Electronic Supplementary Information

Structure-modulated crystalline covalent organic frameworks for

high-rate Li-ion batteries

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Figure S1. The TGA curves of Tp-DANT-COF (a) and Tb-DANT-COF (b).



Figure S2 Nitrogen sorption isotherm curves of (a) Tp-DANT-COF and (b) Tb-DANT-COF, the pore size distribution of (c) Tp-DANT-COF and (d) Tb-DANT-COF.



Figure S3 The redox reaction of naphthalene diimide unit.



Figure S4 Charge (black)/Discharge (red) capability and Coulombic efficiency (blue) of Tp and DANTB electrodes upon continuous cycling at 200 mA g⁻¹.



Figure S5 a) Discharge-charge curves of Tp-DANT-COF electrode at the rate of 1.5 C; Cycling performance of Tp-DANT-COF electrode at 3.7 C (b) and 7.5 C (c) (discharge-red, charge-black and efficiency-blue).



Figure S6 IR spectra of fresh Tp-DANT-COF electrode before cycling (red) and Tp-DANT-COF electrode after 600 cycles (blue). The Tp-DANT-COF electrode before cycling was immersed in the electrolyte for 24 h.



Figure S7 IR spectra of Tp-DANT-COF and Tp-DANT-COF electrodes at different current densities after cycles. The Tp-DANT-COF electrode was washed with NMP to remove traces of electrolyte and binder.



Figure S8 Cycling performance of Tb-DANT-COF electrode at 0.34C (a) and 3.4C (b) (discharge-red, charge-black and efficiency-blue).



Figure S9 Discharge-charge curves of Tp-DANT-COF (black) and Tb-DANT-COF (red) electrode at the rate of 200 mA g^{-1} .

	Active material/Conductive additive/binder	Conductive additive	Binder	Electrolyte	Theoretical capacity (mAhg ⁻¹)	Speed	Initial or Max capacity (mAhg ⁻¹)	Number of cycles	Last capacity (mAhg-1	Potential range (V)	ref
	60:30:10	Printex XE2	PTFE	1M LiN(CF ₃ SO ₂) ₂ in DOL/DME (2:1 w/w)	203	0.2C(81mAg ⁻¹)	202	100	183	1.5-3.5	\$1
	60:30:10	Printex XE2	PTFE	1M LiN(CF ₃ SO ₂) ₂ in DOL/DME (2:1 w/w)	184	0.2C(73mAg ⁻¹)	181	100	173	1.5-3.5	S 1
	60/30/10	Super P	PTFE	1M LiN(CF ₃ SO ₂) ₂ in DOL/DME (2:1 v/v)	184	0.1C(367mAg ⁻ 1)	156	-	-	1.5-3.5	S2
	54/6/30/10	Graphene/Supe r P	PTFE	1M LiN(CF ₃ SO ₂) ₂ in DOL/DME (2:1 v/v)	184	0.1C(367mAg ⁻ 1)	172	-	-	1.5-3.5	S2
	49/11/30/10	Graphene/Supe r P	PTFE	1M LiN(CF ₃ SO ₂) ₂ in DOL/DME (2:1 v/v)	184	0.1C(367mAg ⁻ 1)	205	-	-	1.5-3.5	S2
	60:30:10	Printex XE2	PTFE	1M LiN(CF ₃ SO ₂) ₂ in DOL/DME (2:1 w/w)	158	0.2C(63mAg ⁻¹)	163	100	156	1.5-3.5	S 1
	80:15:5	acetylene black	PTFE	1 M LiPF ₆ in EC/EMC/DMC(1:1:1 V:V:V)	115	0.22C(25mAg ⁻ 1)	103.4	30	68.5	1.5-4.2	\$3
{0}}8{{0}~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	7:2:2	Super P	PVDF	1 M LiPF ₆ in EC/DMC(1:1 V:V)	82.4	2.4C(200mAg ⁻ 1)	42	30	21	1.5-3.5	S4
	7:2:2	Super P/CNT	PVDF	1 M LiPF ₆ in EC/DMC(1:1 V:V)	82.4	2.4C(200mAg ⁻ 1)	70	700	70	1.5-3.5	S4
	6:2:2	Super P	PVDF	1 M LiPF ₆ in DMC/EC/EMC(1:1:1 V:V:V)	134	3.7C(500mAg ⁻ 1)	94	200	89.4	1.5-4.0	This wor k
	6:2:2	Super P	PVDF	1 M LiPF ₆ in DMC/EC/EMC(1:1:1 V:V:V)	134	7.5C(1000mAg ¹)	84.7	600	71.7	1.5-4.0	This wor k
	6:2:2	Super P	PVDF	1 M LiPF ₆ in DMC/EC/EMC(1:1:1 V:V:V))	145.7	1.4C(200mAg ⁻ 1)	123.7	100	87.9	1.5-4.0	This wor k
	6:2:2	Super P	PVDF	1 M LiPF ₆ in DMC/EC/EMC(1:1:1 V:V:V)	145.7	3.4C(500mAg ⁻ 1)	107.9	300	80.1	1.5-4.0	This wor k

Table S1 Summary of the representative polymer performance of naphthalimide organic cathodes in Li-Ion Batteries.

-: not determined, PVDF: poly(vinylidenedifluoride), PTFE: poly(tetrafl uoroethylene), DOL: 1,3-dioxolane, DME: 1,2-dimethoxyethane, EC: ethylene carbonate, EMC: ethylmethyl carbonate, DMC: dimethyl carbonate.

Synthesis

Synthesis of 1,3,5-Triformylphloroglucinol (Tp):

Tp was synthesized according to previously literature procedure^{S5} and characterization matched that in the literature. ¹H NMR (300 MHz, CDCl₃): δ, [ppm]: 10.14 (s, 3H), 14.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ, [ppm]: 191.36 (*C*HO), 173.16 (Ar*C*), 103.21 (Ar*C*).



Figure S11. The ¹³C NMR spectrum of Tp

Synthesis of 1,3,5-Triformylbenzene(Tb):

Tb was synthesized according to previously literature procedure^{S6} and characterization matched that in the literature. ¹H NMR (300 MHz, CDCl₃): δ,[ppm]: 8.63 (s, 3H), 10.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ, [ppm]: 189.12 (*C*HO), 137.84 (Ar*C*), 134.58 (Ar*C*).



Figure S13. The ¹³C NMR spectrum of Tb

Synthesis of 2,7-diaminobenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (DANT):

DANT was synthesized according to previously literature procedure^{S7} and characterization matched that in the literature. ¹H NMR (300 MHz, DMSO- d_6): δ , [ppm]: 8.66 (s, 4H).



Figure S14. The ¹H NMR spectrum of DANT

Synthesis of reference compound 1:

1,3,5-Triformylphloroglucinol(Tp) (0.105 g, 0.5 mmol) and 2-amino-1H-benzo[de]isoquinoline-1,3(2H)-dione (0.572 g, 2.7 mmol) were added in 70 mL ethanol. This mixture was reacted under refluxing condition for 24 h. After being cooling to ambient temperature, the precipitate was collected by filtration and washed with ethanol for 3 times, dried under vacuum to get pale yellow solid. (0.33 g, 82.5 %). **FT-IR**: 1680 (s), 1583 (s), 1462 (m), 1301 (s), 1240 (s), 1189 (m),769 (m) cm⁻¹.

Synthesis of monomer compound (DANTB):

2,7-diaminobenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (DANT) (0.2 g, 0.67 mmol) and benzaldehyde (0.172 g, 1.62 mmol) were added in 50 mL ethanol. This mixture was reacted under refluxing condition for 24 h. After being cooling to ambient temperature, the precipitate was collected by filtration and washed with ethanol for 3 times, dried under vacuum to get light orange solid. (0.29 g, 93%).

Synthesis of reference compound 2:

1,3,5-Triformylbenzene (Tb) (0.1 g, 0.617 mmol) and 2-amino-1H-benzo[de]isoquinoline-1,3(2H)dione (0.699 g, 3.3 mmol) were added in 70 mL ethanol. This mixture was reacted under refluxing condition for 24 h. After being cooling to ambient temperature, the precipitate was collected by filtration and washed with ethanol for 3 times, dried under vacuum to get pale yellow solid. (0.3 g, 65.3 %).

Synthesis of Tp-DANT-COF

Tp-DANT-COF was synthesized under solvothermal condition. Tp (21 mg, 0.1 mmol) and DANT (45 mg, 0.15 mmol) were added to the mixture of 3 mL dimethylacetamide and 3mL o-dichlorobenzene. This mixture was sonicated for 10 min in order to get a homogenous dispersion and sealed under argon in a 15 mL glass tube. The tube was kept at 120°C without disturbance for 5 day to get a brown solid at the bottom of the tube. After being cooling to room temperature, the solid was collected by filtration and washed with dimethylacetamide and acetone for 10 times respectively, then dried under dynamic vacuum at 140°C for 24 h to get a brown solid in ~70% isolated yield. **FT-IR**: 1680 (s), 1583 (s), 1443 (m), 1306 (s), 1256 (s), 1196 (m),762 (m) cm⁻¹.

Synthesis of Tb-DANT-COF

Tb-DANT-COF was synthesized by adding Tb (16 mg, 0.1 mmol) and DANT (45 mg, 0.15 mmol) into the mixture of 3 mL mesitylene and 3 mL 1,4-dioxane. This mixture was sonicated for 10 min in order to get a homogenous dispersion and sealed under argon in a 15 mL glass tube. The tube was kept at 120°C without disturbance for 5 day to get a brown solid at the bottom of the tube. After being cooling to room temperature, the solid was collected by filtration and washed with dimethylacetamide and acetone for 10 times respectively, then dried under dynamic vacuum at 140°C for 2 4h to get a brown solid in ~81% isolated yield. **FT-IR**: 1710 (s), 1670 (s), 1577 (s), 1437 (m), 1304 (s), 1240 (s), 1194 (m) cm⁻¹.

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