## **Supporting Information for**

# Precise synthesis of BN embedded perylene diimide oligomers for fast-charging and long-life potassium–organic batteries

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# **Experimental Procedures**

# **1.** General Information

All chemical reactions were conducted in oven-dried or flame-dried glassware. All the

chemicals and starting materials were purchased from commercial sources without further treatment unless specially noted. Compounds **1**, **2**, **3** are synthesized according to literature procedures. Solvents for chemical synthesis were purified according to the standard procedures. Triethylamine (Et<sub>3</sub>N) and 1,2-dichlorobenzene (DCB) was freshly distilled from calcium hydride under nitrogen prior to use. Toluene was redistilled from sodium under nitrogen and degassed by three freeze-pump-thaw cycles. Column chromatography was performed with silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel-coated glass sheets with F254 indicator. All yields given referred to isolated yields. Conductive additives (super P) and carboxymethyl cellulose (CMC) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd.. The ethylene glycol dimethyl ether (DME) and potassium hexafluorophosphate (KPF<sub>6</sub>) were purchased from duoduochem Co., Ltd., respectively.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on Bruker DRX 500. MALDI-TOF Mass spectrum was measured with AB Sciex 5800. UV-vis spectrum was recorded on Shimadzu UV-1800. Fluorescence measurements were carried out using a Shimadzu RF-6000 spectrophotometer. The cyclic voltammetry (CV) in solution were measured using CHI660E, with a polished platinum-disk electrode as the working electrode, a platinum-wire as counter electrode, an Ag/Ag<sup>+</sup> electrode as reference electrode, using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as internal standard and tetrabutylammonium hexafluorophosphate as electrolyte. Fourier transform infrared spectroscopy (FTIR) was used Thermos Scientific Nicolet 6700 spectrometer.

Thermogravimetric analysis (TGA) was carried out on a tainstruments SDT Q-600 under a nitrogen atmosphere at a heating rate of 10 °C/min. The alky chains were replaced by methyl groups to reduce the computation cost. All the optimized ground-state structures were shown to be minimum by the absence of imaginary frequencies.

A mixture, fabricated by the active materials, conductive additives (Super P) and binder (carboxymethyl cellulose in deionized water) in a weight ratio of 6:3:1, was coated on the surface of copper foil current collectors to fabricate the cathode. Subsequently, the electrode film was then dried at 100 °C overnight and cut into circles with diameter of 0.8 cm. It is worth noting that the loading mass of active materials in each coin cell is *ca.* 1.3  $\pm$  0.2mg cm<sup>-2</sup>. The cathode was assembled in 2032–type coin cells with potassium metal as the counter electrode under the argon atmosphere. The glass fiber filters (Whatman GF/F) acted as separators and 1 M KPF<sub>6</sub> dissolved in ethylene glycol dimethyl ether (DME) served as electrolytes. The Land–2001A (Wuhan, China) automatic battery tester was used to evaluated the galvanostatic charge/discharge performance and the cyclic voltammograms (CVs), electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) tests were investigated by the VSP multichannel potentiostatic-galvanostatic system (Bio–Logic SAS, France).

Generally, the measured current (i) and scan rate (v) in CV curves obey the power law:

$$i = av^b$$
 (Equations S1)  
 $\log i = \log a + b \log v$  (Equations S2)

*a* and *b* are adjustable parameters, and the limiting cases of the *b*-value estimates kinetic limitations, where a *b*-value of 0.5 indicates a total diffusion-driven behavior and a *b*-value of 1 demonstrates to a surface-controlled capacitive-controlled electrochemical process.

#### 2. Material Synthesis

#### 2.1 Synthesis of PDI2BN, trans- and cis-PDI3BN



Scheme S1. Synthetic route of compound PDI2NH.

**Synthesis of PDI2NH:** A Schlenk flask was charged with **2** (1.39 g, 2.40 mmol),  $Cs_2CO_3$  (1.17 g, 3.60 mmol),  $Pd(OAc)_2$  (13.47 mg, 0.06 mmol) and DPE-phos (64.63 mg, 0.12 mmol), then added 100 mL degassed anhydrous toluene at 0 °C. In an additional flask, the compound **1** (1 g, 1.20 mmol) was also dissolved in 60 mL degassed anhydrous toluene and then dropwise to the Schlenk flask at 0 °C. After stirred at 0 °C for more 30 minutes, the reaction was warm to room temperature slowly and then further stirred at 80 °C for 2 h. After cool down to room temperature, the mixture was filtered through celite. The organic solvent was dried over

anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated using vacuum rotary evaporator and obtained black solid. The crude materials were purified with column chromatography (eluent: PE:DCM from 3:1 to 1:2), 1.17 g target **PDI2NH** was obtained as black solid yield of 64%.

**PDI2NH:** <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.04 (s, 2H), 8.75-8.58 (m, 10H), 8.36-8.31 (m, 2H), 7.55 (s, 1H), 5.07-5.17 (m, 4H), 2.13 (s, 8H), 1.77 (s,8H), 1.32-1.16 (m, 64H), 0.85-0.75 (m, 24H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 164.7, 164.6, 164.1, 163.7, 163.0, 140.6, 134.7, 133.9, 131.9, 131.2, 130.2, 129.7, 129.0, 127.5, 126.7, 125.6, 124.8, 124.3, 123.8, 123.3, 122.9, 122.7, 122.4, 122.2, 55.1, 54.7, 32.4, 32.3, 31.7, 31.7, 29.2, 29.2, 27.0, 26.9, 22.6, 22.6, 14.1, 14.0. HRMS (MALDI-TOF) *m/z*: [M]<sup>+</sup> calcd for [C<sub>100</sub>H<sub>123</sub>N<sub>5</sub>O<sub>8</sub>]<sup>+</sup> 1522.9405, found 1522.9457.



Scheme S2. Synthetic route of compound PDI2BN.

**Synthesis of PDI2BN**: In a pressure-resistant reaction tube, the dried compound **PDI2NH** (300 mg, 0.20 mmol), triethylamine (1.5 mL), 10 mL anhydrous DCB and 1.5 mL boron trichloride in DCM was added under nitrogen atmosphere. The black reaction mixture was turned to red while stirred at 190 °C for 40 min. After cool down to room temperature, the mixture was extracted with DCM and washed with brine. Combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude materials were purified with column chromatography (eluent: PE:DCM from 3:1 to 1:1), 229.17 mg target **PDI2BN** was obtained as red solid yield of 76%.

**PDI2BN**: <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 10.40 (d, *J* = 23.7 Hz, 2H), 9.55 (s, 2H), 9.23 (dd, *J* = 13.0, 8.2 Hz, 4H), 9.15-9.00 (m, 4H), 5.35 (s, 2H), 5.23 (s, 2H), 2.45-2.14 (m, 8H), 2.04-1.81 (m, 8H), 1.31 (m, 62H), 0.92 (m, 12H), 0.74 (m, 12H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 165.0, 164.8, 164.4, 163.9, 163.2, 138.6, 137.9, 135.9, 135.0, 134.6, 133.8, 132.3, 131.5, 130.4, 129.9,

129.6, 125.8, 124.4, 123.9, 123.5, 123.1, 122.7, 122.4, 122.3, 55.1, 32.9, 32.6, 32.4, 32.2, 31.9,
31.8, 29.6, 29.3, 29.2, 27.2, 27.0, 26.8, 22.8, 22.7, 22.6, 14.2, 14.0. HRMS (MALDI-TOF) *m/z*:
[M+H]<sup>+</sup> calcd for [C<sub>100</sub>H<sub>121</sub>BN<sub>5</sub>O<sub>8</sub>]<sup>+</sup> calculated for 1530.9308, found 1530.9247.



Scheme S3. Synthetic route of compound trans-PDI3NH<sub>2</sub>.

**Synthesis of** *trans*-PDI3NH<sub>2</sub>: A Schlenk flask was charged with **2** (1 g, 1.02 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.66 g, 5.10 mmol), Pd(OAc)<sub>2</sub> (44.90 mg, 0.20 mmol) and DPE-phos (219.73 mg, 0.41 mmol), then added 100 mL degassed anhydrous toluene at 0 °C. In an additional flask, the compound **3** (1.57 g, 2.04 mmol) was also dissolved in 60 mL degassed anhydrous toluene and then dropwise to the Schlenk flask at 0 °C. After stirred at 0 °C for more 30 minutes, the reaction was warm to room temperature slowly and then further stirred at 80 °C for 6 h. After cool down to room temperature, the mixture was filtered through celite. The organic solvent was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated using vacuum rotary evaporator and obtained black solid. The crude materials were purified with column chromatography (eluent: PE:DCM from 3:1 to 1:2), 1.26 g target *trans*-PDI3NH<sub>2</sub> was obtained as black solid yield of 54%.

*trans*-PDI3NH<sub>2</sub>: <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 9.03-8.28 (m, 20H), 5.10 (d, *J* = 36.4 Hz, 6H), 2.19-2.12 (m, 12H), 1.82 (s, 12H), 1.25-1.20 (m, 98H), 0.87-0.78 (m, 36H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 164.7, 164.6, 164.1, 163.7, 163.1, 162.9, 140.4, 139.7, 134.7, 134.0, 133.6, 132.1, 131.3, 130.4, 129.8, 127.5, 126.7, 126.5, 124.9, 124.4, 124.0, 123.5, 123.2, 123.0, 122.5, 122.5, 122.3, 54.9, 54.7, 32.3, 31.7, 31.7, 31.7, 29.2, 29.2, 29.1, 27.0, 26.9, 22.6, 22.6, 22.6, 14.0, 14.0, 14.0. HRMS (MALDI-TOF) *m/z*: [M]<sup>+</sup> calcd for [C<sub>150</sub>H<sub>184</sub>N<sub>8</sub>O<sub>12</sub>]<sup>+</sup> 2290.4067, found 2290.4643.



Scheme S4. Synthetic route of compound trans-PDI3BN.

**Synthesis of** *trans*-**PDI3BN**: In a pressure-resistant reaction tube, the dried compound *trans*-**3PDINH**<sub>2</sub> (300 mg, 0.13 mmol), triethylamine (1.5 mL), 10 mL anhydrous DCB and 2.5 mL boron trichloride in DCM was added under nitrogen atmosphere. The black reaction mixture was turned to red while stirred at 190 °C for 40 min. After cool down to room temperature, the mixture was extracted with DCM and washed with brine. Combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude materials were purified with column chromatography (eluent: PE:DCM from 3:1 to 1:1), 126.9 mg target *trans*-**PDI3BN** was obtained as red solid yield of 42%.

*trans*-PDI3BN: <sup>1</sup>H NMR (500 MHz, Toluene-*d*<sub>8</sub>)  $\delta$  11.11 (d, *J* = 43.7 Hz, 2H), 10.90 (d, *J* = 22.9 Hz, 2H), 10.25 (d, *J* = 33.2 Hz, 2H), 9.94 (d, *J* = 20.9 Hz, 2H), 9.13 (s, 2H), 8.99 (s, 2H), 8.46 (t, *J* = 8.8 Hz, 4H), 5.71-5.61 (m, 6H), 2.85-2.49 (m, 12H), 2.03-1.96 (m, 12H), 1.54-1.06 (m, 94H), 0.97-0.90 (m, 12H), 0.85-0.56 (m, 24H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  165.07, 164.8, 163.9, 163.6, 163.3, 137.3, 136.4, 135.8, 135.6, 135.3, 134.8, 133.9, 132.4, 131.6, 130.9, 130.4, 130.0, 129.7, 129.6, 127.5, 126.8, 125.9, 125.9, 125.7, 124.5, 124.5, 124.0, 123.6, 123.2, 122.7, 122.3, 112.3, 122.0, 55.5, 55.2, 53.5, 32.9, 32.3, 31.9, 31.8, 29.6, 29.4, 29.2, 27.2, 26.9, 26.7, 22.8, 22.7, 22.5, 14.2, 14.0. HRMS (MALDI-TOF) *m/z*: [M]<sup>+</sup> calcd for [C<sub>150</sub>H<sub>178</sub>B<sub>2</sub>N<sub>8</sub>O<sub>12</sub>]<sup>+</sup> 2306.3784, found 2306.3881.



Scheme S5. Synthetic route of compound cis-PDI3NH<sub>2</sub>.

**Synthesis of** *cis*-**PDI3NH**<sub>2</sub>: A Schlenk flask was charged with **2** (500 mg, 0.48 mmol), Cs<sub>2</sub>CO<sub>3</sub> (782.97 mg, 2.40 mmol), Pd(OAc)<sub>2</sub> (22.45 mg, 0.10 mmol) and DPE-phos (107.19 mg, 0.20 mmol), then added 100 mL degassed anhydrous toluene at 0 °C. In an additional flask, the compound **3** (739.27 g, 0.96 mmol) was also dissolved in 60 mL degassed anhydrous toluene and then dropwise to the Schlenk flask at 0 °C. After stirred at 0 °C for more 30 minutes, the reaction was warm to room temperature slowly and then further stirred at 80 °C for 6 h. After cool down to room temperature, the mixture was filtered through celite. The organic solvent was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated using vacuum rotary evaporator and obtained black solid. The crude materials were purified with column chromatography (eluent: PE:DCM from 3:1 to 1:1), 659.86 mg target *cis*-**PDI3NH**<sub>2</sub> was obtained as black solid yield of 60%.

*cis*-PDI3NH<sub>2</sub>: <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 9.00-8.64(m, 16H), 8.40 (m, 4H), 5.20- 5.07 (m, 6H), 2.19 (s, 12H), 1.81 (s, 12H), 1.60-1.19 (m, 98H), 0.78 (m, 36H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 164.6, 164.2, 163.6, 163.1, 163.0, 141.7, 134.6, 134.3, 134.0, 131.9, 131.6, 131.1, 130.4, 130.0, 139.9, 129.0, 127.5, 126.9, 125.6, 124.5, 124.3, 124.0, 123.5, 123.3, 122.8, 122.5, 121.4, 55.3, 55.1, 54.7, 32.4, 32.3, 32.2, 31.8, 31.7, 31.7, 31.6, 31.6, 29.7, 29.2, 29.2, 29.1, 29.0, 27.0, 26.9, 26.8, 22.6, 22.6, 22.6, 22.6, 22.50, 14.1, 14.0, 14.0. HRMS (MALDI-TOF) *m/z*: [M]<sup>+</sup> calcd for [C<sub>150</sub>H<sub>184</sub>N<sub>8</sub>O<sub>12</sub>]<sup>+</sup> 2290.4067, found 2290.3775.

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Scheme S6. Synthetic route of compound cis-PDI3BN.

**Synthesis of** *cis*-**PDI3BN**: In a pressure-resistant reaction tube, the dried compound *cis*-**PDI3NH**<sub>2</sub> (300 mg, 0.13 mmol), triethylamine (1.5 mL), 10 mL anhydrous DCB and 2.5 mL boron trichloride in DCM was added under nitrogen atmosphere. The black reaction mixture was turned to red while stirred at 190 °C for 40 min. After cool down to room temperature, the mixture was extracted with DCM and washed with brine. Combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude materials were purified with column chromatography (eluent: PE:DCM from 3:1 to 1:1), 117.8 mg target *cis*-**PDI3BN** was obtained as red solid yield of 39%.

*cis*-PDI3BN: <sup>1</sup>H NMR (500 MHz, Toluene-*d*<sub>8</sub>) δ 11.24 (d, *J* = 20.7 Hz, 2H), 10.88 (s, 2H), 10.18-9.85 (m, 4H), 9.05 (d, *J* = 65.7 Hz, 4H), 8.47-8.44 (m, 4H), 5.81-5.57 (m, 6H), 2.74-2.48 (m, 12H), 2.07 (m, 12H), 1.71-1.18 (m, 98H), 0.98-0.49 (m, 36H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 165.0, 163.9, 136.9, 136.4, 135.3, 134.8, 133.9, 131.6, 130.4, 130.0, 129.7, 129.4, 125.6, 125.3, 124.5, 123.5, 123.2, 122.8, 122.4, 122.0, 121.6, 121.2, 55.5, 55.2, 33.0, 32.9, 32.6, 32.3, 32.3, 31.9, 31.8, 29.7, 29.6, 29.4, 29.2, 27.2, 27.1, 22.7, 22.5, 14.1, 14.1, 14.1, 14.0. HRMS (MALDI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for [C<sub>150</sub>H<sub>178</sub>B<sub>2</sub>N<sub>8</sub>NaO<sub>12</sub>]<sup>+</sup> 2329.3682, found 2329.3459.

#### 2.2 Preparation of the PTCDI oligomers

The pure PDI oligomers were heated at 400 °C for 2 h to remove those soluble alkyl chains in tube furnace under the protection of nitrogen. Afterwards, the materials after the reaction were cooled to room temperature naturally to obtain targeted **PTCDI** oligomers.



Scheme S7. Synthetic route of PTCDI2BN.



Scheme S8. Synthetic route of *trans*-PTCDI3BN.



Scheme S9. Synthetic route of *cis*-PTCDI3BN.



Scheme S10. Synthetic route of PTCDI2.



3. Normalized UV-vis absorption spectra of of PDI3, trans- and cis-PDI3BN

Figure S1. Normalized UV-vis absorption spectra of of PDI3, trans- and cis-PDI3BN

4. Cyclic Voltammograms (CVs) of PDI2, PDI2BN, trans-PDI3BN and cis-PDI3BN.





Figure S2. CV of PDI2 vs (Fc/Fc<sup>+</sup>), PDI2BN vs (Fc/Fc<sup>+</sup>), *trans*-PDI3BN vs (Fc/Fc<sup>+</sup>) and *cis*-PDI3BN vs (Fc/Fc<sup>+</sup>) (a) at multiple scanning and (b) at different scan rates in dichloromethane solution.

Table S1. Photoluminescence quantum yields of PDI2, PDI2BN, trans-PDI3BN and cis-PDI3BN in toluene.

FLQY	PDI2	PDI2BN	Trans-PDI3BN	cis-PDI3BN	
Tol	74%	67.8%	58.2%	43.9%	

5. <sup>1</sup>H, <sup>13</sup>C NMR and HRMS Spectra



Figure S3. <sup>1</sup>H NMR spectra of PDI2NH. (500 MHz)



Figure S4. <sup>13</sup>C NMR spectra of PDI2NH. (126 MHz)



Figure S5.<sup>1</sup>H NMR spectra of PDI2BN. (500 MHz)



Figure S6. <sup>13</sup>C NMR spectra of PDI2BN. (126 MHz)



Figure S7. <sup>1</sup>H NMR spectra of trans-PDI3NH<sub>2</sub>. (500 MHz)



Figure S8. <sup>13</sup>C NMR spectra of trans-PDI3NH<sub>2</sub>. (126 MHz)



Figure S9. <sup>1</sup>H NMR spectra of trans-PDI3BN. (500 MHz)



Figure S10. <sup>13</sup>C NMR spectra of trans-PDI3BN. (126 MHz)



Figure S11. <sup>1</sup>H NMR spectra of *cis*-PDI3NH<sub>2</sub>. (500 MHz)



Figure S12. <sup>13</sup>C NMR spectra of *cis*-PDI3NH<sub>2</sub>. (126 MHz)



Figure S13. <sup>1</sup>H NMR spectra of *cis*-PDI3BN. (500 MHz)



Figure S14. <sup>13</sup>C NMR spectra of *cis*-PDI3BN. (126 MHz)



Figure S15. Mass Spectrum of PDI2NH.



Figure S16. Mass Spectrum of PDI2BN.



Figure S17. Mass Spectrum of trans-PDI3NH<sub>2</sub>.



Figure S18. Mass Spectrum of trans-PDI3BN.



Figure S19. Mass Spectrum of cis-PDI3NH<sub>2</sub>.



Figure S20. Mass Spectrum of *cis*-PDI3BN.

# 6. Electrochemical Data



**Figure S21**. Thermogravimetric analysis (TGA) plots of PDI2, PDI2BN, *trans*-PDI3BN and *cis*-PDI3BN in N<sub>2</sub> atmosphere at a scan rate of 10  $^{\circ}$ C min<sup>-1</sup>.



**Figure S22**. The contrastive FTIR spectrum of PDI oligomers before and after vacuum thermolysis.

The resulting organics were then identified through fourier transform infrared (FTIR) spectroscopy, in which, those vibrational modes of alkyl chains (between 2856 and 2927 cm<sup>-1</sup>) disappear, accompanied by new signals indexed to N–H stretching vibration (range from 3034 to 3165 cm<sup>-1</sup>) emerging.



Figure S23. The d(Q) / d(V) image of PTCDI2, PTCDI2BN, trans-PTCDI3BN and cis-PTCDI3BN.



Figure S24. GITT curves and the calculated average overpotential of oligomers.



Figure S25. Nyquist plots and its simulation lines during the initial three cycles of oligomers.



Figure S26. The CV curves at different scan rates of PTCDI derivates.



Figure S27. The log(*i*) vs log(v) plots for cathodic and anodic peaks of PTCDI oligomers.

<b>Rct (</b> Ω <b>)</b>	1st	2nd	3rd
PTCDI2	27.7	142.0	160.0
PTCDI2BN	21.5	26.4	34.9
trans-PTCDI3BN	8.9	15.4	21.3
cis-PTCDI3BN	17.23	20.74	23.65

Table S2. Charge transfer resistance of PTCDI2, PTCDI2BN, trans-PTCDI3BN and cis-PTCDI3BNduring the initial three cycles.