Electronic Supplementary Information

Organic conjugated polyanthraquinonylimide cathodes for rechargeable magnesium batteries

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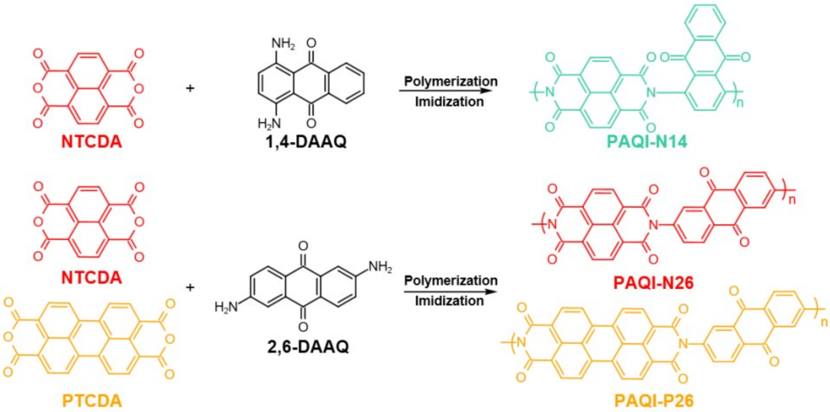


Fig. S1 Synthesis of PAQIs.

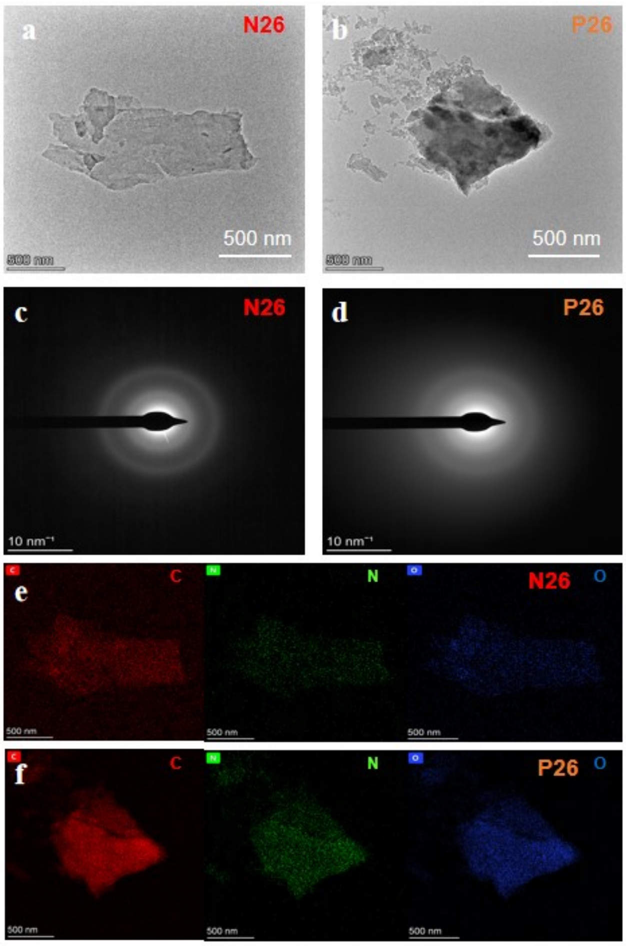


Fig. S2 TEM images of (a) N26 and (b) P26. ED patterns of (c) N26 and (d) P26. EDS images of (e) N26 and (f) P26.

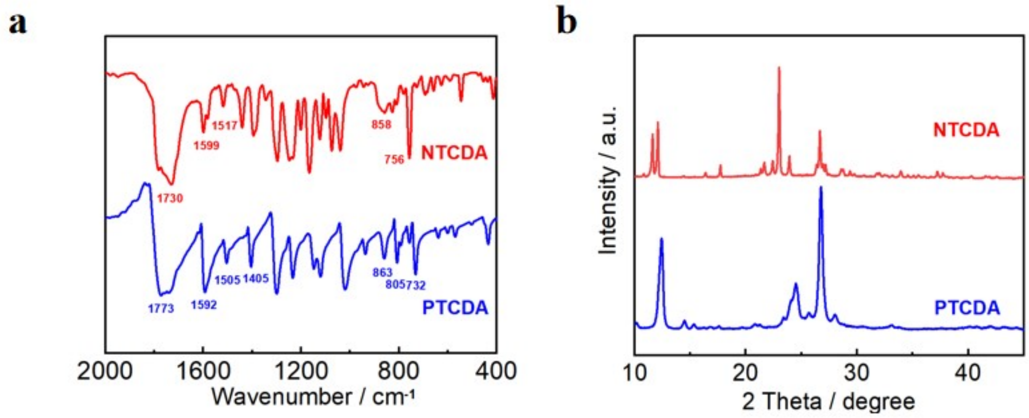


Fig. S3 (a) IR spectra and (b) XRD patterns of NTCDA and PTCDA.

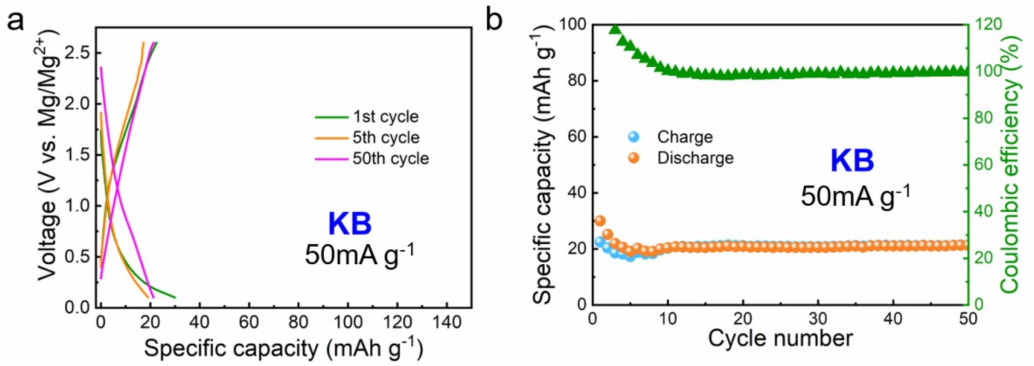
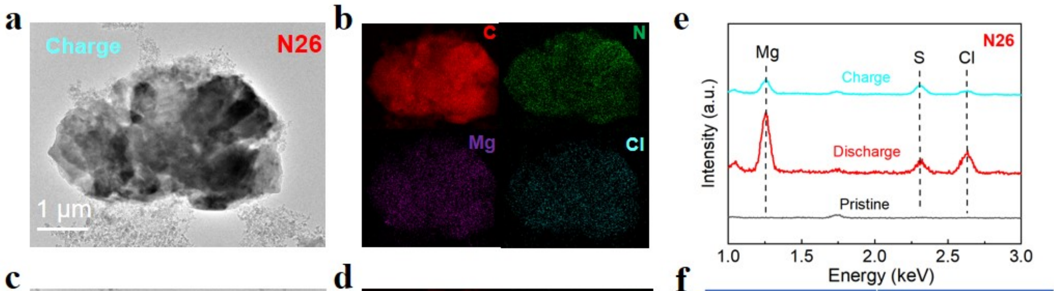


Fig. S4 (a) Charge/discharge curves and (b) cycling performance of KB solely. The mass of KB was the same as that contained in the PAQI cathodes, and the mass of the active material was set the same as the PAQI electrode for a comparison.



Charge		Discharge	
Element	Atomic Fraction (%)	Element	Atomic Fraction (%)
C	83.00	C	79.55
N	2.72	N	2.53
O	13.49	O	15.72
Mg	0.44	Mg	1.48
S	0.23	S	0.25
Cl	0.12	Cl	0.47

Fig. S5 (a) STEM and (b) EDS images of N26 at charge state (20th cycle). (c) STEM and (d) EDS images of N26 at discharge state (20th cycle). (e) EDS spectra of N26 at pristine/charge/discharge states. (f) Relative atomic fractions of N26 at charge/discharge states.

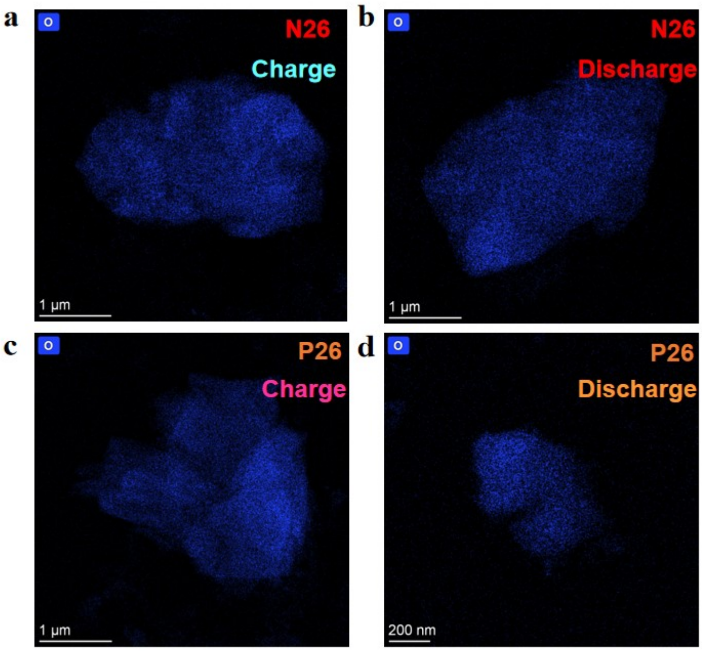


Fig. S6 EDS O images for (a) charge and (b) discharge state of N26 (20th cycle). EDS O images for (c) charge and (d) discharge state of P26 (20th cycle).

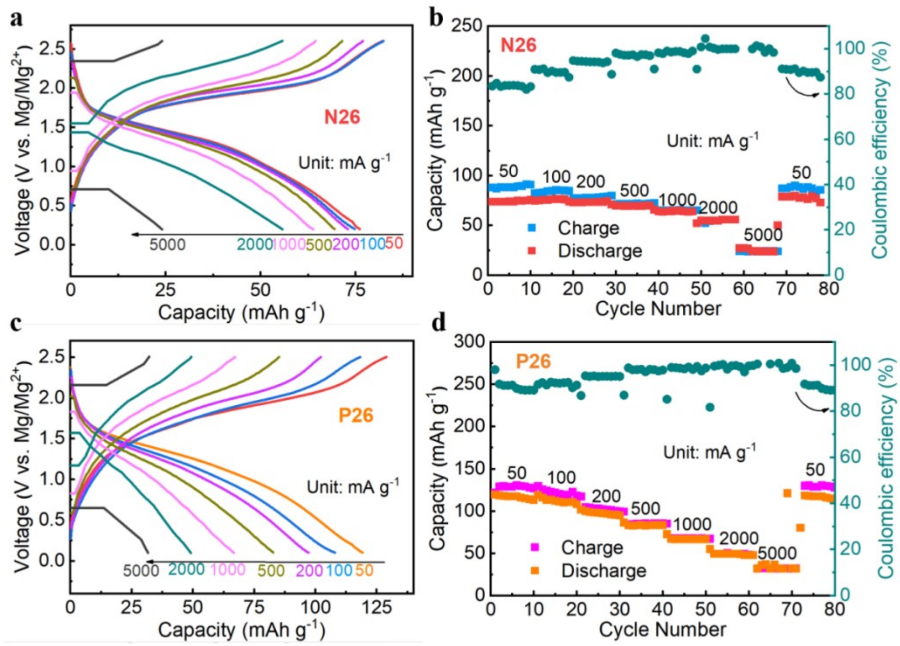


Fig. S7 (a) Charge/discharge curves and (b) cycling performance of N26, (c) charge/discharge curves and (d) cycling performance of P26 at different current densities (0.1–2.6 V) with chlorine-free electrolyte of $Mg(TFSI)_2$ (0.5 M) dissolved in a mixed solvent of DME and 1-methoxy-2-propylamine (w/w=3.84/1).

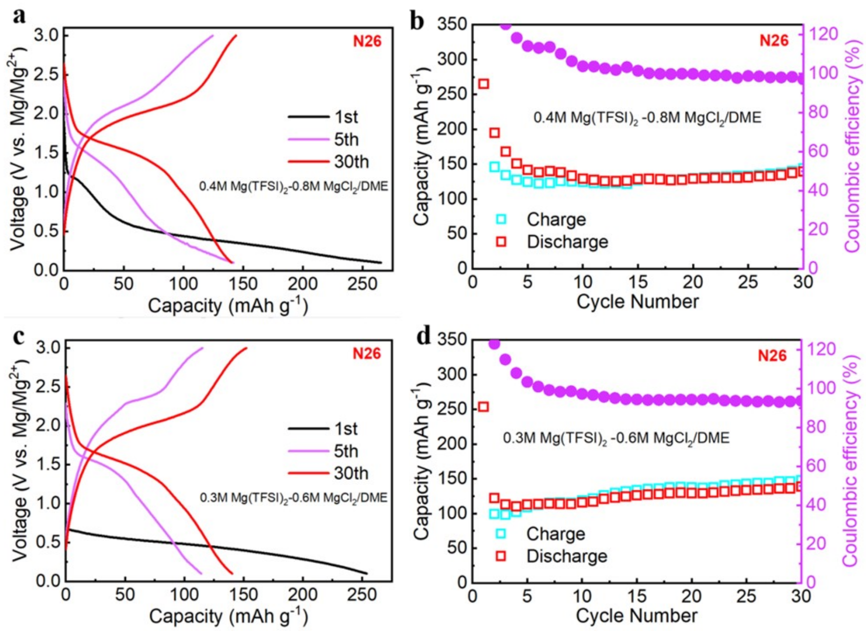


Fig. S8 (a) Charge/discharge curves and (b) cycling performance of N26 in electrolyte of $Mg(TFSI)_2$ (0.4 M)-$MgCl_2$ (0.8 M)/DME at 50 mA g^{-1}. (c) Charge/discharge curves and (d) cycling performance of N26 in electrolyte of $Mg(TFSI)_2$ (0.3 M)-$MgCl_2$ (0.6 M)/DME at 50 mA g^{-1}.

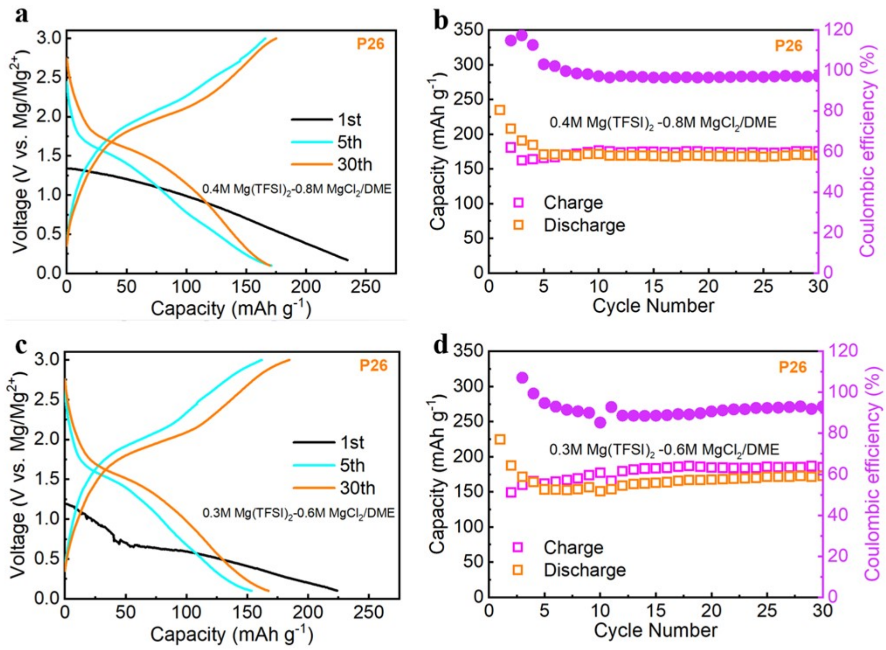


Fig. S9 (a) Charge/discharge curves and (b) cycling performance of P26 in electrolyte of $Mg(TFSI)_2$ (0.4 M)-$MgCl_2$ (0.8 M)/DME at 50 mA g^{-1}. (c) Charge/discharge curves and (d) cycling performance of P26 in electrolyte of $Mg(TFSI)_2$ (0.3 M)-$MgCl_2$ (0.6 M)/DME at 50 mA g^{-1}.

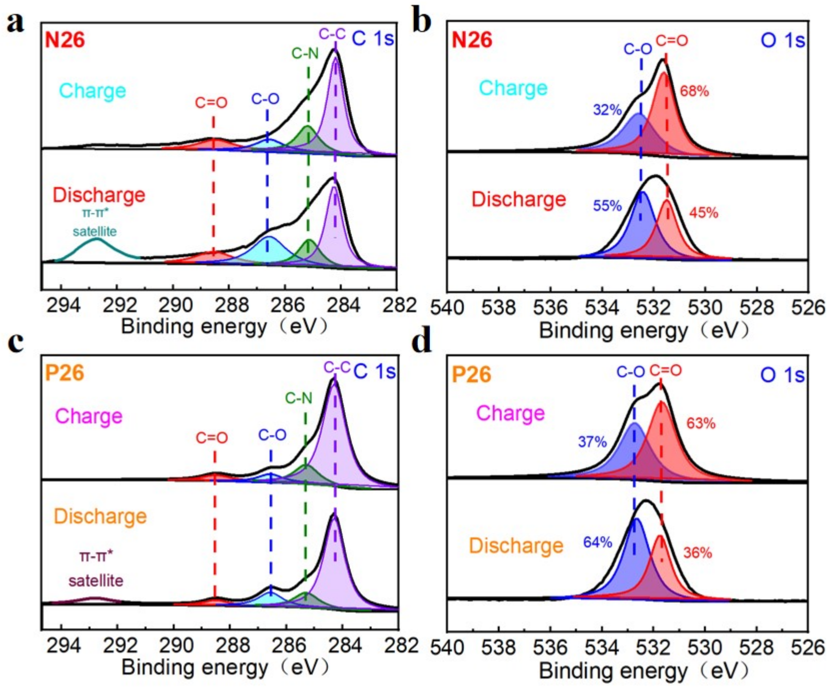


Fig. S10 (a) Ex-situ C 1s and (b) O 1s XPS spectra of N26, and (c) ex-situ C 1s and (d) O 1s XPS spectra of P26 in chlorine-free electrolyte of $Mg(TFSI)_2$ (0.5 M) dissolved in a mixed solvent of DME and 1-methoxy-2-propylamine (w/w=3.84/1). The electrodes were cycled between 0.1 and 2.6 V. The electrodes at the 10th cycle were used.

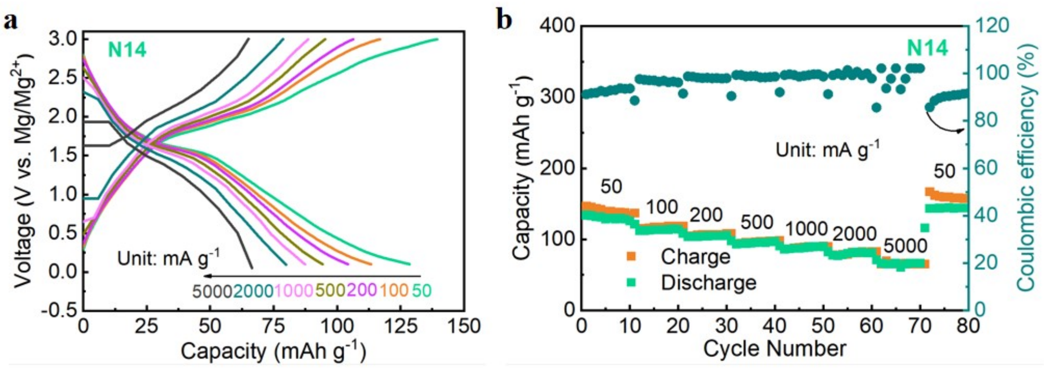


Fig. S11 (a) Charge/discharge curves and (b) rate performance of N14 in the chlorine-containing electrolyte.

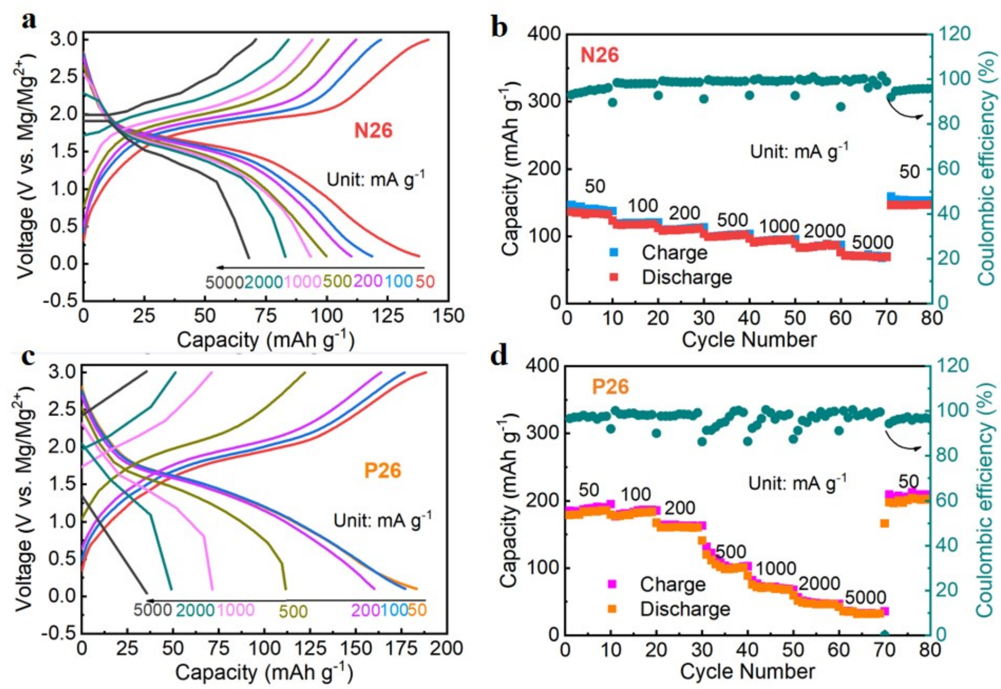


Fig. S12 (a) Charge/discharge curves and (b) rate performance of N26, (c) charge/discharge curves and (d) cycling performance of P26 at different current densities in the chlorine-containing electrolyte.

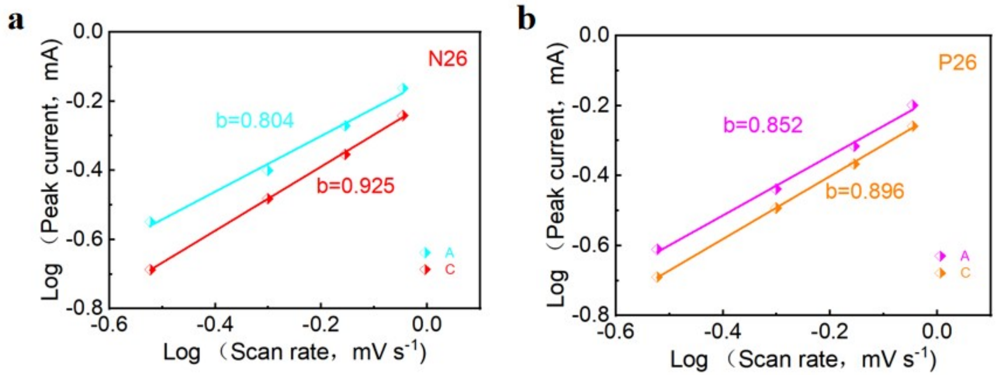


Fig. S13 log(i) vs. –log(v) plots for the redox peaks of (a) N26 and (b) P26.

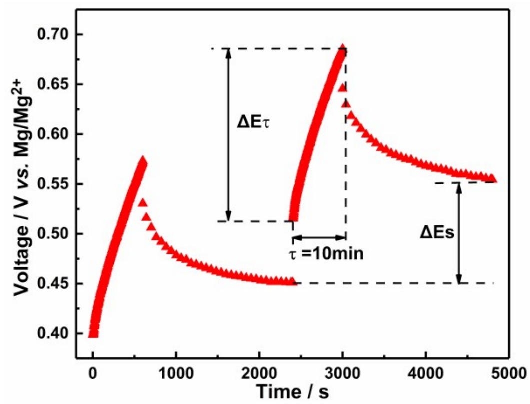


Fig. S14 Calculation details of GITT.

The Mg^{2+} diffusivity can be calculated via the following formula:

$$D^{GITT} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\triangle E_s}{\triangle E_\tau}\right)^2$$

Where τ refers to constant current pulse time, m_B and M_B are the mass, molar mass of the cathode material, respectively. V_m is the molar volume of the compound and S is the area of electrode-electrolyte interface. $\triangle E_S$ is voltage difference during a single-step experiment, and $\triangle E_\tau$ is the total change of cell voltage during a constant current pulse.

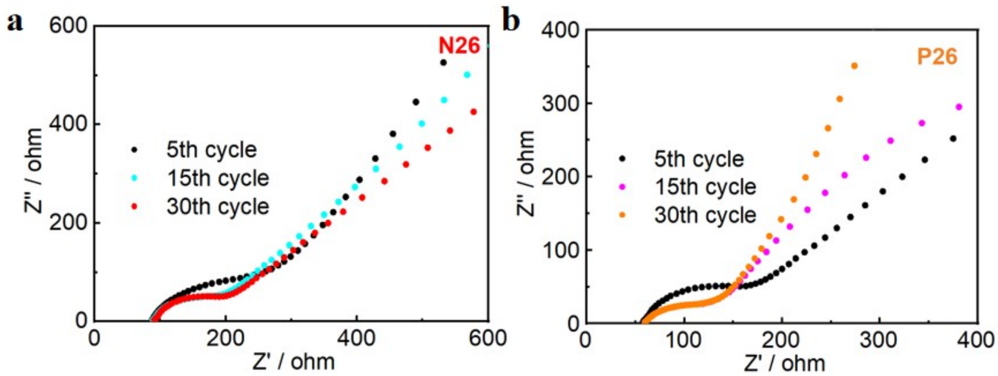
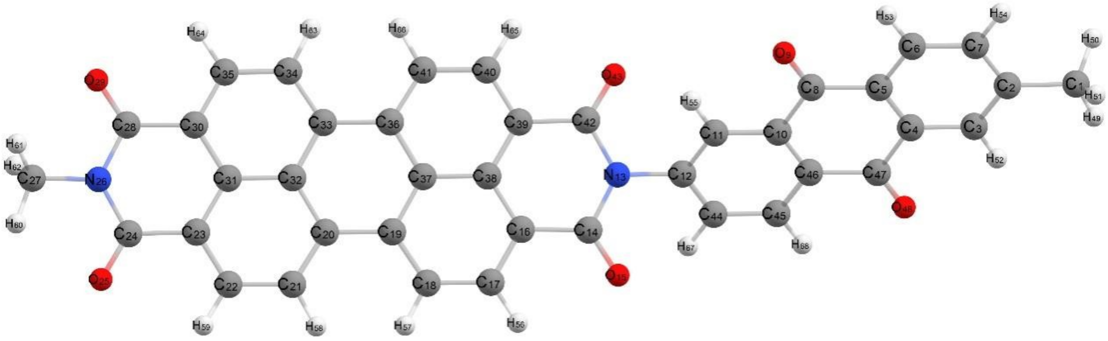


Fig. S15 Electrochemical impedance spectra (EIS) of N26(a) and P26(b) electrodes at different cycles.

Table S1 Computation results



Atom	Pristine	Discharged	Variation
1(C)	-0.07543973	-0.1096145	-0.03417
2(C)	0.01966735	-0.0773481	-0.09702
3(C)	-0.03030071	-0.0808679	-0.05057
4(C)	-0.01698273	-0.0897151	-0.07273
5(C)	-0.0209518	-0.0877938	-0.06684
6(C)	-0.02306288	-0.0746217	-0.05156
7(C)	-0.02891419	-0.1441371	-0.11522
8(C)	0.1554729	0.04066678	-0.11481
9(O)	-0.22954959	-0.4344722	-0.20492
10(C)	-0.01318038	-0.0626536	-0.04947
11(C)	-0.02161011	-0.0544052	-0.0328
12(C)	0.05155272	-0.0043392	-0.05589
13(N)	-0.03898309	-0.0438552	-0.00487
14(C)	0.18494121	0.15107532	-0.03387
15(O)	-0.25576375	-0.3288077	-0.07304
16(C)	-0.02211017	-0.0802506	-0.05814
17(C)	-0.01038368	-0.0645602	-0.05418
18(C)	-0.02765687	-0.1080069	-0.08035
19(C)	0.01092653	-0.0290819	-0.04001
20(C)	0.00891847	-0.0485259	-0.05744
21(C)	-0.02692885	-0.0982571	-0.07133
22(C)	-0.01154882	-0.0904926	-0.07894
23(C)	-0.01990395	-0.0966925	-0.07679
24(C)	0.18362934	0.12589362	-0.05774
25(O)	-0.26260758	-0.3800031	-0.1174
26(N)	-0.03589264	-0.050496	-0.0146
27(C)	-0.02784118	-0.048355	-0.02051
28(C)	0.18134666	0.12523638	-0.05611
29(O)	-0.26386081	-0.3806505	-0.11679
30(C)	-0.0199705	-0.0961631	-0.07619
31(C)	-0.00207967	-0.0167371	-0.01466
32(C)	0.00036148	-0.0129961	-0.01336

33(C)	0.00884774	-0.04786	-0.05671
34(C)	-0.02682782	-0.0974118	-0.07058
35(C)	-0.01148378	-0.0899698	-0.07849
36(C)	0.0108551	-0.0284007	-0.03926
37(C)	0.00067235	-0.0102071	-0.01088
38(C)	-0.00123407	-0.0148555	-0.01362
39(C)	-0.02182749	-0.0783224	-0.05649
40(C)	-0.00975366	-0.0618324	-0.05208
41(C)	-0.02729338	-0.1064381	-0.07914
42(C)	0.18554295	0.15344994	-0.03209
43(O)	-0.25260572	-0.3187577	-0.06615
44(C)	-0.02128673	-0.0959353	-0.07465
45(C)	-0.01884967	-0.0755392	-0.05669
46(C)	-0.01463145	-0.0693071	-0.05468
47(C)	0.1557727	0.02580665	-0.12997
48(O)	-0.2293476	-0.4585846	-0.22924
49(H)	0.03984136	0.00545353	-0.03439
50(H)	0.04035259	-0.0105681	-0.05092
51(H)	0.04061003	-0.0107913	-0.0514
52(H)	0.04534612	0.00057334	-0.04477
53(H)	0.04967201	0.00554119	-0.04413
54(H)	0.04575818	-0.0276706	-0.07343
55(H)	0.05100093	0.02230754	-0.02869
56(H)	0.05671947	0.01870334	-0.03802
57(H)	0.04799661	0.00501205	-0.04298
58(H)	0.04772002	0.00817139	-0.03955
59(H)	0.05617836	0.0068468	-0.04933
60(H)	0.04381048	0.01937304	-0.02444
61(H)	0.04234162	0.01521812	-0.02712
62(H)	0.04231655	0.01495834	-0.02736
63(H)	0.0478226	0.00891999	-0.0389
64(H)	0.05643963	0.00733874	-0.0491
65(H)	0.05729343	0.02142087	-0.03587
66(H)	0.04813346	0.00596614	-0.04217
67(H)	0.05072452	0.00303264	-0.04769
68(H)	0.05207954	0.00538587	-0.04669

Table S2 EDS element analysis for charged state (3.0V) of the N26 cathode.

Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
C	K	85.30	5.09	80.80	3.16	1.89
N	K	1.71	0.36	1.89	0.39	2.68
O	K	12.03	2.50	15.18	3.08	0.28
Mg	K	0.50	0.10	0.97	0.19	1.57
S	K	0.32	0.06	0.80	0.15	0.38
Cl	K	0.13	0.03	0.37	0.07	1.22

Table S3 EDS element analysis for charged state (3.0V) of the P26 cathode.

Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
C	K	87.19	3.96	83.40	2.34	0.03
N	K	1.37	0.29	1.53	0.32	3.84
O	K	10.90	2.24	13.89	2.82	1.72
Mg	K	0.36	0.07	0.70	0.14	0.32
S	K	0.11	0.02	0.28	0.05	0.78
Cl	K	0.07	0.01	0.19	0.04	1.29

Table S4 EDS element analysis for discharged state (0.1V) of the N26 cathode.

Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
C	K	79.55	5.12	73.32	2.89	0.05
N	K	2.53	0.54	2.71	0.56	3.98
O	K	15.72	3.30	19.30	3.94	0.32
Mg	K	1.48	0.31	2.76	0.56	1.43
S	K	0.25	0.05	0.62	0.12	0.44
Cl	K	0.47	0.09	1.29	0.24	0.36

Table S5 EDS element analysis for discharged state (0.1V) of the P26 cathode.

Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
C	K	86.22	4.37	81.48	2.66	1.33
N	K	1.42	0.30	1.57	0.32	2.82
O	K	10.75	2.22	13.53	2.75	1.69
Mg	K	1.19	0.24	2.28	0.46	0.74
S	K	0.15	0.03	0.38	0.07	1.36
Cl	K	0.27	0.05	0.76	0.14	0.97

Table S6 Calculation details of specific power for different RMB cathodes.

Specific capacity, voltage, specific energy and specific power of state- of-the-art Mg batteries that store pure Mg^{2+}. Calculation of specific energy is based on the equation of $E_s = E \times (C_c^{-1} + C_a^{-1})^{-1}$, where C_a is the specific capacity of Mg metal anode (2205 mAh g^{-1}), and C_c is cathode specific capacity. Calculation of specific power is based on the equation of $P_s = E_s \times (C_c \times CD^{-1})^{-1}$. CD is current density. The selected data is based on the maximum specific power of the material.The data of N26 and P26 are based on the rate performance of the cathodes in chlorine-containing electrolyte.

Cathode Materials	CD/mA g^{-1}	C_c/mAh g^{-1}	E/V	E_S/Wh kg^{-1}	P_S/ W kg^{-1}
Mo_6S_8 (R.T.)	258	56	0.92	50	231
Mo_6S_8 (50 °C)	258	94	1.09	98	270
Ti_2S_4 (R.T.)	4.8	130	1.1	135	5
Ti_2S_4 (60 °C)	4.8	190	1.15	201	51
I_2	211	135	1.8	229	358
COFs	2280	39	1.17	45	2870
P14AQ	450	112	1.2	128	897
PTO	20400	210	1.63	313	30361
N26(this work)	50	142	1.67	222	78
	2000	86	1.45	119	2780
P26(this work)	50	184	1.53	258	70
	2000	50	1.25	62	2431

Table S7 Calculation of Mg^{2+} diffusion coefficients at 1.1 mV s^{-1}

peak	N26		P26	
	i_p (mA)	D ($\times10^{-10}$ cm^2 s^{-1})	i_p (mA)	D ($\times10^{-10}$ cm^2 s^{-1})
A	0.7721	1.40	0.7459	1.37
C	–0.7356	1.35	-0.6829	1.24

The diffusion coefficient of Mg^{2+} is calculated by the following Randles-Sevcik Equation:

$$i_p=2.69\times10^5 n^{3/2} A D^{1/2} v^{1/2} C_0$$

where i_p is the peak current (A), n is the number of electrons per molecule during the reaction, A is the contact area between the electrode and electrolyte , D is the diffusion coefficient of Mg^{2+} (cm^2 s^{-1}), C_0 is the concentration of Mg^{2+} ion in the electrode material, and v is the scan rate (V s^{-1}).