Supplementary Information (SI) for RSC Advances.
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SUPPROTING INFORMATION

Tweaking electrochemical potential of nitrogen-rich Ce-PTA-MOF by reduced graphene oxide for hybrid supercapacitor

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Synthesis of Ce-PTA-MOF

Pyridine-2,4,6-tricarboxylic acid (0.6 mmol) and cerium (III) nitrate hexahydrate (0.6 mmol) were dissolved in deionized water separately by stirring at 50 °C.After mixing both the solutions, the mixture was sonicatedfor 30 minutes at 20 kHz frequency and 20 µm amplitude. After filtration, the filtrate was kept at room temperature and yellow crystals of Ce-PTA-MOF appeared after 10 days which were washed with distilled water to remove any impurities and dried at room temperature (25 °C) (**Fig.1**). Calc. for $C_{48}H_{51}Ce_4N_7O51$ (2102.44): N, 4.66; C, 27.40; H, 2.42; Found: N, 4.52;C, 27.33; H, 2.22.

Ce-PTA-MOF Structure:

The asymmetric unit of **Ce-PTA-MOF** consists of two Ce(III) ions, three coordinated water molecules, two non-coordinated water molecules, one ammonia molecule and two pyridine-2,4,6-tricarboxylic (PTA) ligands. The Ce1 atom is nine-coordinated by two nitrogen atoms (N1 and N2) from two pyridine rings, five oxygen atoms (O1, O6, O7, O12 and $O5^{i}$) from five carboxylic groups and two oxygen atoms (O14 and O15) from water molecules. The Ce2 and N3 atoms located on 3-fold symmetry centers. The Ce2 atom is ten-coordinated by six oxygen atoms (O11, O12, $O11^{ii}$, $O12^{ii}$, $O11^{iii}$ and $O12^{iii}$) from three carboxylic groups, three oxygen atoms (O13, $O13^{ii}$ and $O13^{iii}$) from water molecules and one nitrogen atom (N3) from ammonia molecule ((i) -x+1, -y, z-1/2; (ii) -x+y+1, -x+1, z; (iii) -y+1, x-y, z). X-ray analysis has revealed that **Ce-PTA-MOF** consists of 3D coordination polymer (Fig. 3). In the first of these coordination polymers running parallel to the [001] direction, Ce1 is coordinated by the oxygen atom ($O5^{i}$) of carboxylic group from a symmetrically related pyridine-2,6-dicarboxylic anion. In the second coordination polymer running parallel to the [100] and [010] directions, Ce1 atoms bond to Ce2 atoms via oxygen atom (O12) from carboxylic groups. The adjacent Ce1···Ce2, and Ce1···$Ce1^{ii}$ distances are 5.151 and 8.289 Å. The Ce-N bond distances have values of 2.617(7), 2.668(9) and 2.458(17) Å, respectively, while the Ce-$O_{carboxylate}$ bond distances ranged between 2.441(8) and 2.764(7) Å, respectively. The N-Ce-N bond angle is 152.1(3)°, respectively. These values are comparable to those observed in other Ce(III) complexes [1],[2]. The pyridine ring mean planes from are approximately

planar, with maximum deviations of 0.0233(74) Å for N1 atom and 0.0091(68) Å for N2 atom, respectively.

Table S1. Crystal data and structure refinement parameters for Ce-PTA-MOF

Empirical formula	$C_{48}H_{51}Ce_4N_7O_{51}$
Formula weight	2102.44
Temperature (K)	296
Crystal system	Hexagonal
Space group	$P6_3$
a (Å)	24.9991 (7)
b (Å)	24.9991 (7)
c (Å)	7.0302 (2)
V (Å^3)	3804.93 (18)
Z	2
Absorption coefficient (mm^{-1})	2.46
D_{calc}(Mg m^{-3})	1.835
Theta range for data collection (º)	1.6–26.0
Measured reflections	25434
Independent reflections,R_{int}	4986, 0.086
Observed reflections [I > 2σ(I)]	3847
Refinement method	
Final R indices (all data)	R1 = 0.052 wR2 = 0.141
Goodness–of–fit on F^2	1.07
$\Delta\rho_{max}$ (eÅ^{-3})	1.22
$\Delta\rho_{min}$(eÅ^{-3})	–1.38

Table S2. Selected bond distances in Ce-PTA-MOF(Å, º)

Ce1-O1	2.524 (7)
Ce1-O6	2.522 (7)
Ce1-O7	2.512 (7)
Ce1-O12	2.637 (7)
Ce1-O14	2.561 (9)
Ce1-O15	2.504 (8)

Ce1-O5^{i}	2.441 (8)
Ce1-N1	2.617 (7)
Ce1-N2	2.668 (9)
Ce2-O11	2.483 (7)
Ce2-O12	2.764 (7)
Ce2-O13	2.590 (7)
Ce2-N3	2.458 (17)

Symmetry codes: (i) −x+1, −y, z−1/2 for Ce-PTA-MOF

Table S3. Hydrogen-bond parameters for Ce-PTA-MOF(Å, º)

D-H· · ·A	D-H	H···A	D···A	D-H···A
Ce-PTA-MOF				
O10-H10A···O8^{v}	0.82	1.60	2.418 (10)	172
O13-H13A···O2^{vi}	0.84	2.10	2.850 (11)	149
O13-H13B···O15^{iv}	0.84	2.49	3.114 (11)	132
O14-H14B···O2^{iv}	0.84	1.99	2.787 (11)	158
O15-H15A···O17	0.84	2.00	2.718 (10)	144
O16-H16A···O3^{iv}	0.84	2.18	3.009 (17)	168
O16-H16B···O4^{ii}	0.84	2.18	3.008 (16)	169
O17-H17A···O7^{vii}	0.84	2.35	3.090 (9)	147
O17-H17A···O10^{iii}	0.84	2.36	2.932 (10)	126
O17-H17B···O6^{vii}	0.84	2.05	2.779 (10)	145
O17-H17B···O5^{vii}	0.84	2.57	3.361 (11)	158
N3-H3A···O1^{iii}	0.83 (2)	2.46 (4)	3.268 (8)	166 (11)
O17-H17A···O6^{viii}	0.82 (2)	2.06 (6)	2.795 (10)	150 (11)

Symmetry codes: (ii) −x+1, −y, z−1/2; (iii) −x+y+1, −x+1, z; (iv) −y+1, x−y, z; (v) y+1, −x+y+1, z+1/2; (vi) −x+y+1, −x+1, z+1; (vii) −x+1, −y, z+1/2 for Ce-PTA-MOF.

FTIR Spectroscopy

Fourier transform infrared spectrum was measured using ATR sample compartment on Bruker Tensor-27 spectrophotometer (Billerica, MA, USA) in the range of 400-4000 cm^{-1}. 3204 br, 1651s, 1555s, 1510 m, 1356 m,1294 m, 1132 s, 879 m, 758 m, 421 m. These lower values of C=O indicates that ligand is coordinated with cerium as well as broad band at 3204 also indicates presence of water molecules.

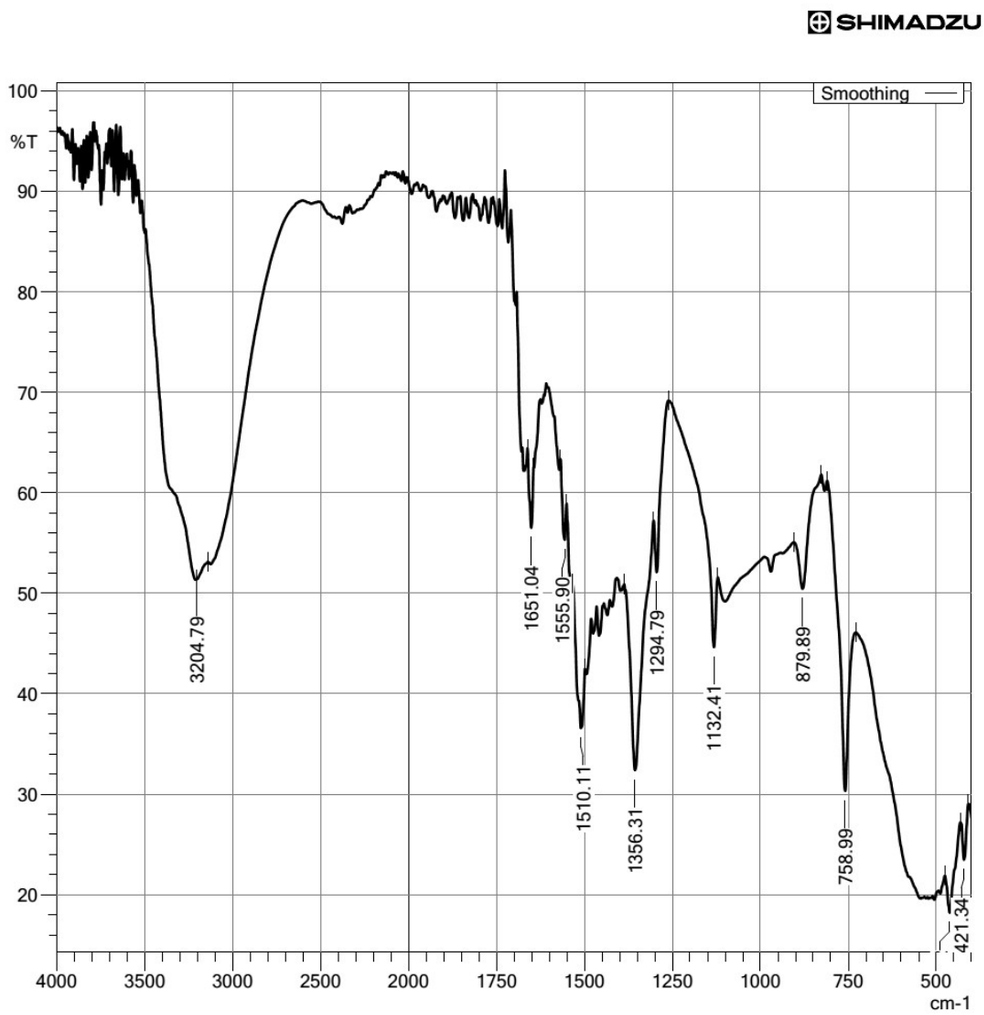

Fig. S1.FTIR spectra of Ce-PTA-MOF

Thermal Analysis

Thermogravimetric analysis (TGA) was carried on TA Instruments with a ramp-rate of 10°C min^{-1} using a SDT Q 600 instrument, thermal analyzer under N_2 atmosphere and temperature range of 25°C to 1000°C.

The decomposition pattern of complex 16Ce-PTA-MOF is illustrated in **Fig. S2**. At the first stage ammonia and water was released with weight loss of about 13.4% (calculated value 13.8%) for 9 coordinated water and 1 ammonia and 6 noncoordinated water molecules up to 210 °C. TGA curve passes through a flat up to 390 °C and the polymer

starts to decomposed due to successive release of PTA up to 1000 °C assuming 30.8 %as residue may be attributed to Ce_2O_3(calcd. 31.2%).

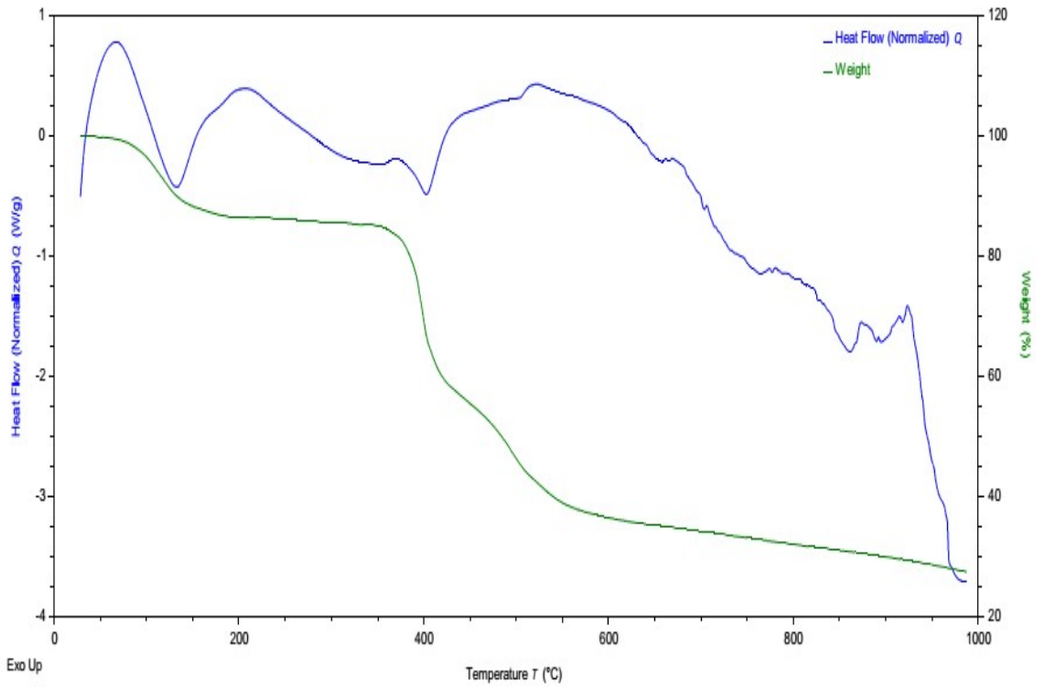

Fig. S2. Thermogram of Ce-PTA-MOF

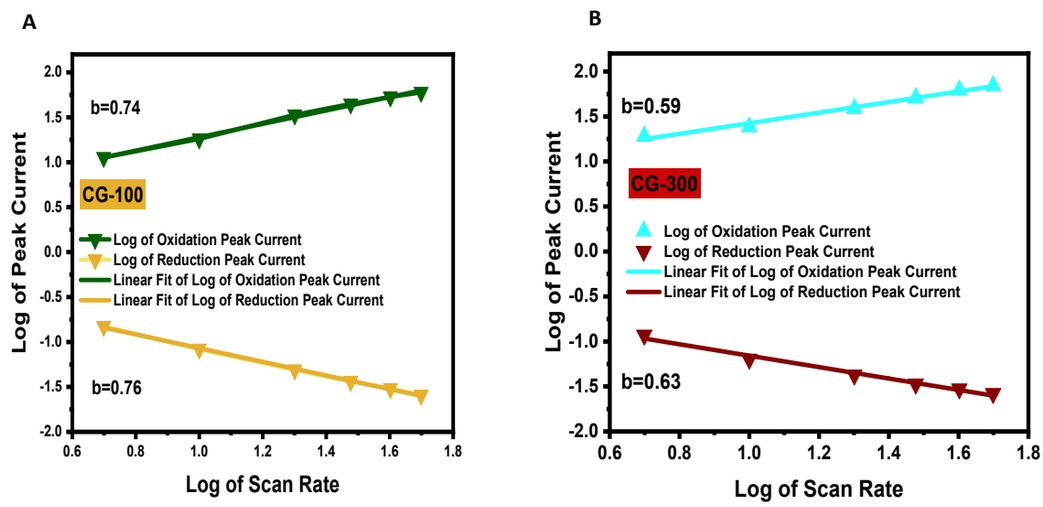

Fig.S3 (A)b-value for CG-100 and (B) CG-200

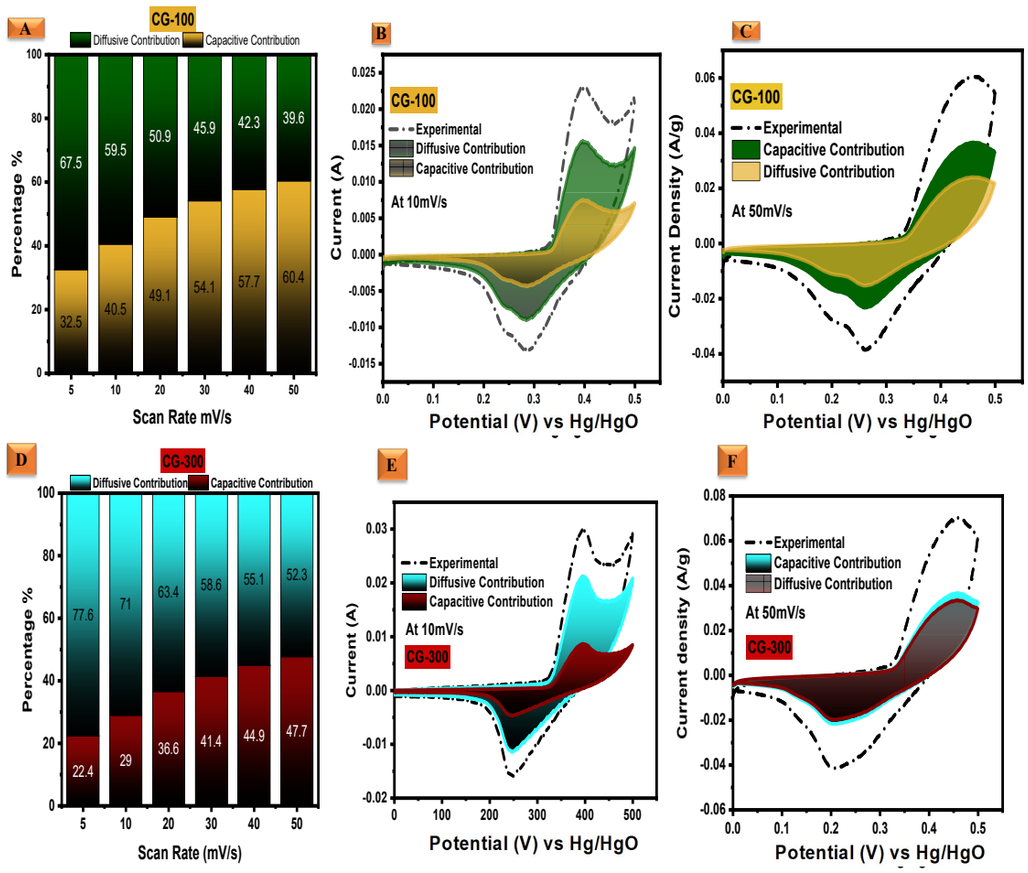

Fig.S4(a) Bar graph of diffusive and capacitive contribution for CG-100 (b) Diffusive, capacitive and experimental current CG-100 at 10 mV/s and (c) 50 mV/s (d) Bar graph of diffusive and capacitive contribution for CG-300 (e) Diffusive, capacitive and experimental current CG-300 at 10 mV/s and (f) 50 mV/s.

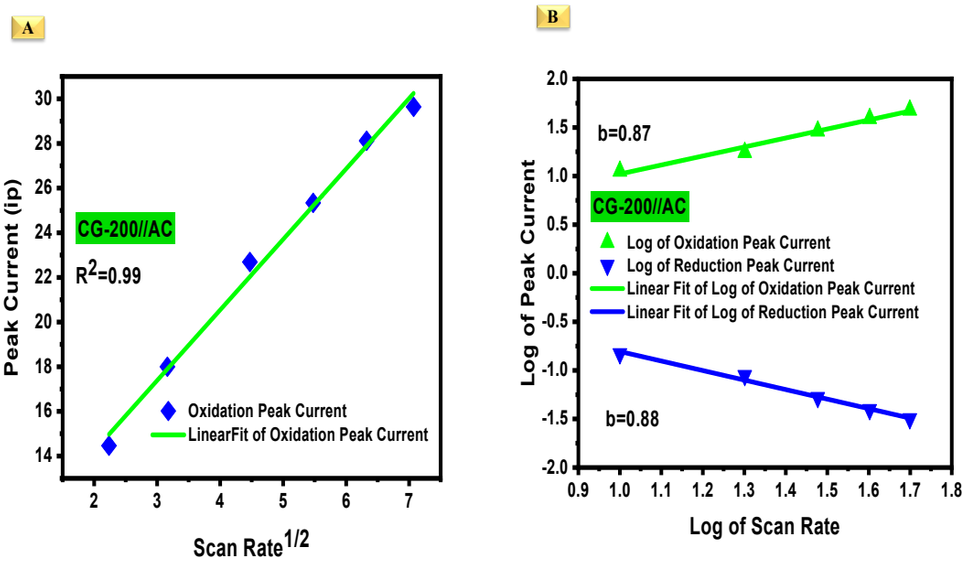

Fig.S5(a) Value of R^2 and (b) b-value for hybrid device.