

## Supplementary Information

# **An extended $\pi$ -conjugated bipolar polymer cathode for rechargeable magnesium batteries: high capacity contributed by n- and p-doping and charge delocalization**

Shuai Cui<sup>a</sup>, Zhen Qin<sup>a</sup>, Hongda Gui<sup>b</sup>, Ting Li<sup>a,\*</sup>, Daohong Zhang<sup>a,\*</sup>, Fei Xu<sup>b,\*</sup>

<sup>a</sup> Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, South-Central Minzu University, Wuhan 430074, China.

<sup>b</sup> Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China.

<sup>c</sup> Hubei Key Lab of Electrochemical Power Sources, College of Chemistry & Molecular Science, Wuhan University, Wuhan 430072, China.

\* E-mail: Ting Li ([liting@mail.scuec.edu.cn](mailto:liting@mail.scuec.edu.cn)); Daohong Zhang ([daohong.zhang@scuec.edu.cn](mailto:daohong.zhang@scuec.edu.cn)); Fei Xu ([xufei2058@whu.edu.cn](mailto:xufei2058@whu.edu.cn))

## Experimental section

### *Preparation of PI-P-tBA*

**PI-P-tBA** was prepared by perylenetetracarboxylic dianhydride (PTCDA, aladdin, 98%), tris(4-aminophenyl)amine (TAPA, aladdin, 98%) and imidazole (aladdin, 98%) at 200 °C for 24 h (Fig. S1). The obtained precipitates were washed with *N,N*-dimethylformamide (DMF), aqueous NaOH solution (1.0 mol L<sup>-1</sup>), water and ethanol. The final products were dried under vacuum at 70 °C for 24 h.

### *Characterization*

Infra-red spectrometer (FT-IR, FTIR-5700), Raman (DXR2 XI), X-ray photoelectron spectroscopy (XPS, EscaLab Xi+), fluorospectrophotometer (LS-55) and X-ray powder diffractometer (XRD, D8-ADVANCE) were applied for the structure analysis. Ex-situ characterization was conducted for the cycled electrodes after removal of residual electrolyte by being washed with 1,2-dimethoxyethane (DME).

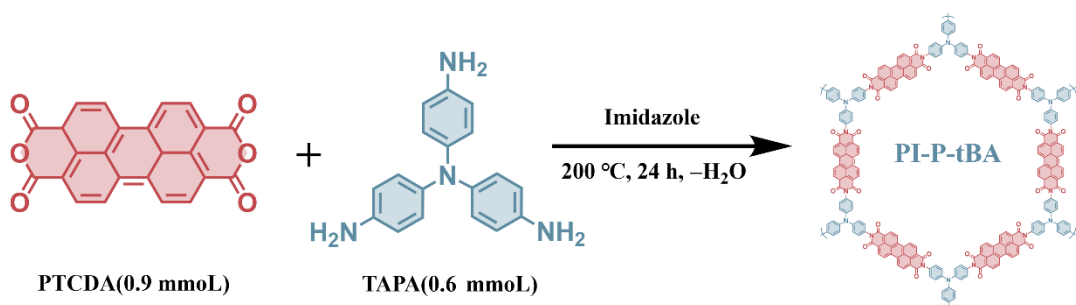
### *Electrochemical measurements*

An isopropanol slurry was prepared via mixing the active material, conductive carbon (Ketjen-black) and polytetrafluoroethylene with a proportion of 6: 3: 1, and coated on carbon paper current collector. After being dried under vacuum for 24 h at 70 °C, the cathodes were cut into circular discs (12 mm, 1.0 mg cm<sup>-2</sup>). The cathode, a Whatman separator and a metallic Mg anode were assembled into CR2032 coin cells in a glove box (Ar, H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm). A circular molybdenum foil (19 mm) was inserted at the cathode side to prevent electrochemical corrosions. The electrolyte was prepared by dissolving 2.5 mmol of Mg(TFSI)<sub>2</sub> (DoDoChem, 99.5%) and 5.0 mmol of MgCl<sub>2</sub> (Alfa Aesar, 99%) in 10 mL of DME. Galvanostatic cycling and cyclic voltammogram (CV) were conducted on LAND testers and CHI-660e electrochemical workstations, respectively. The specific capacity was calculated based on the mass of **PI-P-tBA**.

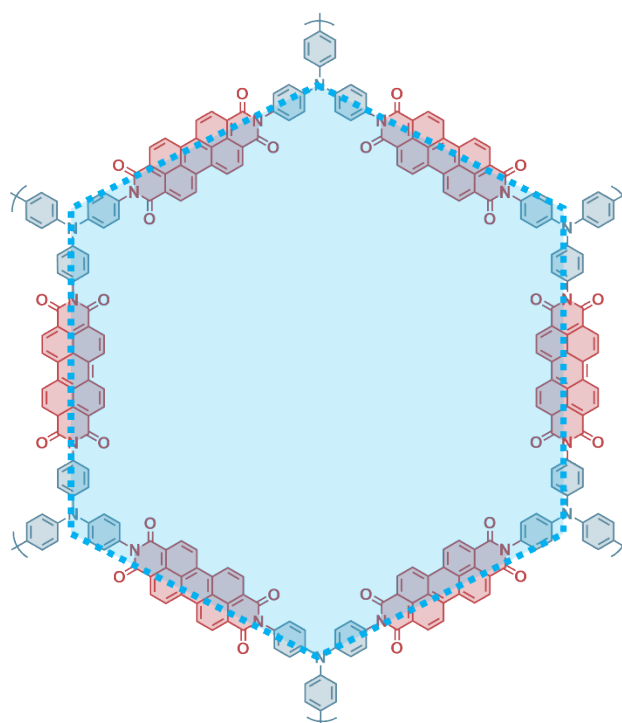
### *Theoretical computations*

Computation was conducted using Gaussian 16 software.<sup>1</sup> B3LYP functional<sup>2</sup> was adopted for all computations. Basis set of def2-SVP<sup>3</sup> was employed for geometry optimizations, and the optimal geometry was determined for each structure. A larger

basis set of def2-TZVP was used for the singlet point energy calculations. To improve the calculation accuracy, DFT-D3 dispersion correction with BJ-damping<sup>4,5</sup> was applied to correct the weak interaction. Orbital energy level analysis was performed with Multiwfn software.<sup>6</sup> All wave-functions used to analyze molecular orbitals were verified for stability. VMD software was used for the visualization of the orbitals.<sup>7</sup>

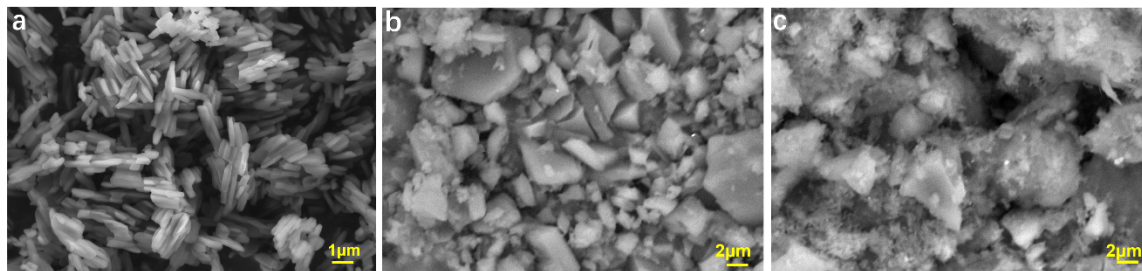


**Fig. S1.** Synthesis of **PI-P-tBA**.

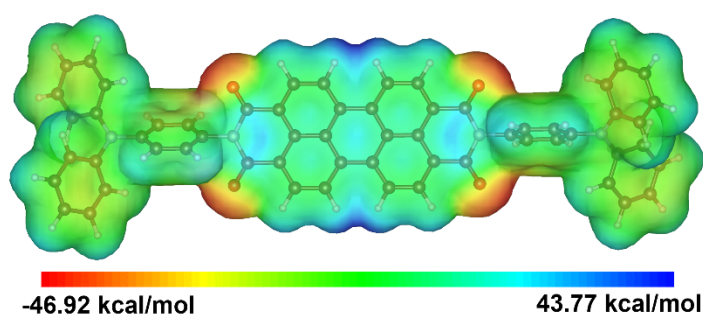


**Fig. S2.** The calculation of theoretical capacities of tBA and PTCDI.

To better calculate the theoretical capacity of **PI-P-tBA**, we selected the repeated unit (shaded in blue) as shown in Fig. S2. The theoretical capacity of **PI-P-tBA** was calculated based on the theoretical capacity of PTCDI and tBA and combined their relative molecular mass ratio and charge transfer ratio in the repeated unit. The theoretical capacities of n-doping are  $104\text{ mAh g}^{-1}$  based on two-electron enolization and  $208\text{ mAh g}^{-1}$  based on four-electron enolization, and  $52\text{ mAh g}^{-1}$  for p-doping of **PI-P-tBA**.

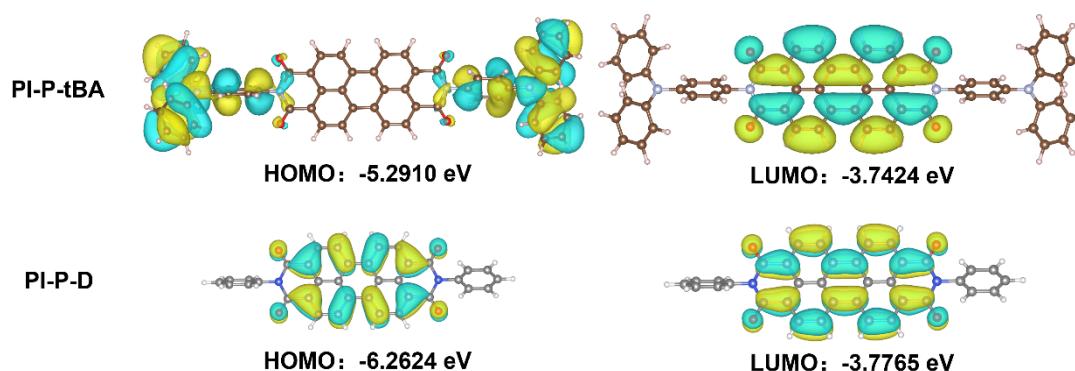


**Fig. S3.** SEM images of (a) PTCDA, (b) TAPA and (c) **PI-P-tBA**.



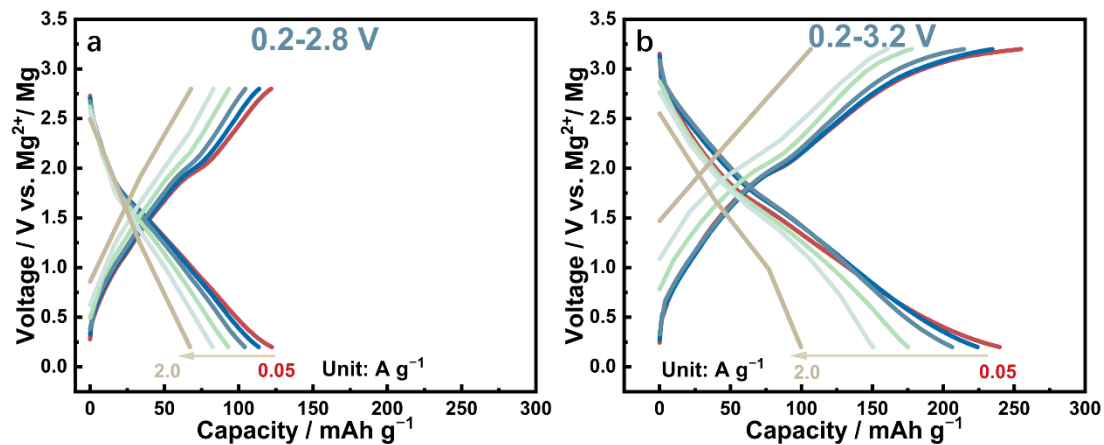
**Fig. S4.** Molecular electrostatic potentials of of PTCDI with two tBA units.

One repeating unit of **PI-P-tBA** is selected for the theoretical calculation. It is observed from its molecular electrostatic potential diagram that low values are observed at the carbonyl oxygen atoms, indicating these are the active sites for cation association.

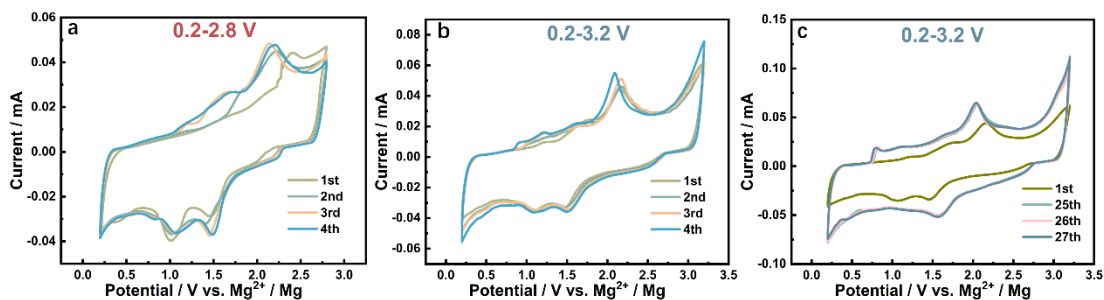


**Fig. S5.** HOMO and LUMO of PTCDI with (a) two tBA units or (b) two benzene units.

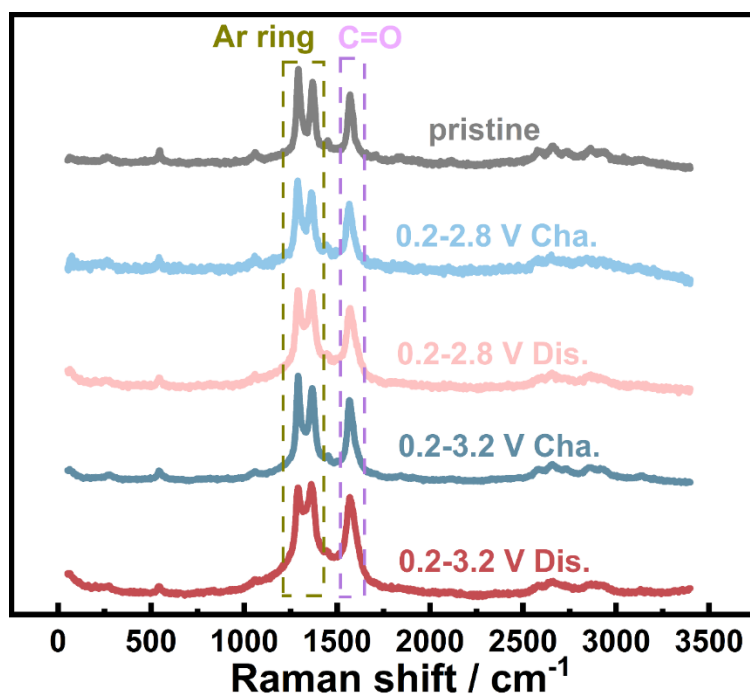
Based on the PTCDI unit, the HOMO and LUMO are calculated when the two ends are connected with tBA or benzene and units. It is observed that when the benzene unit is connected, HOMO and LUMO are mainly distributed in the middle PTCDI unit. When tBA is connected, the HOMO orbital is mainly distributed on the tBA unit, indicating tBA is the p-doping unit. The HOMO energy value of **PI-P-tBA** ( $-5.2910$  eV) is significantly higher than that of **PI-P-D** ( $-6.2624$  eV), indicating p-doping capability of **PI-P-tBA**.



**Fig. S6.** Charge/discharge profiles of **PI-P-tBA** at different current densities with the voltage ranges of (a) 0.2–2.8 V and (b) 0.2–3.2 V.






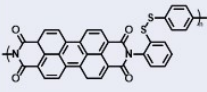
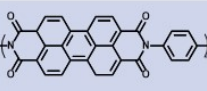
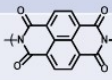
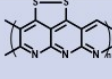


**Fig. S7.** CV profiles of **PI-P-tBA** at  $0.1 \text{ mV s}^{-1}$  with the potential ranges of (a) 0.2–2.8 V and (b) 0.2–3.2 V. (c) Comparison of the CV profiles before and after the activation.



**Fig. S8.** Raman spectra of **PI-P-tBA** at pristine and charge-discharge states with different voltage ranges.

Raman tests were conducted at the charge and discharge state of **PI-P-tBA** with voltage ranges of 0.2–2.8 V and 0.2–3.2 V. Compared with the pristine state, the C=O peak intensity of the discharge state gradually increases, and the change degree of 0.2–3.2 V was higher than that of 0.2–2.8 V, indicating that the enolization degree of **PI-P-tBA** is higher with a wider voltage range. At the same time, it is observed that the peak intensity of the conjugated structure changes obviously at 0.2–3.2 V. That is because the charge delocalization on the conjugated structure also changes due to the introduction of p-doping.

**Table S1.** Reported examples of organic cathodes for magnesium-ion batteries.

Structure	Name	Capacity(mA h g <sup>-1</sup> );Current	Voltage range	Electrolyte	Reference
	DMBQ	226; 20 mA g <sup>-1</sup>	0.5-2.8 V	0.5M Mg(TFSI) <sub>2</sub> 2MgCl <sub>2</sub> /DME	8
	d-PAQS	200; 50 mA g <sup>-1</sup>	0.1-2.6 V	0.5M Mg(TFSI) <sub>2</sub> 2MgCl <sub>2</sub> /DME	9
	26PAQ	122; 50 mA g <sup>-1</sup>	0.5-2.5 V	0.3M Mg(HMDS) <sub>2</sub> 4MgCl <sub>2</sub> /THF	10
	PI-SS	155; 50 mA g <sup>-1</sup>	0.2-2.8 V	0.5M Mg(TFSI) <sub>2</sub> 2MgCl <sub>2</sub> /DME	11
	PI-P-D	150; 50 mA g <sup>-1</sup>	0.2-2.8 V	0.5M Mg(TFSI) <sub>2</sub> 2MgCl <sub>2</sub> /DME	12
	NP	85; 50 mA g <sup>-1</sup>	0.6-2.5 V	0.4M Mg(TFSI) <sub>2</sub> MgCl <sub>2</sub> /TEGDME/DOL	13
	CSM	117.3; 25 mA g <sup>-1</sup>	0.3–2.0 V	0.25 M Mg(AlCl <sub>2</sub> BuEt) <sub>2</sub> /THF	14
	PHBQS	75; 50 mA g <sup>-1</sup>	0.8–3.0 V	0.48 M MgCl <sub>2</sub> and 0.32 M Mg(TFSI) <sub>2</sub> in tetraglyme and 1,3- dioxolane	15
	PI-P-tBA	250; 50 mA g <sup>-1</sup>	0.2-3.2 V	0.5M Mg(TFSI) <sub>2</sub> 2MgCl <sub>2</sub> /DME	This work

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