Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

A phenazine-based conjugated microporous polymer as high performing cathode for aluminium-organic batteries

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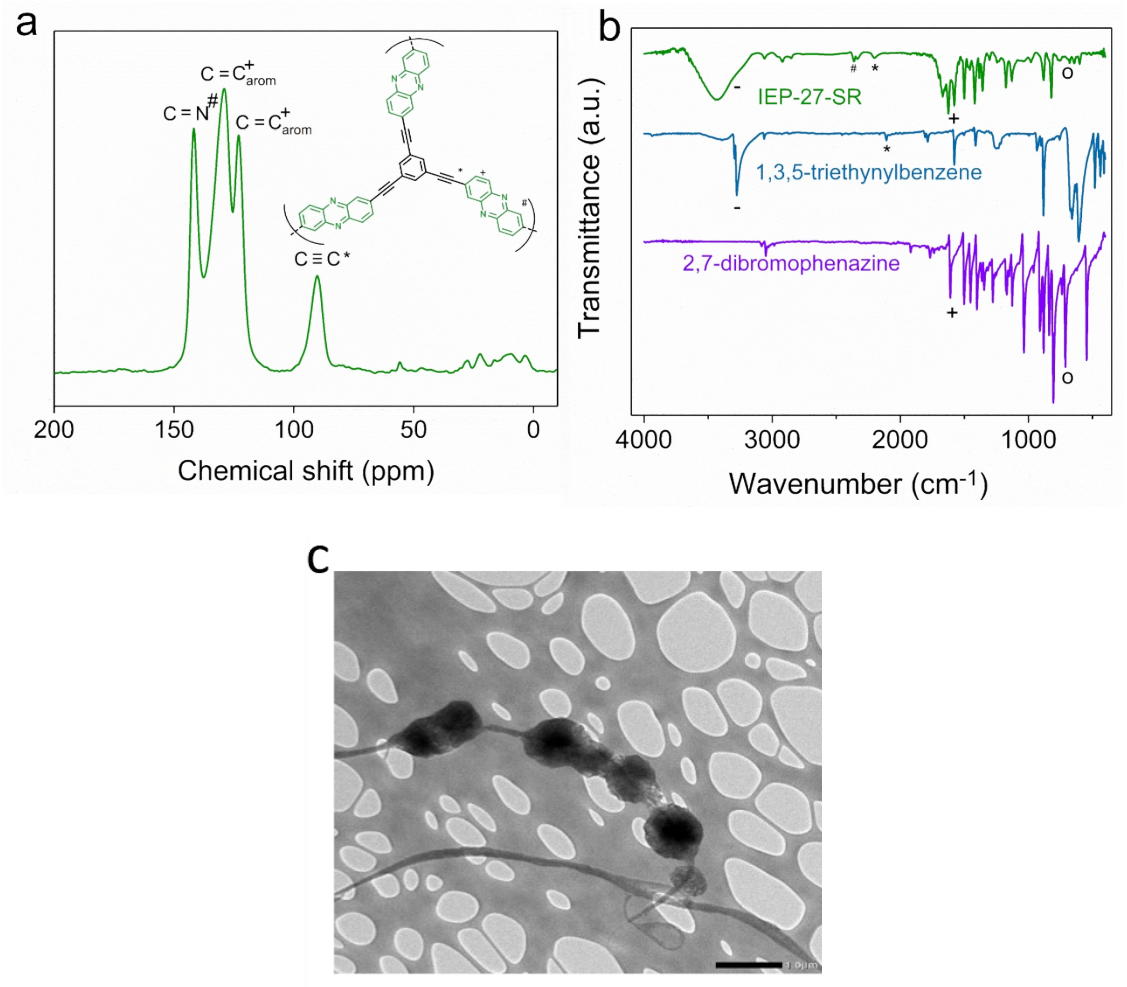
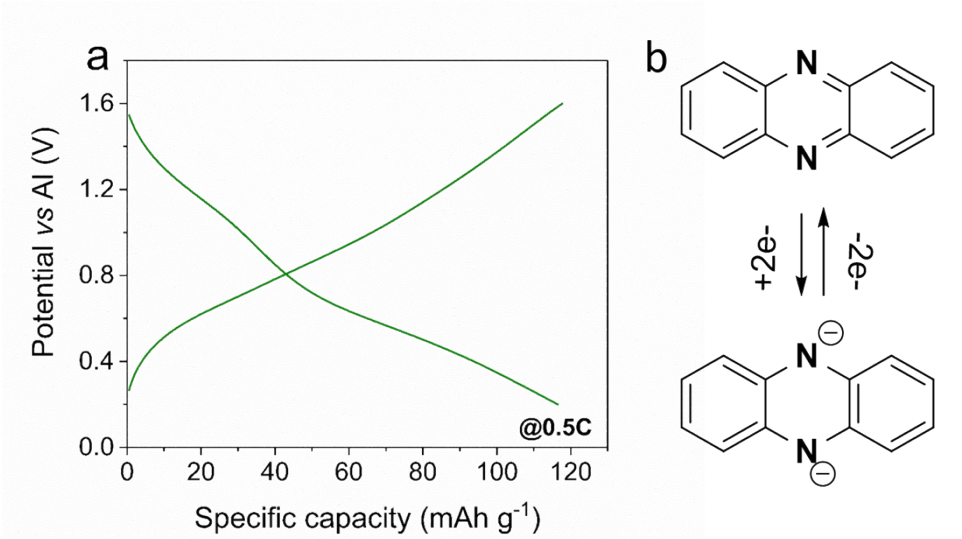


Figures S1. (a) ^{13}C Solid-state NMR of IEP-27-SR. (b) FTIR on IEP-27-SR and monomers made on KBr pellets (Legends are - : C≡C–H, # : CO_2 ambiental,* : C≡C, + : C=N, o : C–Br), (c) TEM picture at 1 µm bar scale.



Figures S2. (a) Galvanostatic test for *ex situ* ATR at 0.5C. (b) Depiction of the generic conversion mechanism of phenazine.

Since carbon additives were included during the synthesis of the IEP-27-SR hybrid (SWCNT and RGO) and an extra amount is added during the preparation of the buckypaper electrodes (SWCNTs), we evaluated the carbon contribution to the total capacity. Long-term galvanostatic charge-discharge cycling (GCD) was performed at 2C on buckypaper with similar mass loading, but containing only SWCNTs and RGO (GCD profile and cyclability are shown in Figure S5). Since the capacity attributed to carbon additives was found to be only 22 mAh g^{-1}, we could assess that most of the capacity is given by the phenazine active units. For this reason, the carbon contribution was considered in this work minor and was not substrated from the specific capacity values obtained for the Al//IEP-27-SR experiments and reported in this work, to allow the comparison with the state of art.

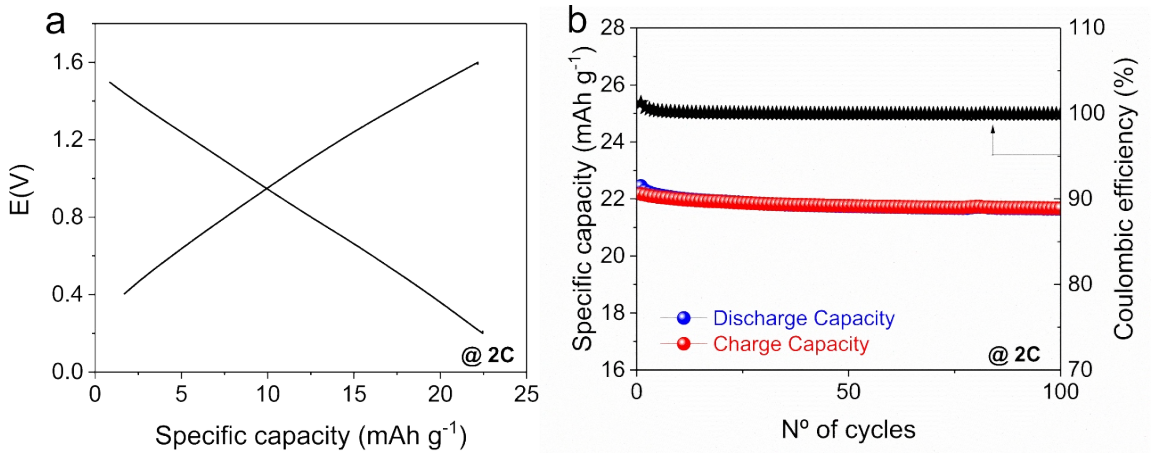


Figure S3. Carbon contribution. (a) GPLC at 2C and (b) cycling (100 cycles) of the carbon electrode. Capacity contribution from the carbon was found to be 22 mAh g^{-1}.

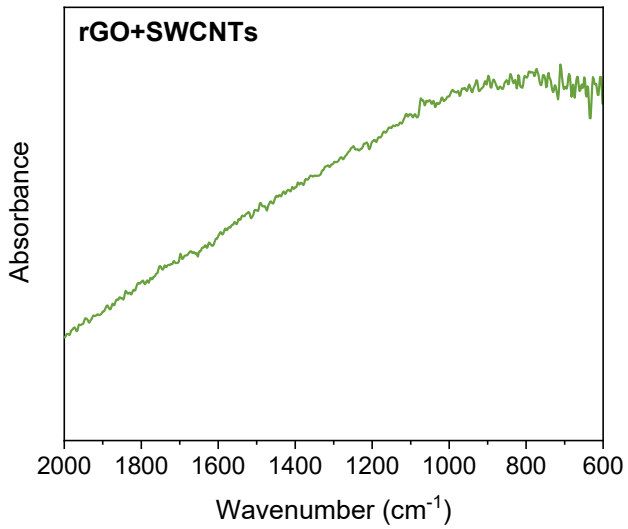


Figure S4. ATR spectra of only carbon (RGO + SWCNTs). No peaks are observed.

Table S1. *Ex situ* EDS data for the Pristine, Soaked, Discharged and Charged electrodes in atomic percents. It be noted that the values reported are the average values obtained over 5 different areas on specific electrodes.

	C	O	N	Al	Si	Cl	Fe	Cu	Br	Pd
Pristine	92.08	3.92	3.38	-	0.07	0.02	0.03	0.10	0.38	0.02
Soaked	89.32	6.95	2.89	0.20	0.30	0.17	0.03	0.04	0.04	0.01
Discharged	91.50	2.89	2.54	0.87	0.07	2.00	0.04	0.03	0.04	0.02
Charged	85.03	9.12	2.69	0.25	0.03	0.22	0.01	0.04	0	0

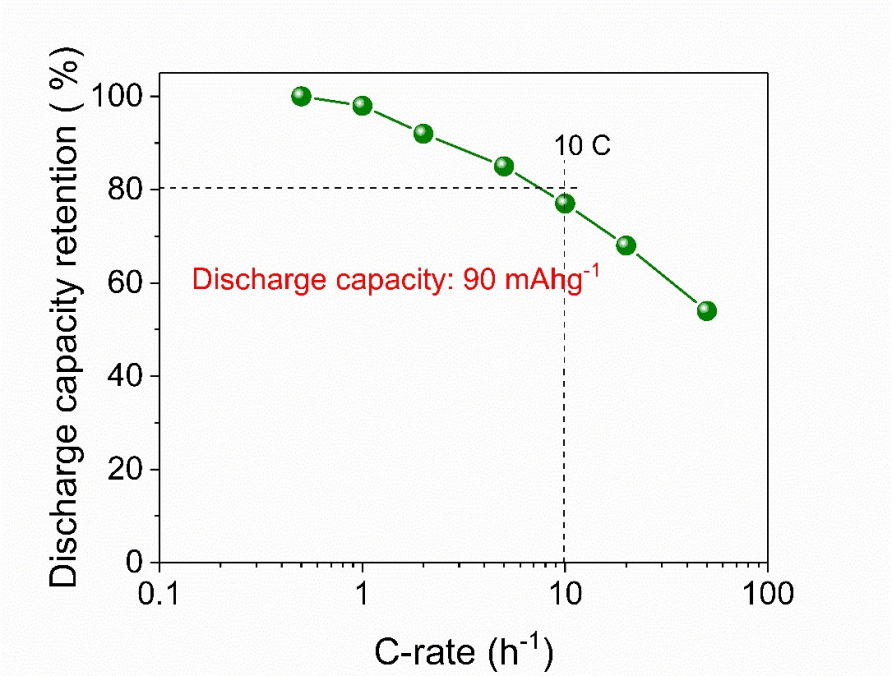


Figure S5. Discharge capacity retention vs C-rate for Al//IEP-27-SR cell in the $AlCl_3$/EMIMCl electrolyte

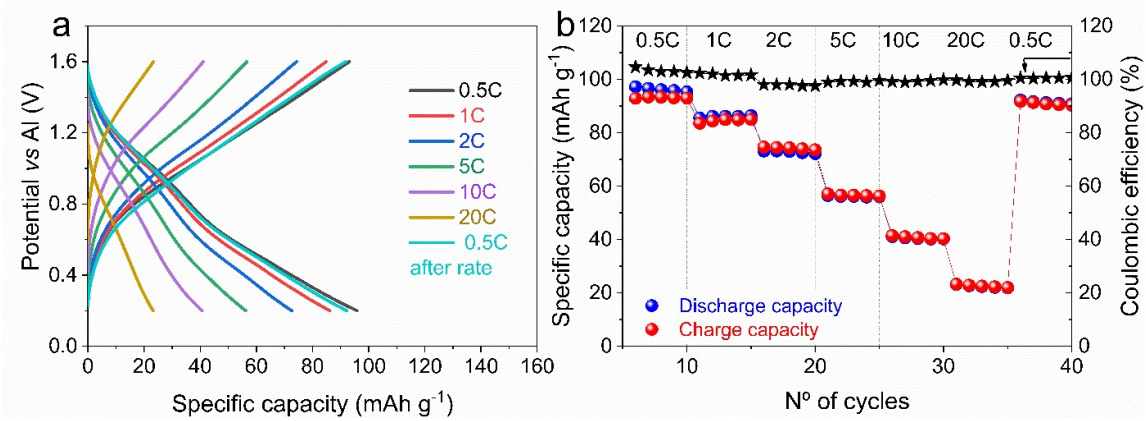


Figure S6. GCDs profiles of Al//IEP-27-SR cell in $AlCl_3$: urea (1.3:1.0, molar ratio) at different current densities. (a) Al//IEP-27-SR cell profiles. (b) Stability and CE (%) at different current densities.

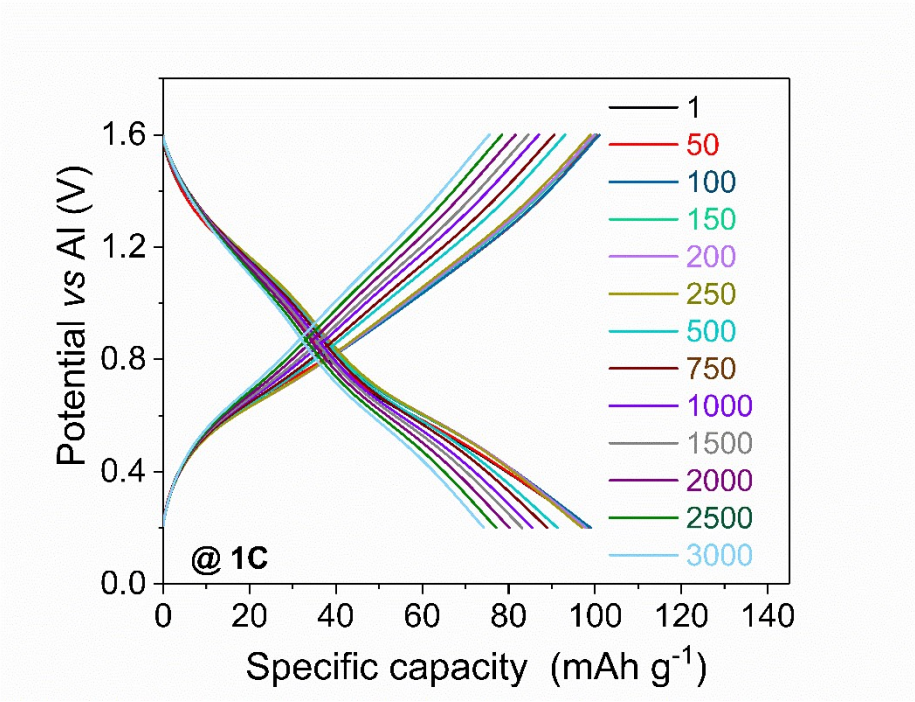
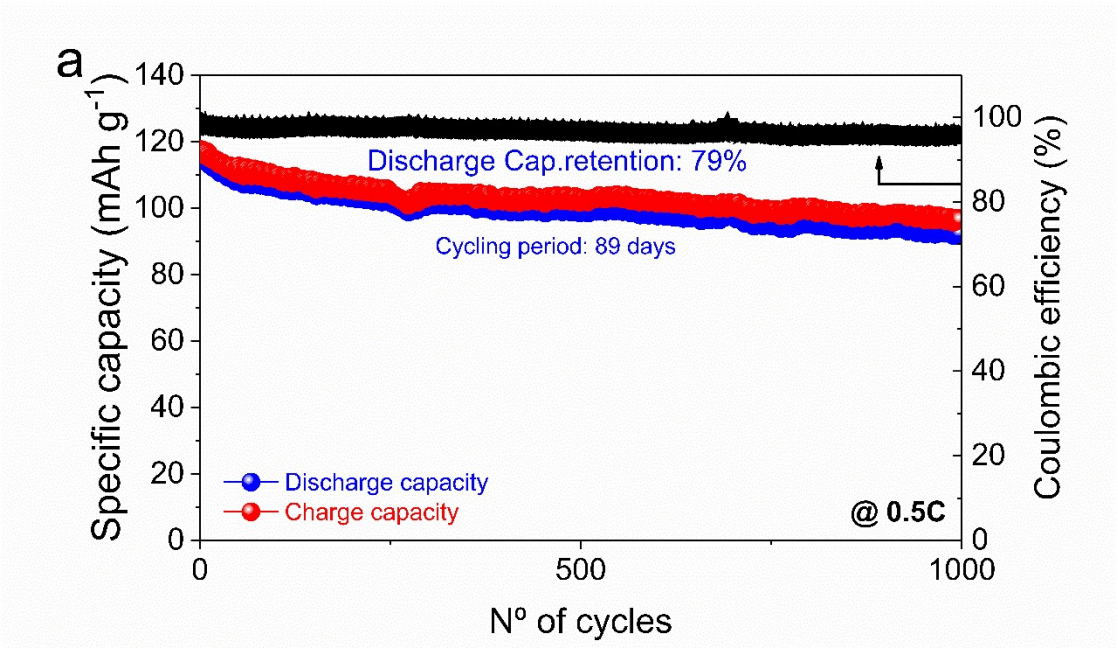


Figure S7. GCDs profiles at 1C from cycle 1 to cycle 3000 in in the $AlCl_3$/EMIMCl electrolyte.



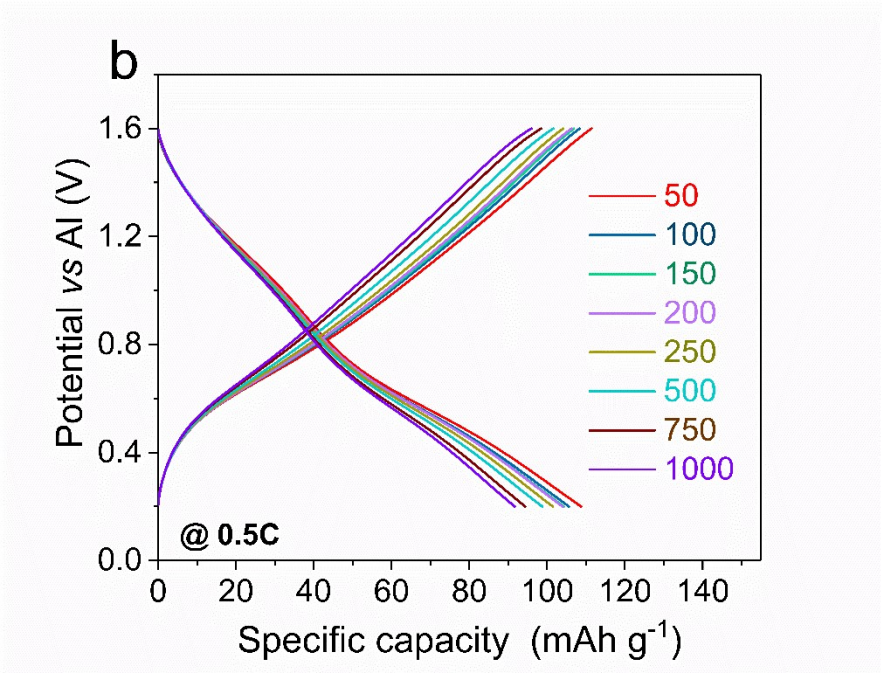
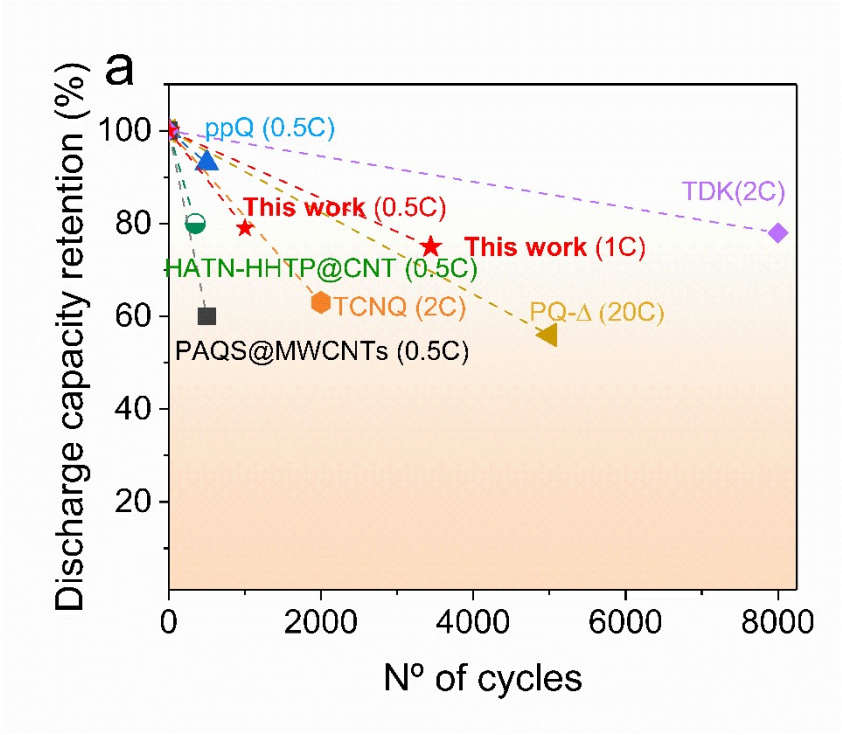


Figure S8. (a)Long cycling at 0.5C for 1000 cycles (corresponding to 89 days of cycling). (b)Charge-discharge profiles at the same current density for different selected cycles.



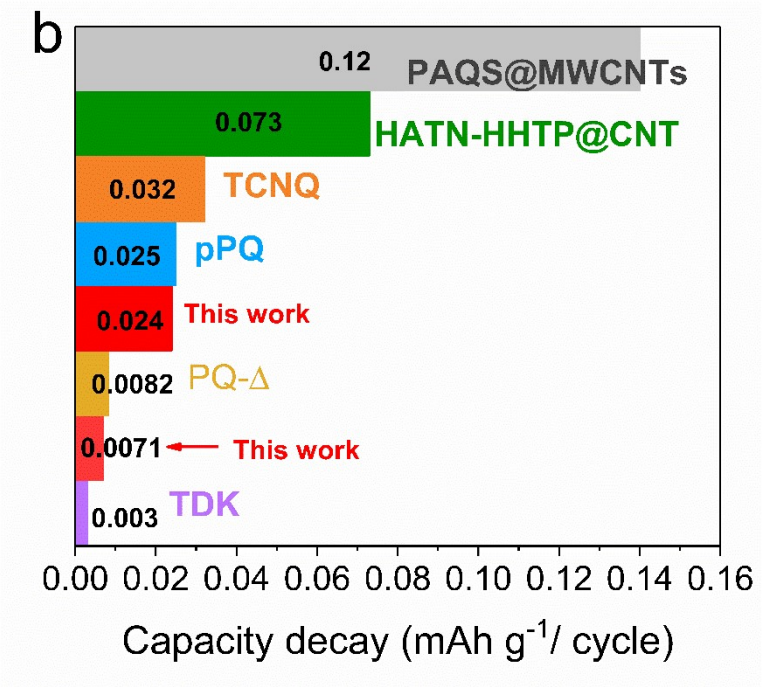
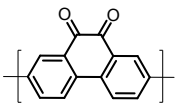
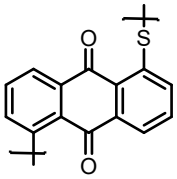
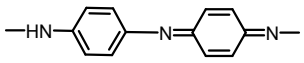
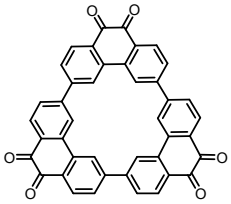
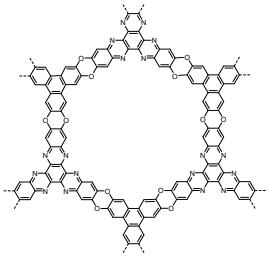
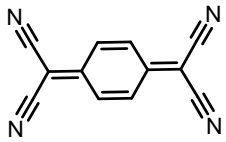
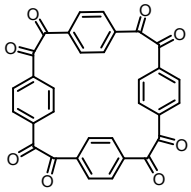
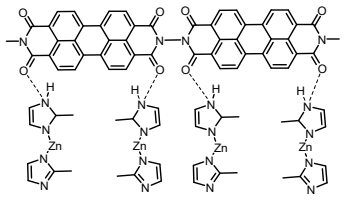
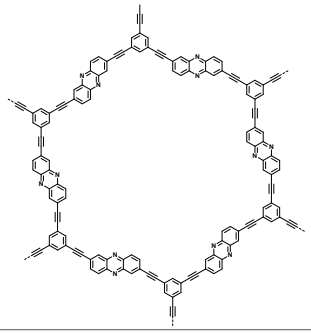


Figure S9. Comparison with the state-of-the-art: (a) discharge capacity retention vs cycle number. (b) Capacity decay per cycle. For this comparison have been selected only some examples from the literature (n-type): "p-type" and "bipolar" types polymers have been excluded. All the examples used for this comparison are reported in Table S2 and are listed here with the respective reference numbers: PAQS@MWCNTS,(1) HATN-HHTP@CNT,(2) TCNQ,(3) ppQ,(4) PQ- Δ,(5) TDK.(6)

Table S2. Table with the most representative examples of RABs with n-type organic cathode materials applied in $AlCl_3$:[EMIm]Cl electrolyte

Organic cathode	Electrode composition and Active material mass loading*[1]	C-max, number of cycles, current density, C_{ret}% and number of days[2]	Rate capability (capacity at max applied current and retention %)
pPQ(4) 	60 : 30 : 10 AM: Printex XE2 CB: PTFE 2 mg cm^{-2}	168 mAh g^{-1} at 0.5C 500 cycles at 0.5C 93% ~52 days	8 $mAhg^{-1}$ 20C 6%
PAQS/MWCNT(1) 	60 : 30 : 10 AM: Printex XE2 CB: PTFE 2 mg cm^{-2}	190 mAh g^{-1} at 0.5C 500 cycles at 0.5C 60% ~41 days	130 $mAhg^{-1}$ 10C 69%
PANI(H^+)@SWCNT(7) 	65 : 35 PANI:SWCNTS 1.1 mg cm^{-2}	200 mAh g^{-1} at 1 A g^{-1} 8000 cycles at 10 A g^{-1} 87.6% //	45 $mAhg^{-1}$ 40 A g^{-1} 22.5%

PQ- Δ (5) 	30: 60: 10 AM: Denka black: PVDF 0.5mg cm^{-2}	110 mAh g^{-1} at 1C 5000 cycles at 20C 56% ~11 days	70 $mAhg^{-1}$ 100C 64%
HATN-HHTP@CNT (40%)(2) 	80: 10: 10 HHTP@CNT (40%): acetylene black: sodium alginate 1 mg cm^{-2}	128 mA h g^{-1} at 100 mA g^{-1} (~0.5C) 350 cycles at 100 mA g^{-1} 80% ~29 days	110 mA h g^{-1} 200 mA g^{-1} (~1C) 86%
TCNQ(3) 	60 : 30 : 10 AM: acetylene black: PVDF 0.5 mg cm^{-2}	180 mAh g^{-1} at 500 mAg^{-1} (~2C) 2000 cycles at 500 mAg^{-1} 63% ~55 days	100 $mAhg^{-1}$ 500 mAg^{-1} (~2C) 83%
TDK(6) 	50:40:10 AM: conductive agent: PVDF 1.5 mg cm^{-2}	226 mAh g^{-1} at 100 mA g^{-1} (~0.25C) 8000 cycles at 1 A g^{-1}(~2.5C) 78% ~65 days	66 mAh g^{-1} 2A g^{-1} (~5C) 36%
PI-MOF(8) 	70 :20: 10 Pi-MOF : Ketjenblack: PVDF 1.7 mg cm^{-2}	83 mAh g^{-1} at 1 A g^{-1} 1800 cycles at 1 A g^{-1} 87% //	40 mA h g^{-1} 10 A g^{-1} 43%
IEP-27-SR (this work) 	50 : 50 IEP-27: SWCNTs (47%):RGO(3.5%) 1 mg cm^{-2}	116 mAh g^{-1} at 0.5C 3440 cycles at 1C 75% ~127 days 1000 cycles at 0.5C 79% ~89 days	50C 62 mAh g^{-1} 54%

*[1] Active material mass loading is calculated considering the amount of polymer excluding any carbon contribution, also in the case of hybrid materials.

*[2]Duration of the cycling expressed as cycling period (days) is calculated considering the C-rate and multiplying the theoretical time by the Capacity utilization (%) at the first cycle and at final cycle and considering the average value. The calculation was possible only when the C-rate was

given or when was possible to convert current density from A/g to C-rate using the theoretical capacity.

References:

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