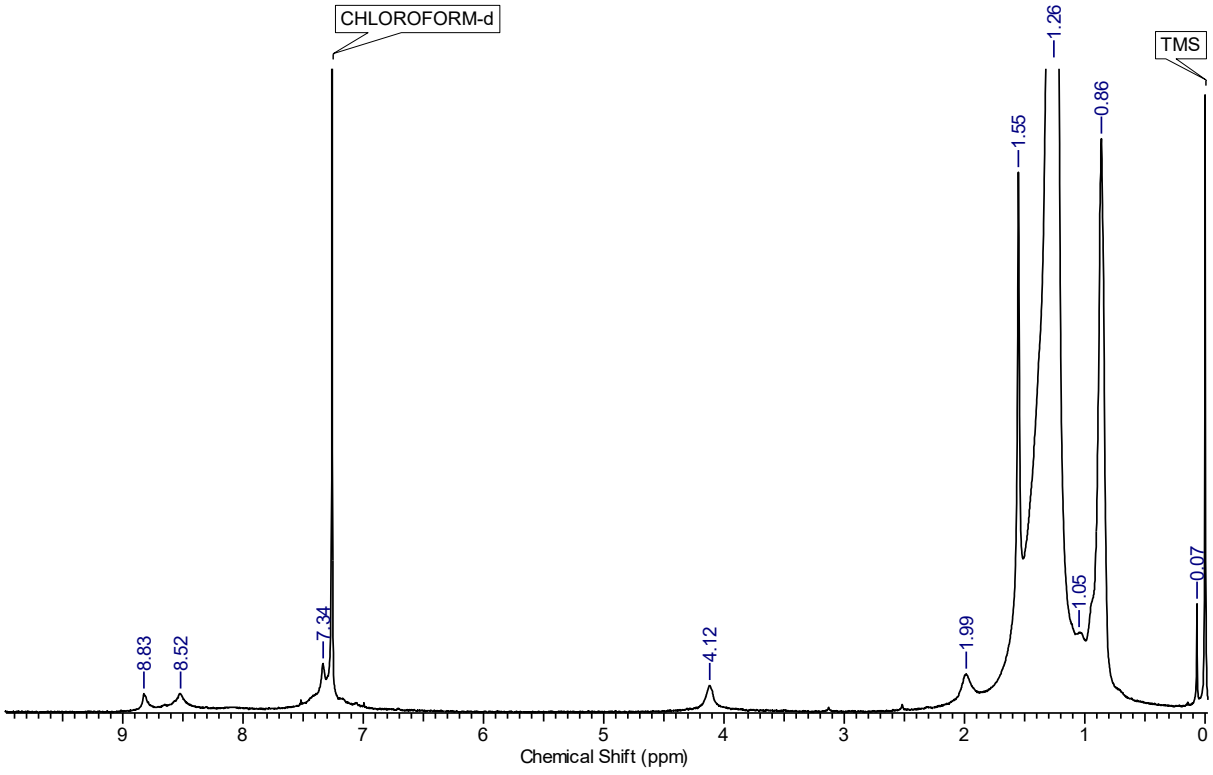


Figure S3. Gel permeation chromatogram (GPC) of P(NDI2OD-T2) and their composites.

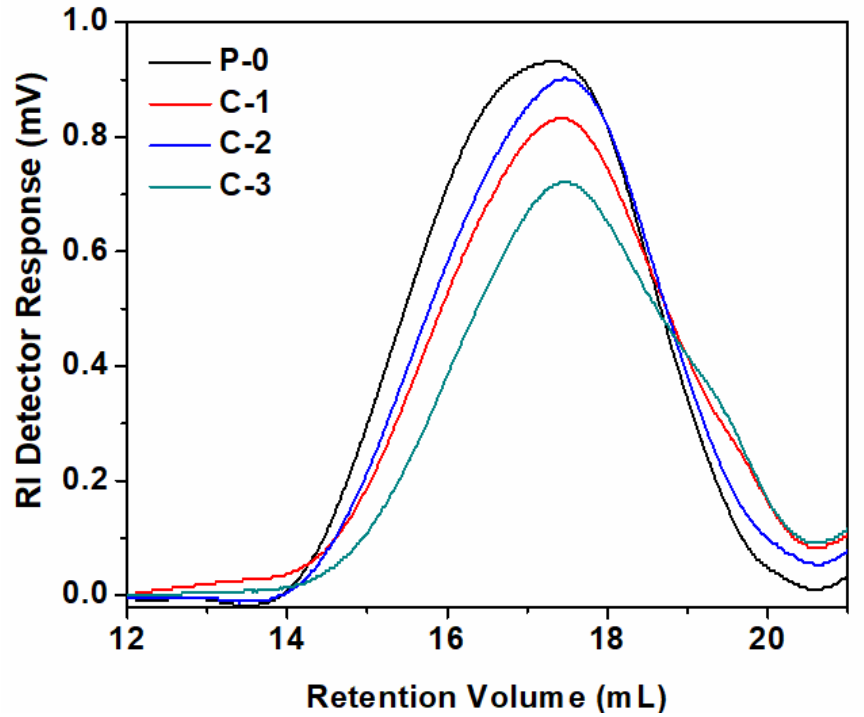
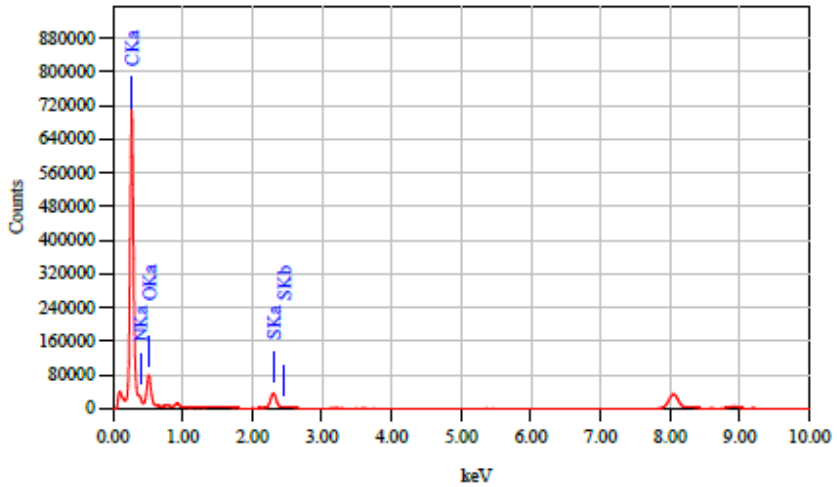


Figure S4. EDX spectra of P(NDI2OD-T2) and their composites.

P(NDI2OD-T2) **P-0**

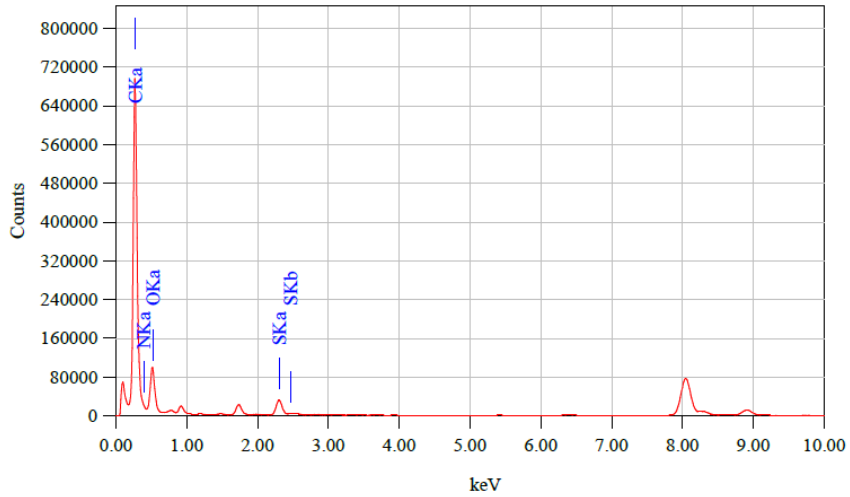


Acquisition Parameter
Instrument : JEM-F200(URP)
Acc. Voltage : 200.0 kV
Probe Current: 7.47500 nA
PHA mode : T3
Real Time : 96.99 sec
Live Time : 50.00 sec
Dead Time : 48 %
Counting Rate: 147201 cps
Energy Range : 0 - 40 keV

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1417

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
C K	0.277	72.53	0.03	78.16				82.8071
N K		ND		ND				
O K	0.525	26.53	0.06	21.46				11.6360
S K	2.307	0.94	0.00	0.38				5.5569
Total		100.00		100.00				

C-1

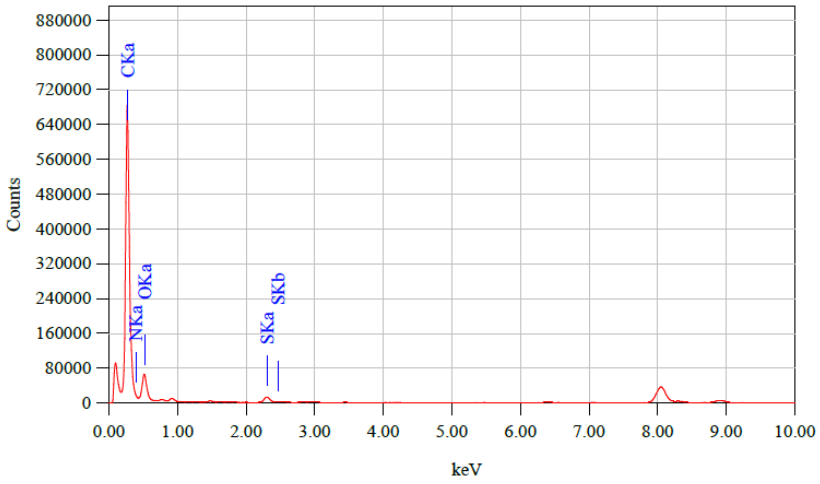


Acquisition Parameter
Instrument : JEM-F200(URP)
Acc. Voltage : 200.0 kV
Probe Current: 7.47500 nA
PHA mode : T3
Real Time : 134.86 sec
Live Time : 50.00 sec
Dead Time : 62 %
Counting Rate: 195164 cps
Energy Range : 0 - 40 keV

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.3138

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
C K	0.277	70.13	0.03	76.03				80.5529
N K		ND		ND				
O K	0.525	29.02	0.06	23.62				14.5488
S K	2.307	0.85	0.00	0.34				4.8983
Total		100.00		100.00				

C-2

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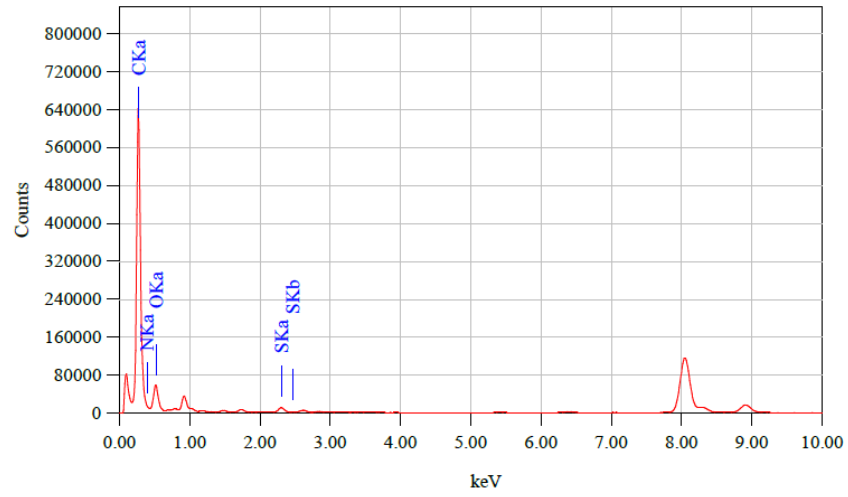
Acquisition Parameter
Instrument    : JEM-F200(URP)
Acc. Voltage : 200.0 kV
Probe Current: 7.47500 nA
PHA mode      : T3
Real Time     : 101.70 sec
Live Time     : 50.00 sec
Dead Time     : 50 %
Counting Rate: 155518 cps
Energy Range :  0 - 40 keV
```

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2691

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
C K	0.277	72.04	0.04	77.56				87.5120
N K		ND		ND				
O K	0.525	27.57	0.07	22.28				10.3310
S K	2.307	0.39	0.00	0.16				2.1570
Total		100.00		100.00				

C-3

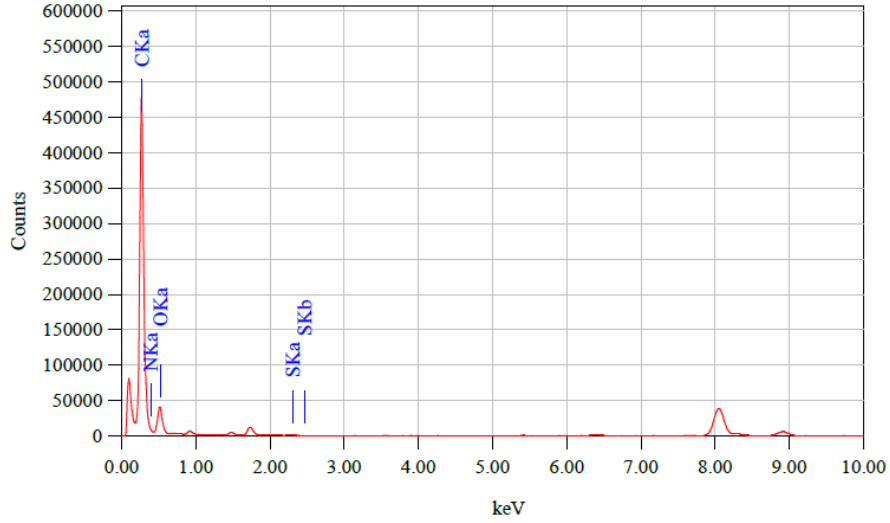



```
Acquisition Parameter
Instrument    : JEM-F200(URP)
Acc. Voltage : 200.0 kV
Probe Current: 7.47500 nA
PHA mode      : T3
Real Time     : 144.27 sec
Live Time     : 50.00 sec
Dead Time     : 65 %
Counting Rate: 199176 cps
Energy Range :  0 - 40 keV
```

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.4307

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
C K	0.277	72.26	0.04	77.73				88.3821
N K		ND		ND				
O K	0.525	27.42	0.07	22.14				9.8400
S K	2.307	0.32	0.00	0.13				1.7780
Total		100.00		100.00				

Ex C-30




```
Acquisition Parameter
Instrument    : JEM-F200(URP)
Acc. Voltage : 200.0 kV
Probe Current: 7.47500 nA
PHA mode      : T3
Real Time     : 83.76 sec
Live Time     : 50.00 sec
Dead Time     : 40 %
Counting Rate: 113560 cps
Energy Range :  0 - 40 keV
```

```
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.3280
Element        (keV)   Mass%    Sigma   Atom%  Compound   Mass%  Cation        K
 C K           0.277   69.41     0.04   75.15                              90.1409
 N K                     ND               ND
 O K           0.525   30.56     0.10   24.84                               9.6786
 S K           2.307    0.03     0.00    0.01                               0.1805
Total                  100.00           100.00
```

Table S1: Atomic percentage of the elements present in CNT, P-0, C-1, C-2, C-3, and Ex C-30 samples obtained from the EDX analysis.

Element Name	CNT atom %	P-0 atom %	C-1 Atom %	C-2 Atom %	C-3 atom %	Ex C-30 atom %
C K	100	78.16	76.03	77.56	77.73	75.15
O K		21.46	23.62	22.28	22.14	24.84
S K		0.38	0.34	0.16	0.13	0.01

Figure S5. TGA curves of the polymer composites.

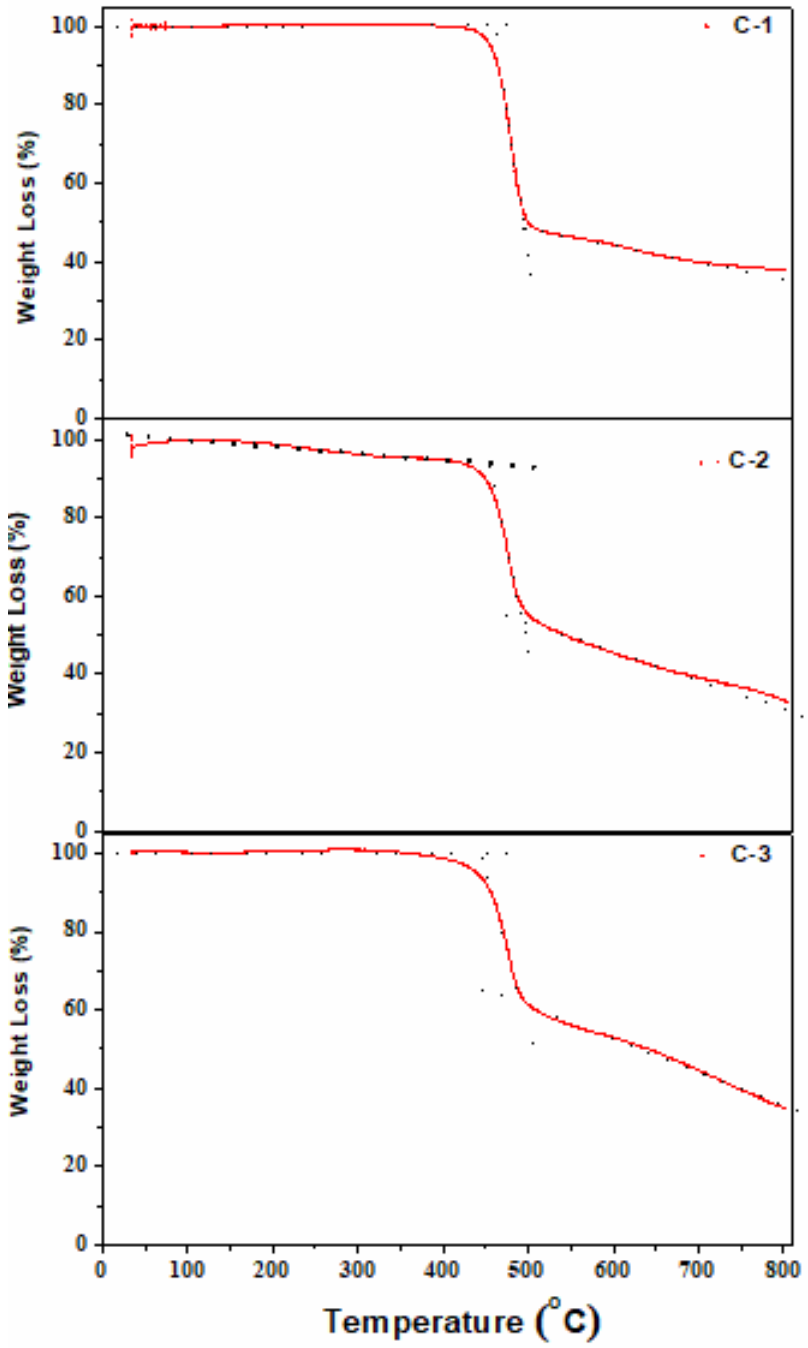
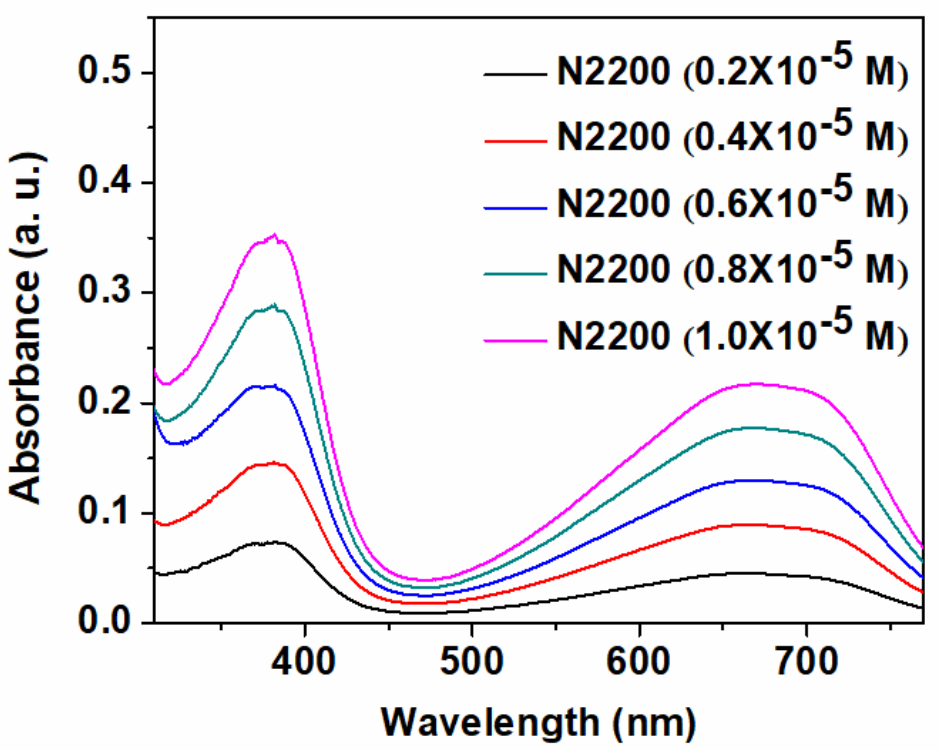


Figure S6. UV-vis absorption spectra for P(NDI2OD-T2).



Section S2. Calculation of molar absorptivity coefficient for P(NDI2OD-T2) polymer and concentration of polymer in the composites C-X using molar absorptivity coefficient.

Molar absorptivity coefficient was calculated at 383 nm by using Lambert-Beers law, $A = \varepsilon cl$

Where, A= Absorbance, C= concentration g/mole, l= path length, ε=35954 L $M^{-1}cm^{-1}$.

The calculation for obtaining the concentration of polymer in the composites is shown below.

- P-0 $C=A/\varepsilon$ A= 0.7826; C= 0.7826/35954 = 2.1767 X 10^{-5} M

1 M = 988 gm of Polymer (repeating unit mass) = 2.1767 X 10^{-5} x 988 = 0.02151 gm, for 1000 ml solution.

As 1 mg polymer was dissolved in 50 ml of chloroform: (0.02151 x 50) /1000 = 1.075 x10^{-3} g = 1 mg

- C-1 A= 0.6086;

C= 0.6086/35954 = 1.6927 X 10^{-5} M = 1.6927 X 10^{-5} x 988 = 0.01672 gm.

In 50 ml: (0.01679 x 50) /1000 = 8.362 x10^{-4} g = 0.836 mg

Amount of CNT = 1mg – 0.839 mg polymer = 0.16 mg CNT

- C-2 A= 0.5292;

C= 0.5292/35954 = 1.4719 X 10^{-5} M = 1.4719 X 10^{-5} x 988 = 0.01454 gm.

In 50 ml: (0.01454 x 50) /1000 = 0.727 mg

Amount of CNT = 1mg – 0.727 mg polymer = 0.273 mg CNT

- C-3 A= 0.4453;

C = 0.4453/35954 = 1.2385 X 10^{-5} M = 1.2385 X 10^{-5} x 988 = 0.012236 gm.

In 50 ml: (0.012236 x 50) /1000 = 0.6118 mg

Amount of CNT = 1mg – 0.6118 mg polymer = 0.388 mg CNT

Figure S7. (a) Pore size distribution profile for P-0, (b) Pore size distribution profile for MWCNT, (c) nitrogen adsorption/desorption isotherm of P-0 sample, and (d) nitrogen adsorption/desorption isotherm of MWCNT sample.

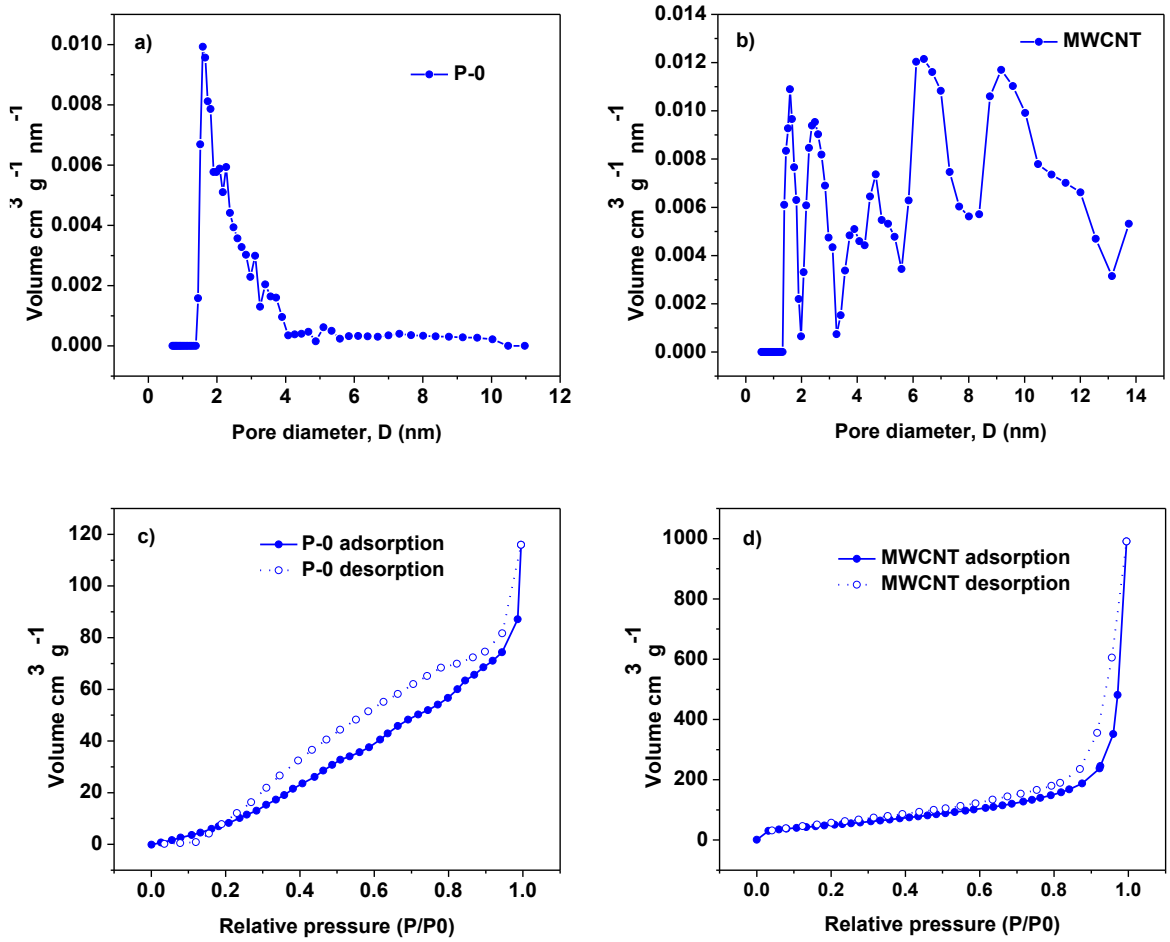


Figure S8. CV profiles of MWCNT recorded at various scan rates.

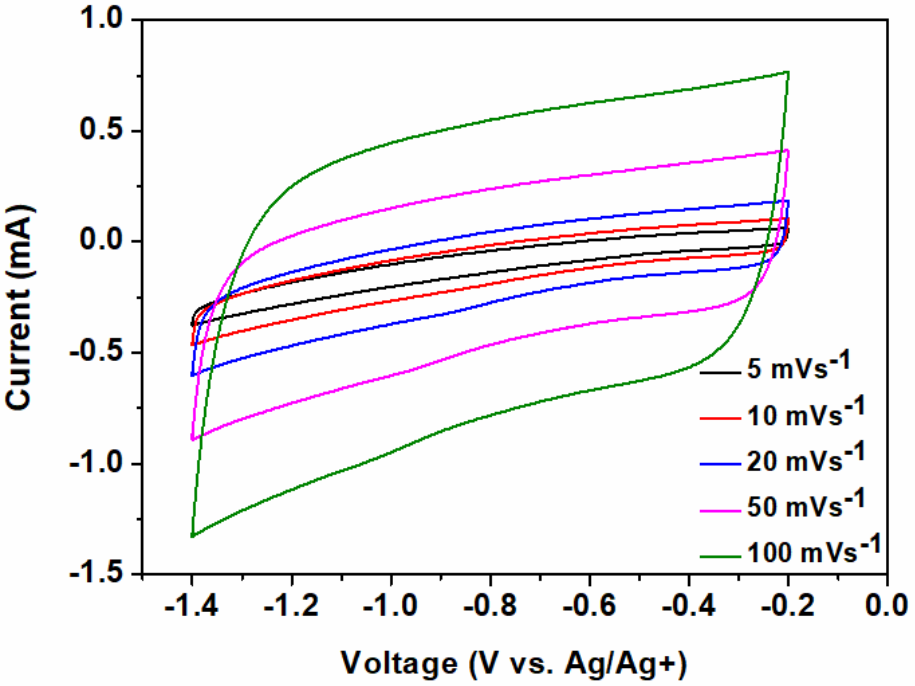


Figure S9. Nyquist plots recorded for the P-0, C-1, and C-2 samples.

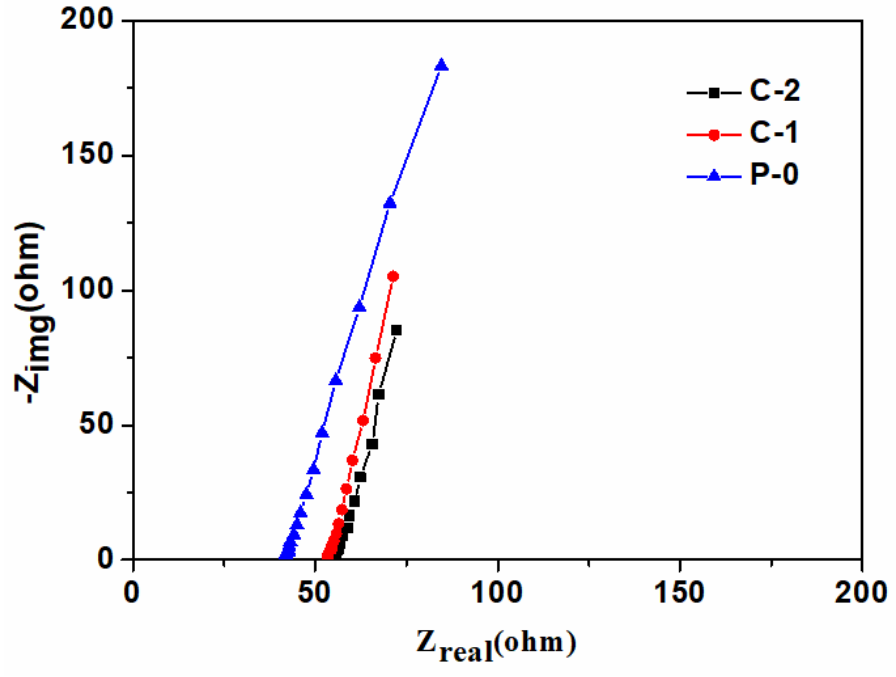


Figure S10. CV profiles recorded at various scan rates for the (a) P-0, (b) Ex C-30, (c) C-1, and (d) C-2 samples.

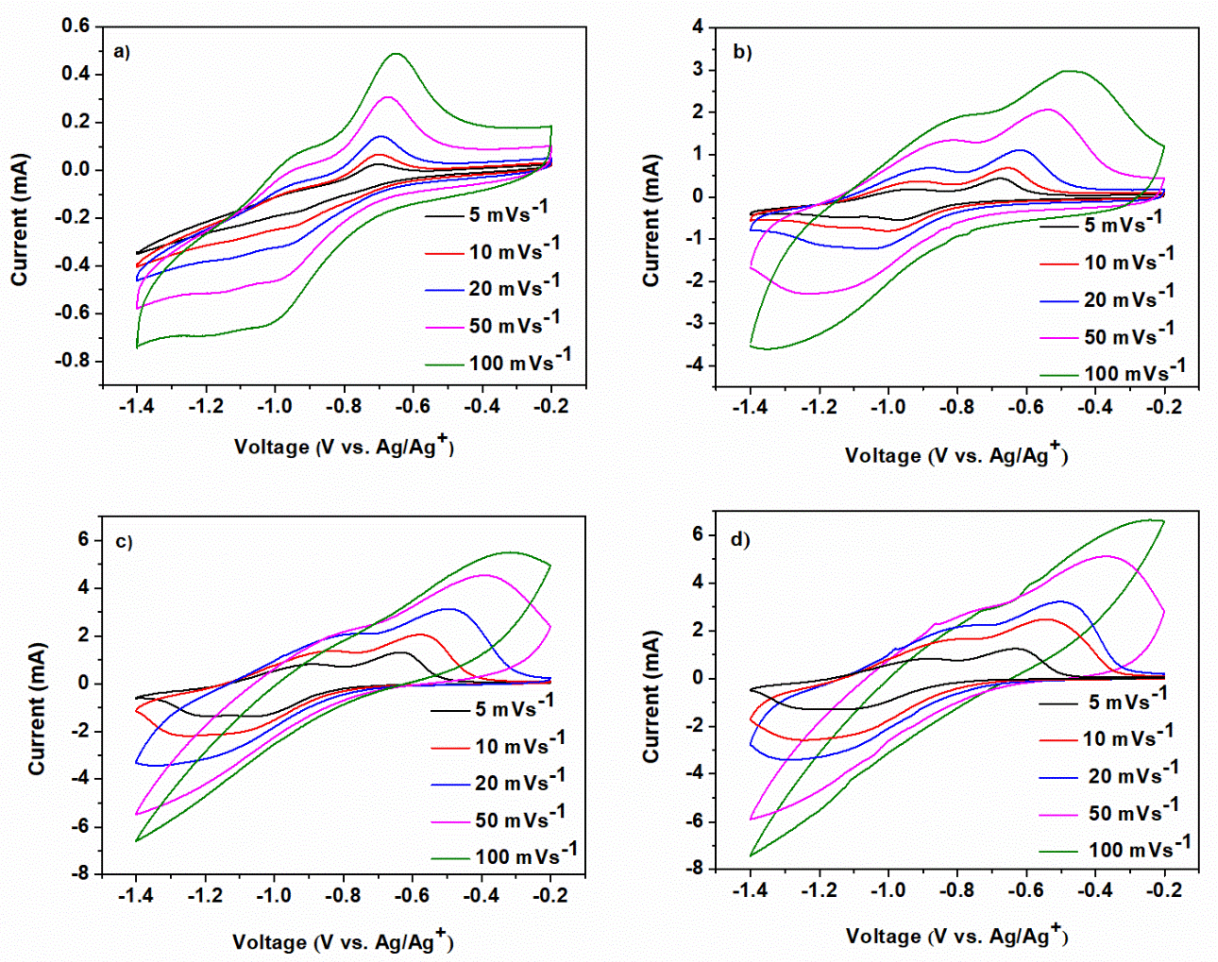


Figure S11. (a) Discharge profiles recorded at various current rates for MWCNT and (b) discharge profiles of P-0, C-1, C-2, C-3, and Ex C-30 samples recorded at 0.5 A g^{-1} considering the total loading of electrode material (1mg cm^{-2}); discharge profiles recorded at various current rates for the (c) P-0, (d) Ex C-30, (e) C-1, and (f) C-2 samples.

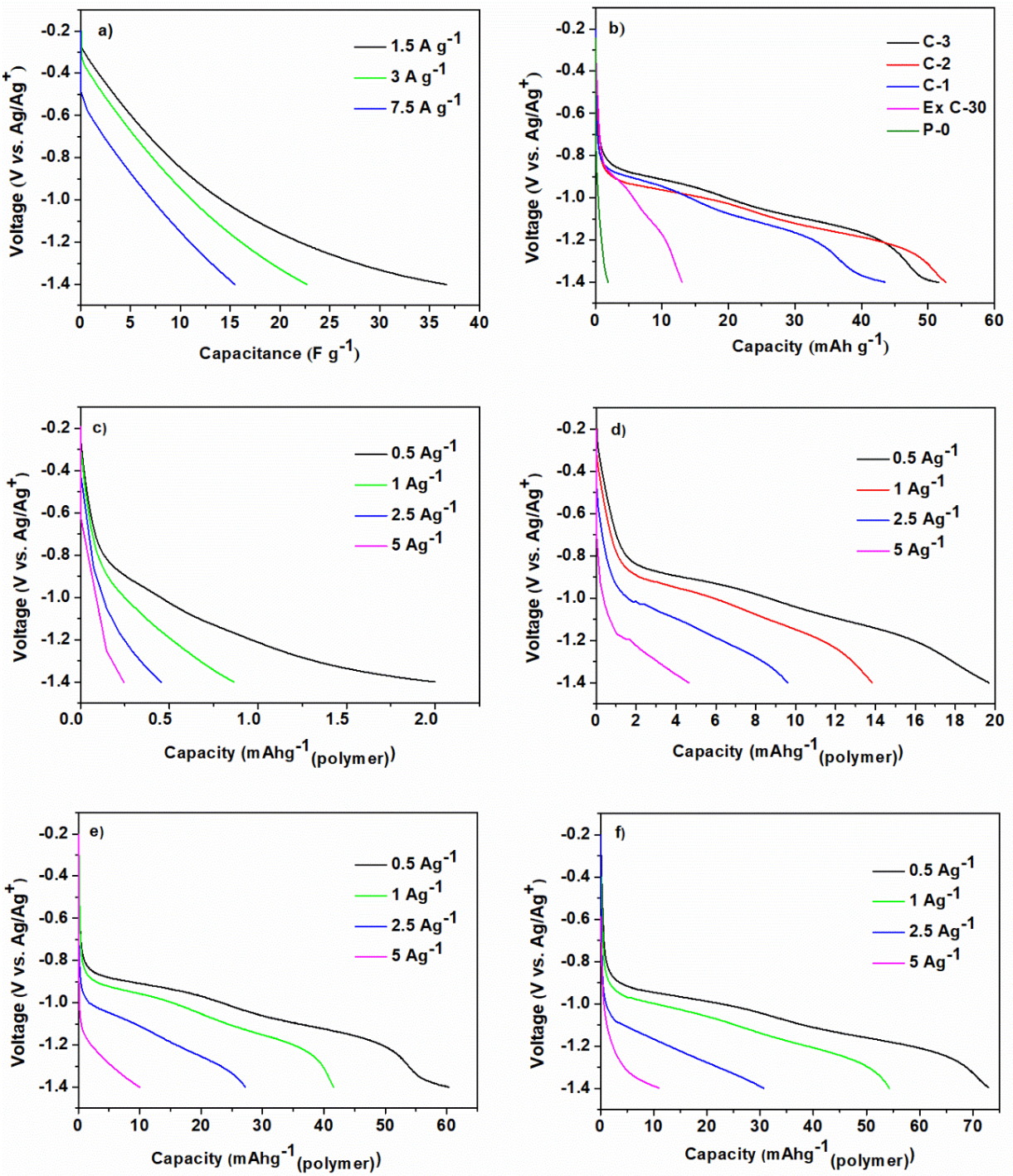


Figure S12. (a) CV data taken for the C-3||C-3 symmetric device at 50 mV s^{-1} scan rate; (b) CV data recorded at 50 mV s^{-1} scan rate and (c) discharge profiles recorded at 0.50 A g^{-1} (considering total loading of electrode material) for the activated carbon (AC) and C-3 samples in three-electrode configuration; (d) CV profiles recorded for the C-3||C-3 symmetric device and AC||C-3 HSC device in 1M $LiClO_4$/PC liquid electrolyte at 50 mV s^{-1} scan rate.

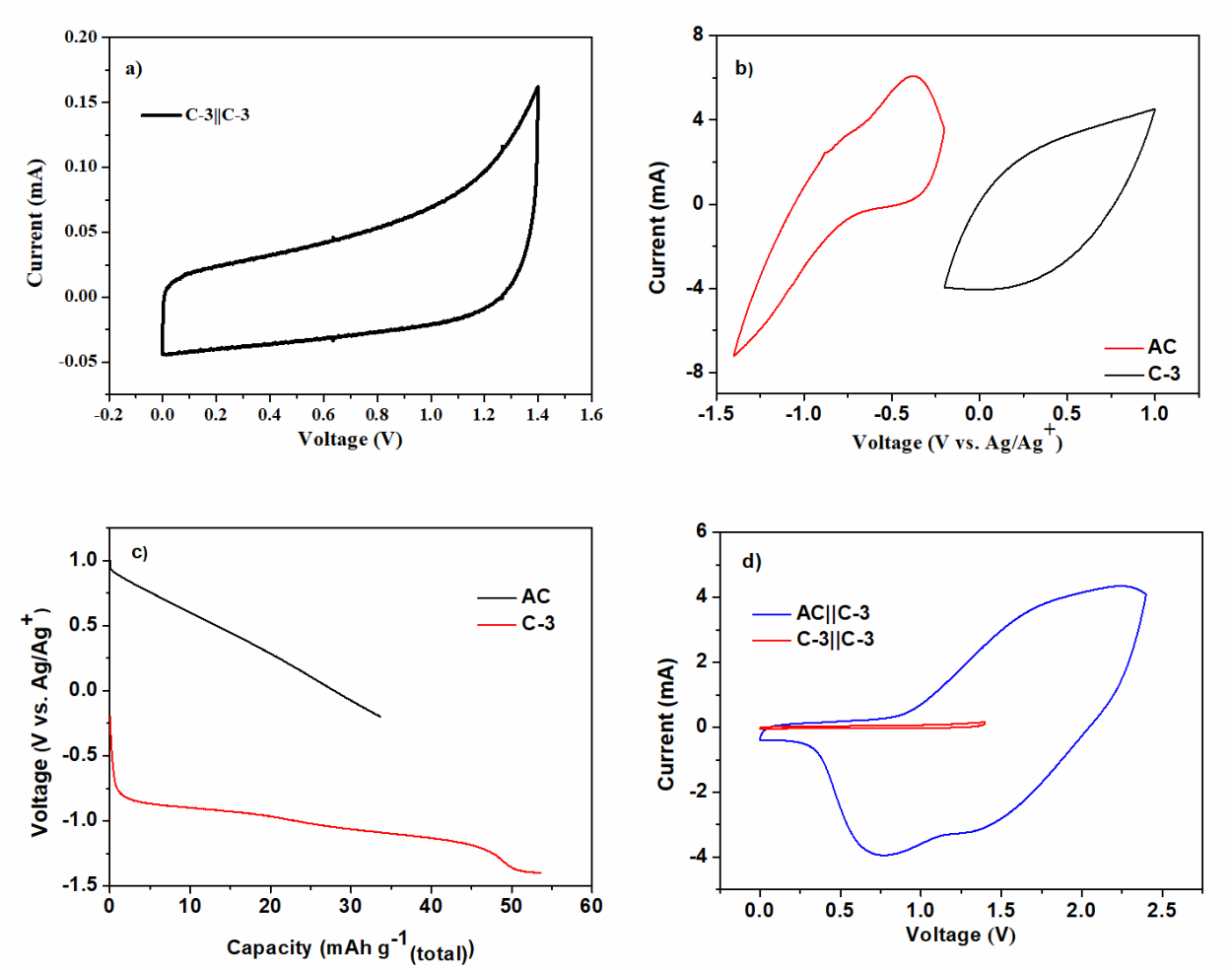


Figure S13. (a) CV profiles recorded at different scan rates, (b) GCD profiles recorded at different current rates, (c) impedance plot, and (d) cycling stability data for the AC||C-3 HSC device in 1M $LiClO_4$/PC (LS-HSC device) recorded at a current rate of 1.0 A g^{-1}.

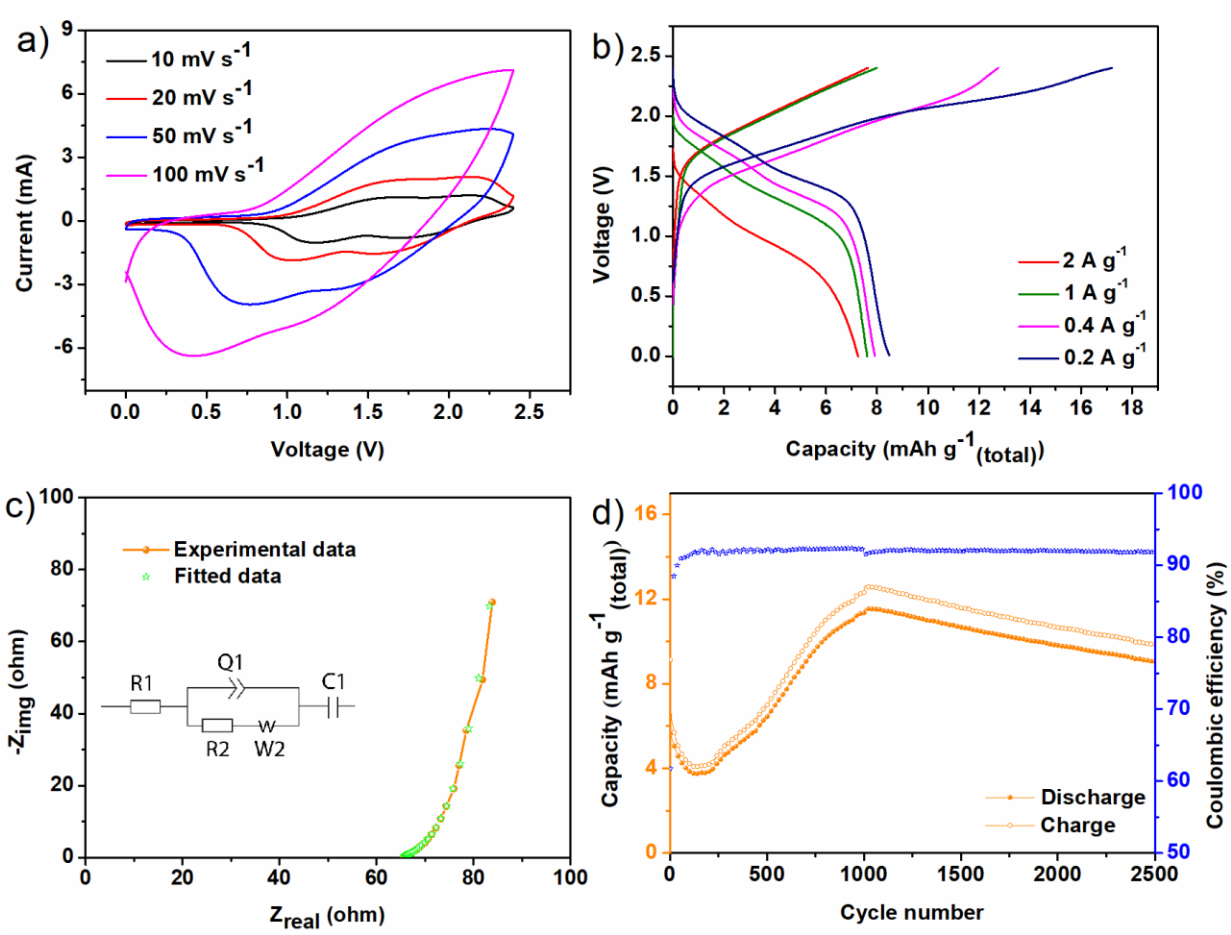


Table S2: The capacitance, voltage window, and cycling stability of C-3 composite in three-electrode cell and HSC device configurations are compared with the performance of some of the previously reported redox active polymers.

Material	Electrolyte	Voltage window	Configuration	Specific capacity or capacitance	Cycling stability	Ref.
PBOTT-BTD/ITO/PET	0.1 M $TBAPF_6$/ACN	-0.2 to 0.6 V	Three-electrode	2.5 mF cm^{-2} (31 F g^{-1}) @ 0.1 mA cm^{-2} (capacity ≈7 mAh g^{-1})[a]	86 % retention after 2000 cycles	**2**
PI-IDT	0.5 M $LiClO_4$/PC	0 to 0.95 V	Three-electrode	6.2 mF cm^{-2} @ 0.05 mA cm^{-2}	68 % retention after 1000 cycles	**3**
P(NDI2OD-OThCNPV) or P2	0.5 M H_2SO_4	-0.7 to 0.5 V	Three-electrode	124 F g^{-1} @ 0.5 A g^{-1} (capacity ≈ 41.3 mAh g^{-1}) [a]	100% retention after 5000 cycles	**4**
P(PDI-alt-BDT)	1 M $LiClO_4$/PC	−1.5 to −0.85 V	Three-electrode	113 F g^{-1} @ 0.5 A g^{-1} (capacity ≈ 31 mAh g^{-1}) [a]	100% retention after 4000 cycles	**5**
PBEDOT-BT-BD	0.1 M Bu_4NPF_6/ACN	-0.5 to 1.1 V	Three-electrode	129.3 F g^{-1} @ 1 A g^{-1} (capacity ≈ 60.1 mAh g^{-1}) [a]	77% retention after 1000 cycles	**6**
PBEDOT-iIBut2	1 M LiBTI/ PMMA/PC	0 to 0.5 V	Device	14 F g^{-1} @ 50 mV s^{-1} (capacity ≈ 1.9 mAh g^{-1}) [a]	80% retention after 10000 cycles	**7**
Ag NW/PDOPEQ	1 M $LiClO_4$/PC	0 to 0.5 V	Three electrode	61.5 F g^{-1} @ 0.1 A g^{-1} (capacity ≈ 8.5 mAh g^{-1}) [a]	~100% retention after 20000 cycles	**8**
TPA1Th-NDI//AC	TEATFB/PC/ DME	0 to 2.0 V	Device	22 F g^{-1} (capacity ≈ 12.2 mAh g^{-1}) [a]	~90% retention over 500 cycles	**9**
P(DEBT/TETPA)	0.1 M $TBAPF_6$/ACN	-0.5 to 0.8 V	Three electrode	149 F g^{-1} @ 10 mV s^{-1} (capacity ≈ 53.8 mAh g^{-1}) [a]	~100% retention over 2000 cycles	**10**
C-3	1 M $LiClO_4$/PC	-1.4 to -0.2 V	Three electrode	80 mAh $g^{-1}_{(polymer)}$ (or 240 F $g^{-1}_{(polymer)}$) @ 0.5 A g^{-1}	80% retention after 2500 cycles	**This work**
AC‖C-3	$LiClO_4$/PMMA/ PC	0 to 2.4 V	Device	11 mAh g^{-1} (or 16.8 F g^{-1} @ 0.4 A g^{-1}	57% retention after 100 cycles	**This work**

a: capacity (mAh g^{-1}) values are calculated from the capacitance (F g^{-1}) provided in the respective reports (capacity (mAh g^{-1}) = $\frac{capacitance\ (F\ g^{-1}) \times voltage\ window}{3600} \times 1000$)

Section S3.

1) Calculation of the specific discharge capacity in the three-electrode cell:

Charge (Q) = $\int i \times t$

where *i* (in A) and *t* (in sec) are current and time, respectively.

Capacity (mAh) = $\frac{Q \times 1000}{3600}$

Therefore, the equation for specific discharge capacity (mAh g^{-1}) can be presented as

$$\text{Specific discharge capacity (mAh g}^{-1}) = \frac{Applied\ current\ (A) \times discharge\ time\ (sec)}{electrode\ loading\ (mg) \times 3600} \times 10^6$$

(**Equation S1**)

As already mentioned, the total loading of the P-0, C-1, C-2, C-3, and Ex C-30 eletrodes were 1.0 mg. In the case of the MWCNT electrode, the total loading was 0.33 mg.

2) Calculation of specific discharge capacity considering the loading of only the redox-active polymer (mAh $g^{-1}_{(polymer)}$)

$$= \frac{Applied\ current\ (A) \times discharge\ time\ (sec)}{loading\ of\ the\ polymer\ (mg) \times 3600} \times 10^6$$ (**Equation S2**)

The loading of the polymer in the respective electrodes is given below:

Sample	MWCNT content (%)	PVDF content (%)	Polymer content (mg)
P-0	0	5	0.95
C-1	14	5	0.8
C-2	24	5	0.7
C-3	35	5	0.6
Ex C-30	30	5	0.65

3) Calculation for balancing the loading in the positive (AC) and negative electrode (C-3) in the hybrid supercapacitor device:

The mass ratio of the electrodes was calculated by following equation,

$$\frac{M_{AC}}{M_{C-3}} = \frac{Q_{C-3}}{Q_{AC}}$$ (**Equation S3**)

where, M_{AC} and M_{C-3} are the total loading of positive and negative electrodes, respectively.[11] Q_{AC} and Q_{C-3} represent the discharge capacity values (considering the total mass-loading in the respective electrode) of the positive and negative electrodes obtained from the three-electrode study.

$$\frac{M_{AC}}{M_{C-3}} = \frac{53\ mAh\ g^{-1}}{34\ mAh\ g^{-1}}$$

$$\frac{M_{AC}}{M_{C-3}} = \frac{1.5}{1.0}$$

Therefore, the total loadings in the positive and negative electrodes were taken as 1.5 mg and 1 mg, respectively.

4) The capacity of the hybrid supercapacitor device was calculated from the follwoing equation:

$$Capacity\left(mAh\ g^{-1}_{(total)}\right) = \frac{Discharge\ time\ (hour) \times applied\ current\ (mA)}{total\ mass-loading\ of\ the\ electrode\ materials\ in\ both\ the\ positive\ and\ negative\ electrodes\ (mg)} \times 1000$$

(**Equation S4**)

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