

Function-Oriented Design of Conjugated Carbonyl Compound Electrodes for High Energy Lithium Batteries

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Supplementary Information

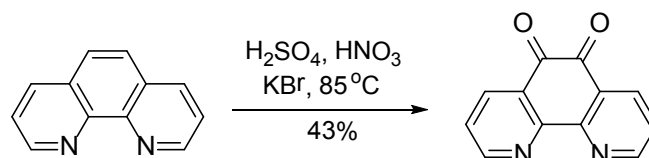
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Synthesis

Phenanthraquinone (PQ)

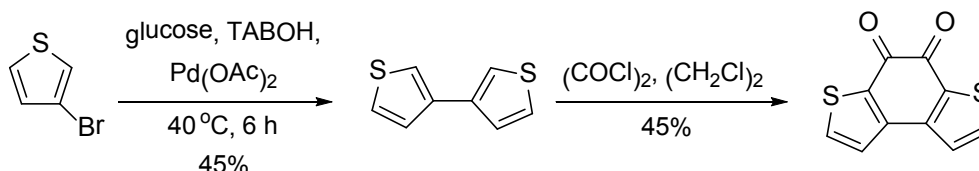
This compound was purchased from Aladdin and used as received. IR (KBr) ν_{\max} 1726, 1651, 1594, 1451, 1293, 1283, 1230, 922, 761 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): 8.18 (2H, m), 8.02 (2H, m), 7.72 (2H, m), 7.47 (2H, dm).

1,10-Phenanthroline-5,6-dione (PhenQ)¹



1,10-phenanthroline hydrate (1 g, 5.04 mmol), HNO_3 (4.6 ml), H_2SO_4 (9.6 ml), and KBr (0.906 g, 7.61 mmol) were mixed at $-5\text{ }^\circ\text{C}$ and then heated at $85\text{ }^\circ\text{C}$ for 2 h. Then the mixture was poured into 400 ml of ice water and neutralized with NaHCO_3 . The mixture was extracted with dichloromethane for three times. Recrystallization from EtOH gave PhenQ (0.459 g, 43%) as yellow needles. IR (KBr) ν_{\max} : 3064, 1659, 1577, 1560, 1459, 1416, 1317, 1295, 1204, 1117, 1014, 927, 816, 739 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): 9.12 (dd, 2H). 8.51 (dd, 2H). 7.59 (q, 2H).

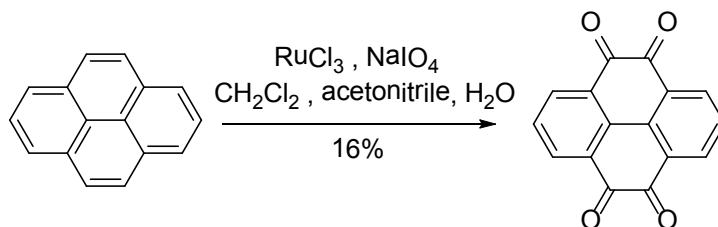
Benzo[1,2-*b*:4,3-*b'*]dithiophene-4,5-quinone (BDTQ)²



To the stirred mixture of 3-Bromothiophene (0.187 ml, 2 mmol), glucose hydrate (0.198 g, 1 mmol), and tetrabutylammonium hydroxide (6.13 ml, 6 mmol, 25%) was added palladium diacetate (0.0135 g, 0.06 mmol) at r.t. The vessel was then sealed and heated at $40\text{ }^\circ\text{C}$ for 6 h. The mixture was then extracted with petroleum ether, and 3,3'-bithiophene (0.074 g, 45%) was obtained upon evaporation.

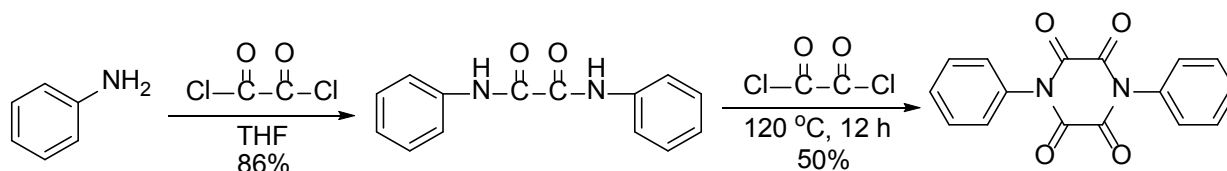
Oxalyl chloride (0.254 ml, 3 mmol), dichloroethane (1.6 ml, 0.18 M), and 3,3'-bithiophene (50 mg, 0.3 mmol) were mixed under Ar and heated at $150\text{ }^\circ\text{C}$ in a sealed vessel for 12 h. After cooling to r.t., the mixture was filtered, washed with PE and EtOH, and dried in air at $80\text{ }^\circ\text{C}$ to afford BDTQ (0.03 g, 45%) as a red powder. IR (KBr) ν_{\max} 3119, 3090, 3078, 1651, 1620, 1416, 1394, 1300, 1256, 1107, 1083, 857, 770, 739, 522 cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 8.24 (d, 2H). 7.70 (d, 2H).

Pyrene-4,5,9,10-tetraone (PTO)³



To the mixture of pyrene (0.813 g, 4 mmol) in dichloromethane/acetonitrile/ H_2O (1:1:1.2, 32.4 ml) was added NaIO_4 (7.01 g, 32.8 mmol). RuCl_3 (0.1 g, 0.482 mmol) was then added in small portions. After stirring at 40 °C for 13 h, the organic solvents were evaporated. The residue was filtered, washed with H_2O , dried, and then purified by column chromatography (4% ethyl acetate in dichloromethane) and treated with boiling $\text{HOAc}/\text{CHCl}_3$ (1:1). Upon cooling, PTO (0.172 g, 16%) was obtained as orange crystals. IR (KBr) ν_{max} 3088, 3068, 1704, 1678, 1690, 1560, 1452, 1423, 1336, 1276, 1283, 1177, 1103, 1057, 999, 963, 910, 809, 710, 479, 417 cm^{-1} ; $^1\text{H NMR}$ (300 MHz, $\text{DMSO}-d_6$): 8.32 (4H), 7.74 (2H).

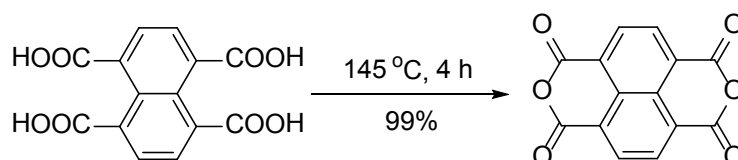
N,N'-Diphenyl-2,3,5,6-tetraketopiperazine (PHP)⁴



To the solution of oxalyl chloride (1.075 ml, 12.7 mmol) in THF (20 ml) was slowly added aniline (2.4 g, 25.8 mmol). After stirring at 80 °C for 2 h, the mixture was filtered and oxanilide (2.6 g, 86%) was obtained as a white solid.

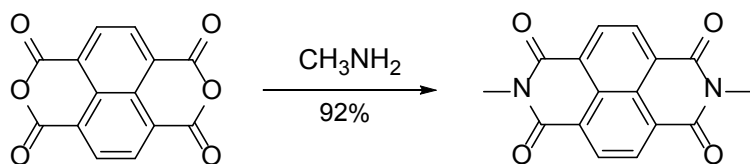
Oxanilide (0.516 g, 2.15 mmol) was heated with oxalyl chloride (2 ml, 23.6 mmol) at 120 °C for 12 h. The mixture was then cooled and washed with 1,2-dichloroethane. The crude product was recrystallized from acetonitrile-toluene (1:1) to afford PHP (0.32 g, 50%) as a white powder. IR (KBr) ν_{max} 3071, 1713, 1699, 1680, 1314, 1287 cm^{-1} ; $^1\text{HNMR}$ (300 MHz, $\text{DMSO}-d_6$): 7.62–7.52 (m, 6H), 7.31 (d, 4H).

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA)



1,4,5,8-Naphthalenetetracarboxylic acid (1 g, 3.29 mmol) was heated in air at 145 °C for 4 h, then cooled to room temperature in a desiccator to afford 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.882 g, 99%) as a yellow powder. IR (KBr) ν_{max} 3122, 3090, 3042, 1779, 1769, 1579, 1517, 1437, 1298, 1235, 1162, 1119, 1037, 756, 698, 544 cm^{-1} ; $^1\text{HNMR}$ (300 MHz, $\text{DMSO}-d_6$): 8.72 (s, 4H).

***N, N'*-Dimethyl-1,4,5,8-naphthalenetetracarboxylic diimide (NTCDM)⁵**



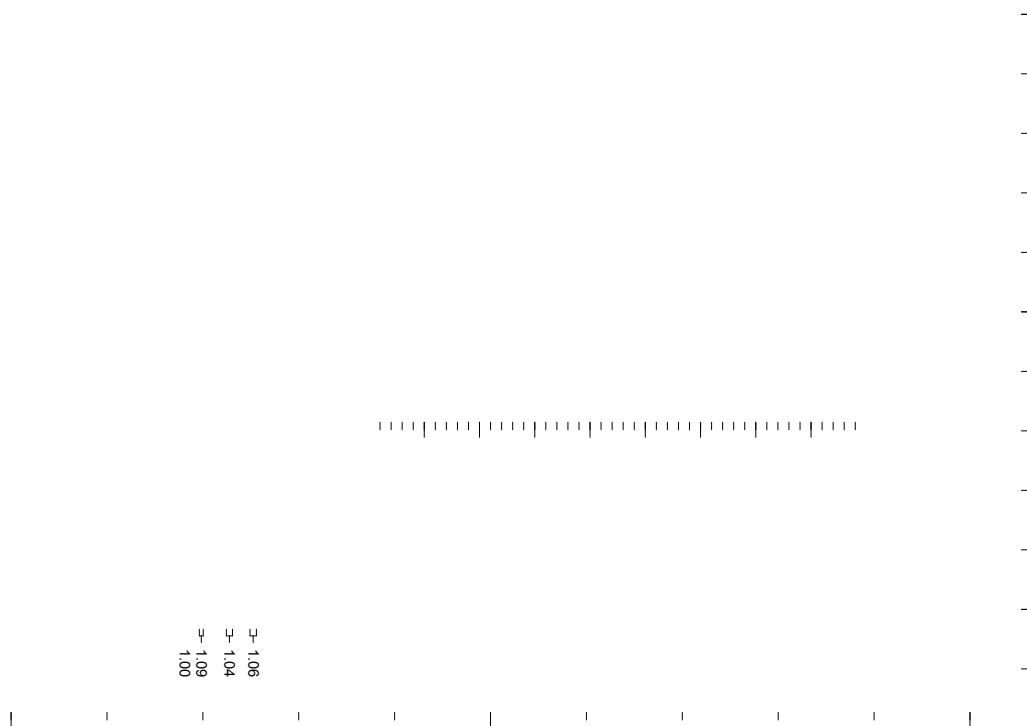
To the stirred CH_3NH_2 (75 ml, aq, 40%) was added 1,4,5,8-naphthalene-tetracarboxylic dianhydride (2 g, 7.46 mmol). After stirring at 50 °C for 2 h, the mixture was filtered, washed with H_2O , and dried in vacuo at 60 °C for 4 h to afford NTCDM (0.468 g, 92%) as a pink solid. IR (KBr) ν_{max} 1711, 1666, 1579, 1454, 1408, 1375, 1346, 1286, 1240, 1158, 1047, 768 cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 8.66 (s, 4H), 3.42 (s, 6H).

Anthraquinone (AQ)

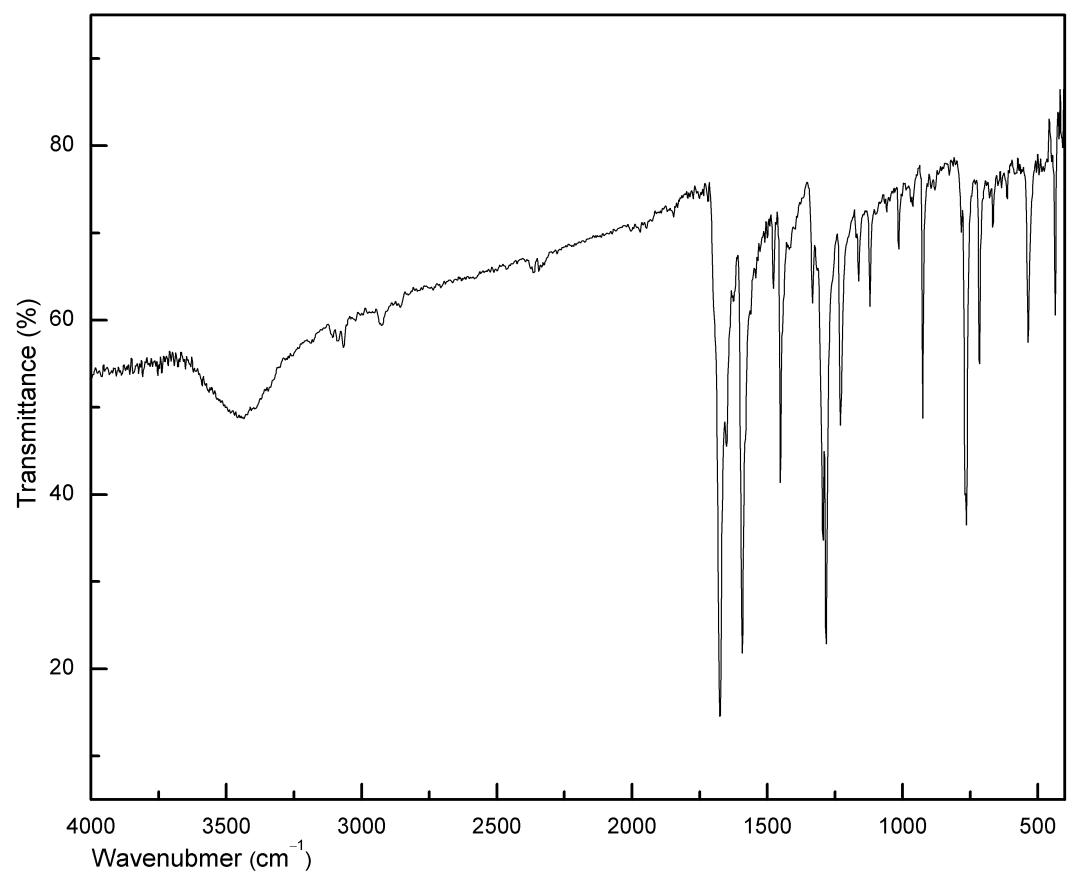
This compound was purchased from Shanghai No. 4 Reagent and used as received. IR (KBr) ν_{max} 1678, 1592, 1581, 1286, 1171, 937, 810, 695 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): 8.35–8.29 (m, 4H), 7.84–7.78 (m, 4H).

Spectra

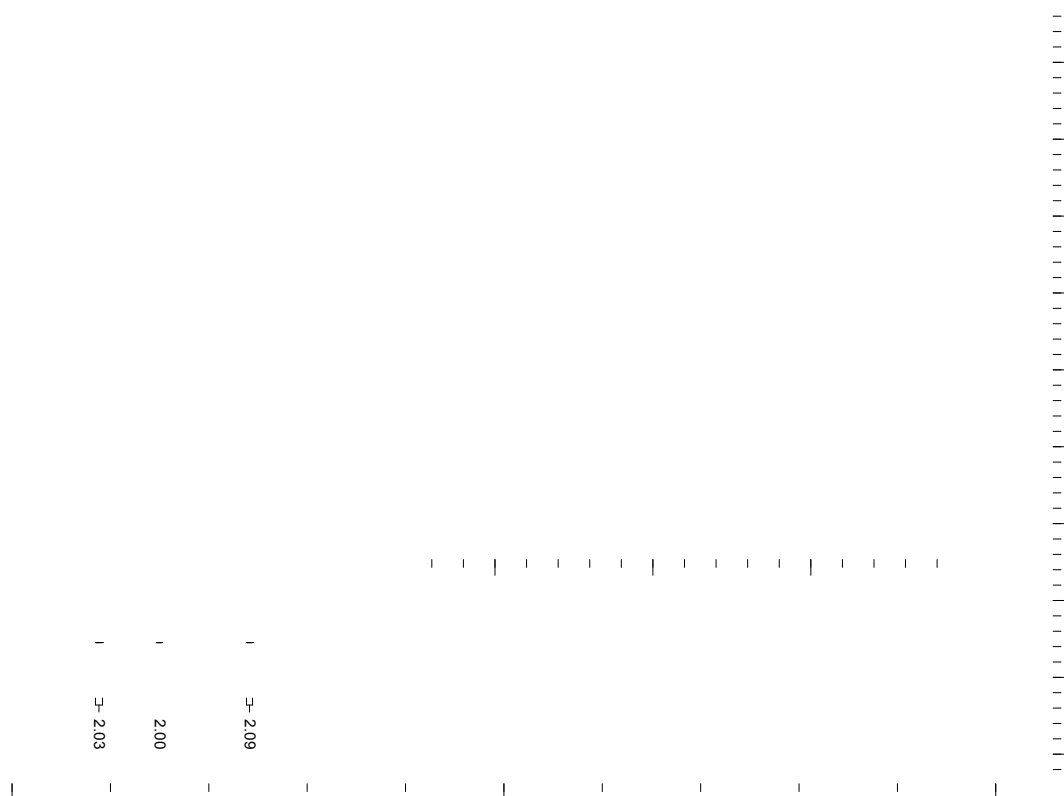
^1H NMR spectrum of PQ



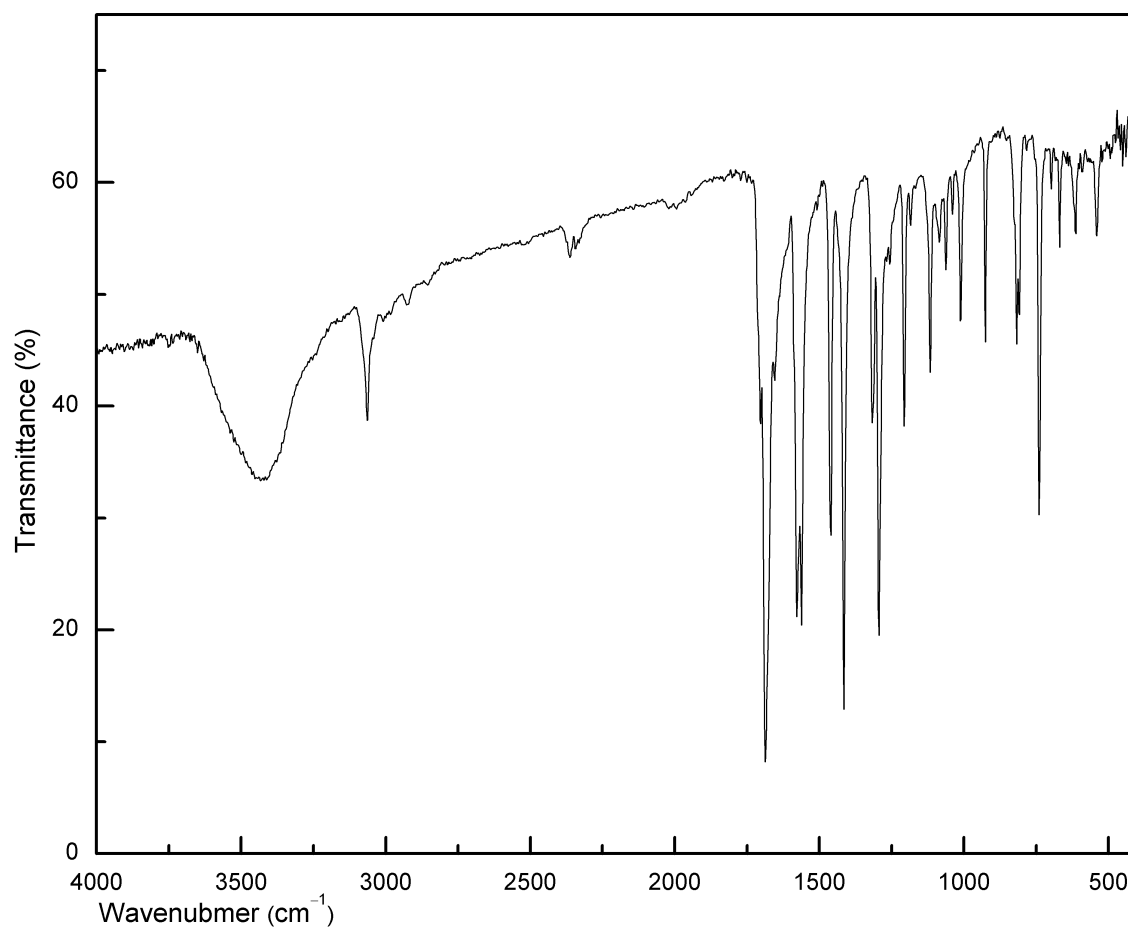
IR spectrum of PQ



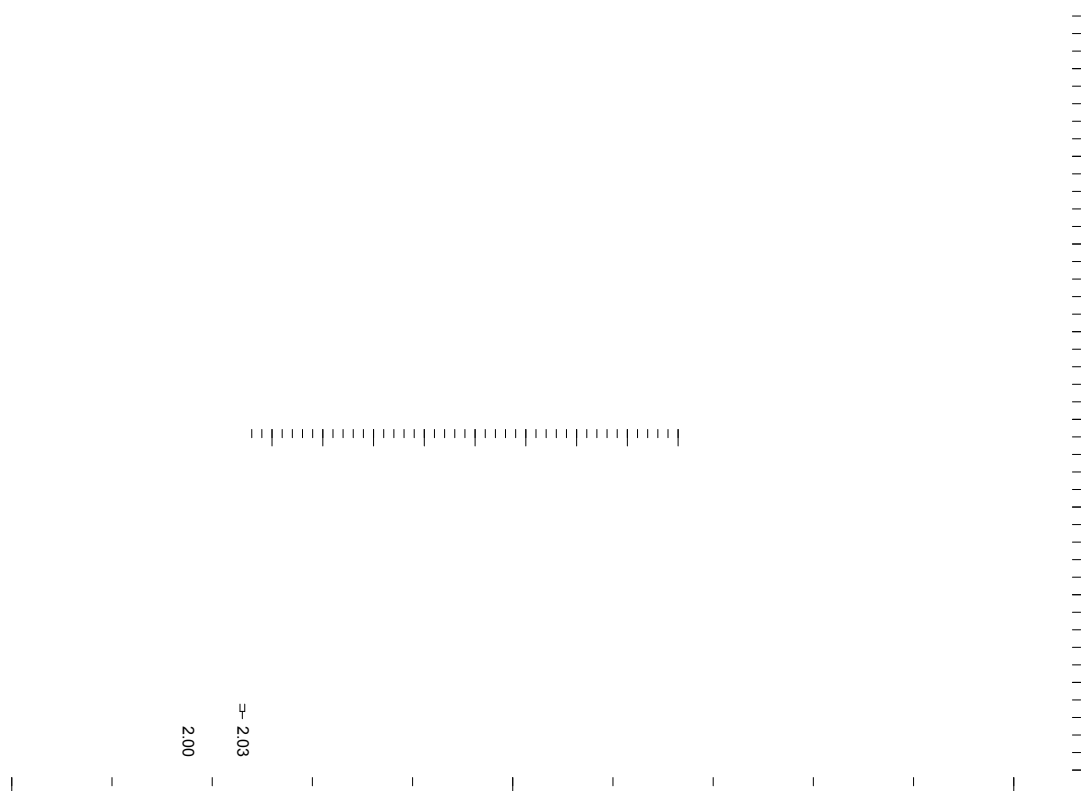
^1H NMR spectrum of PhenQ



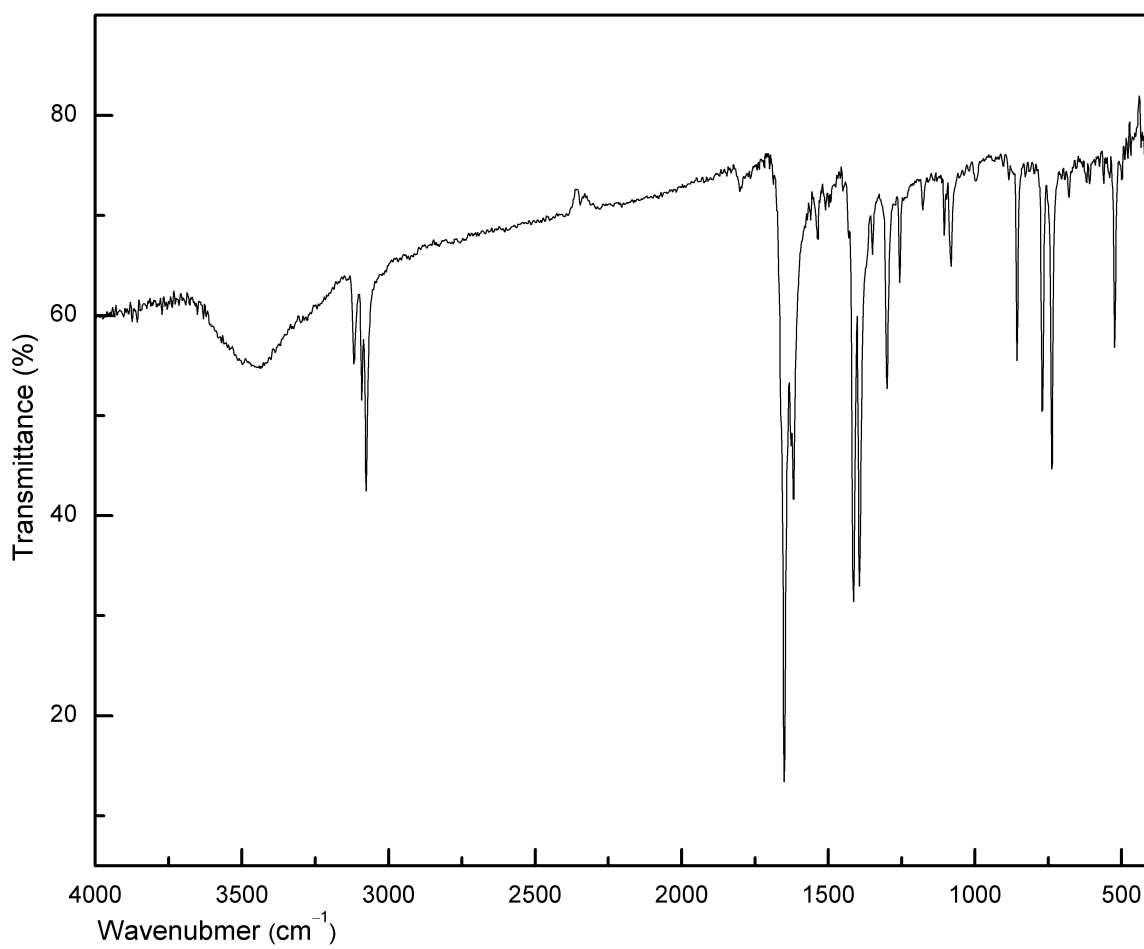
IR spectrum of PhenQ



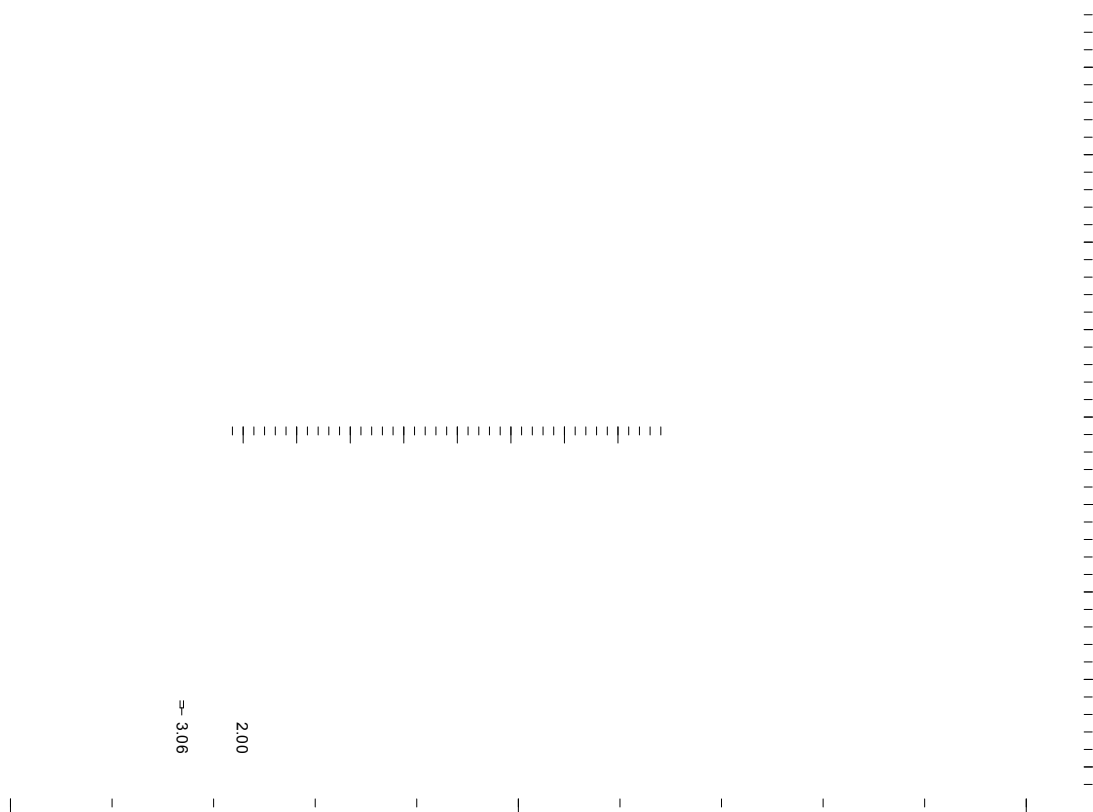
^1H NMR spectrum of BDTQ



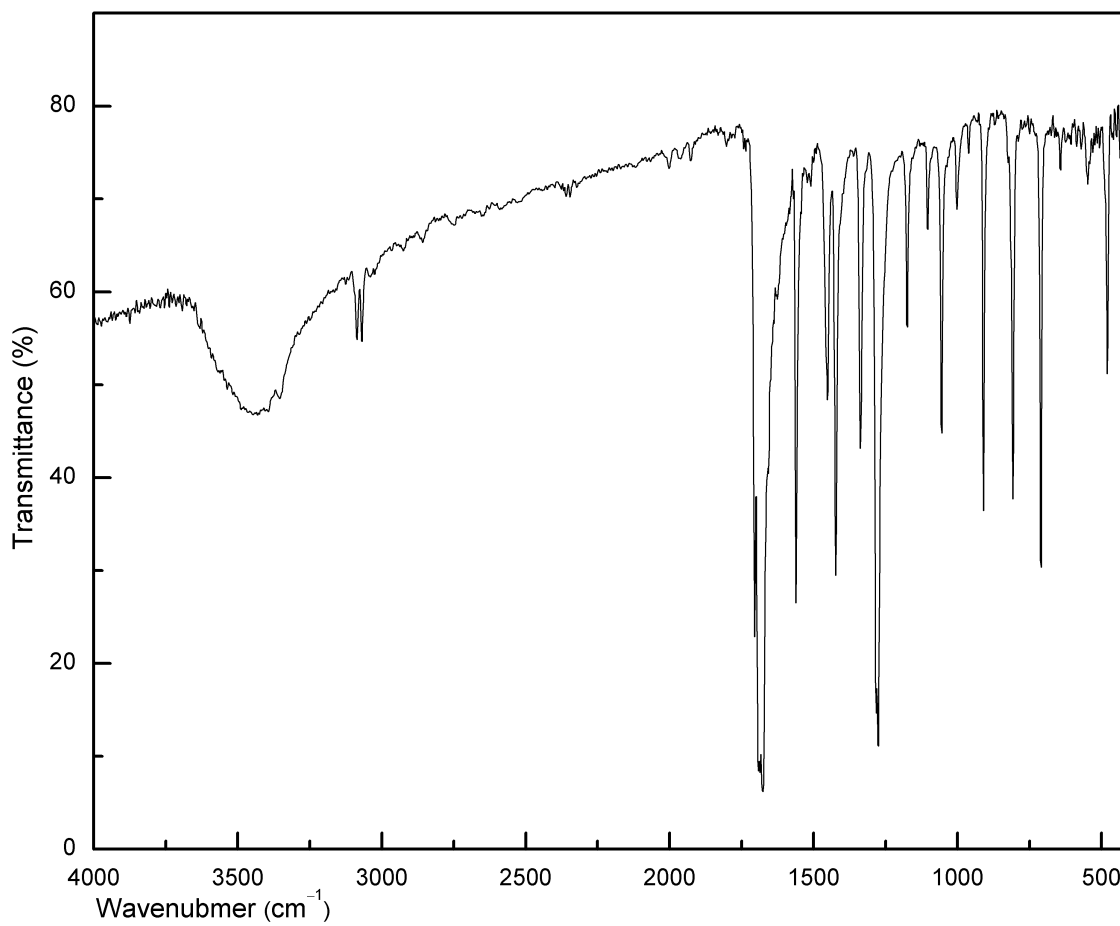
IR spectrum of BDTQ



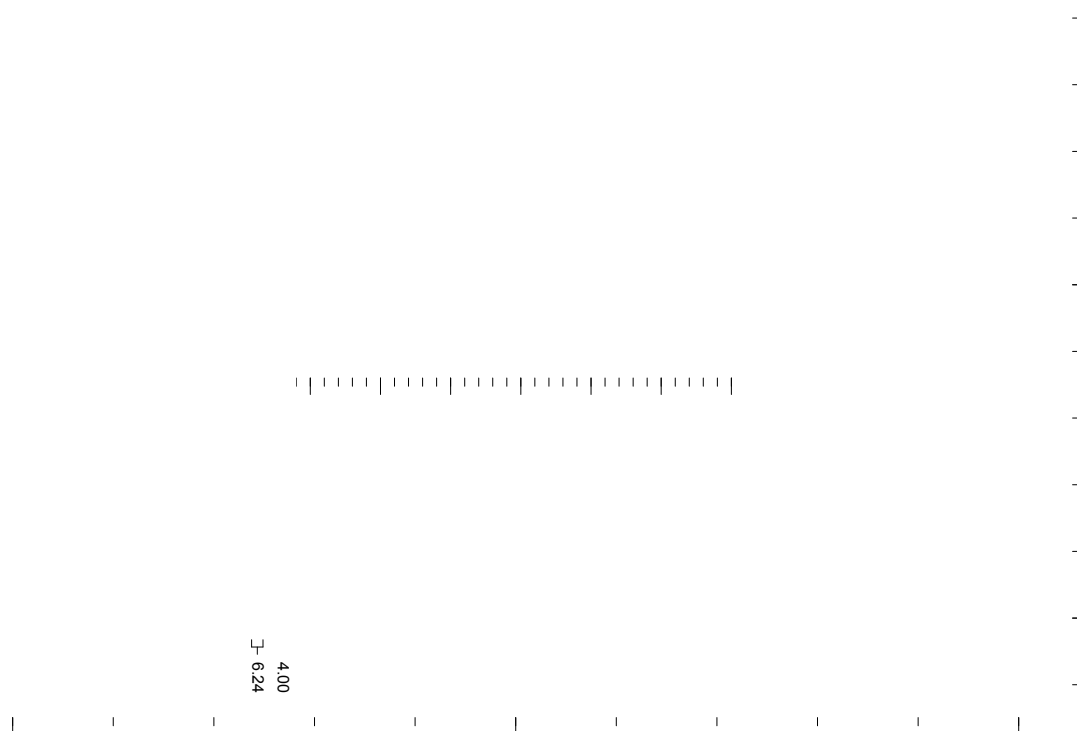
^1H NMR spectrum of PTO



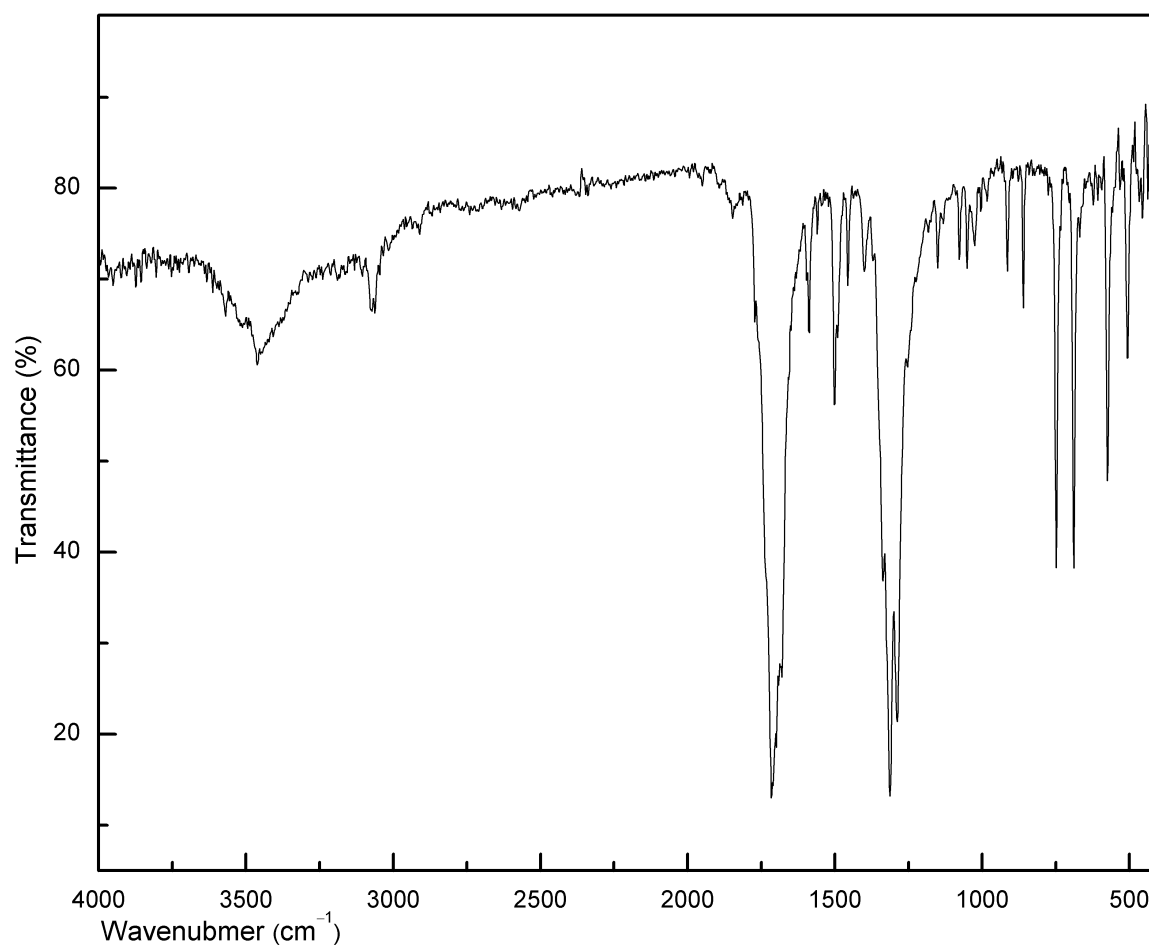
IR spectrum of PTO



^1H NMR spectrum of PHP



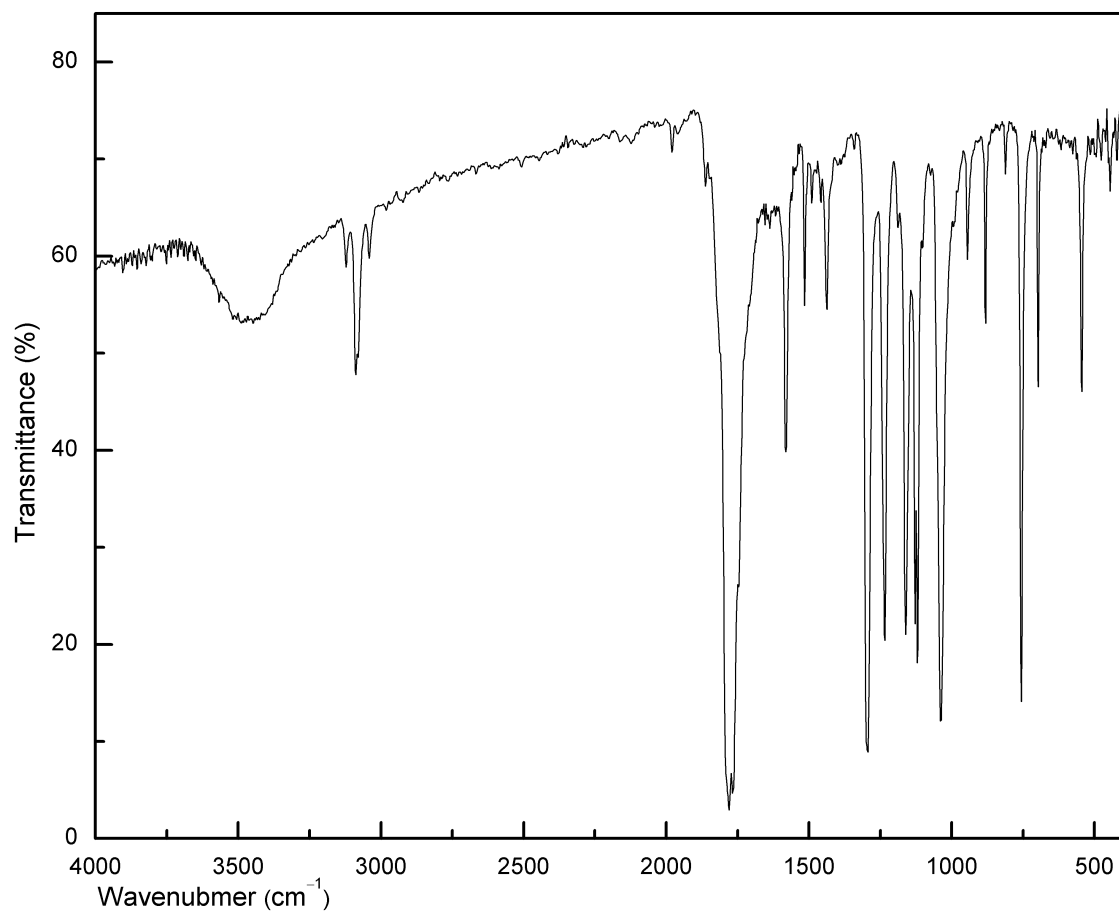
IR spectrum of PHP



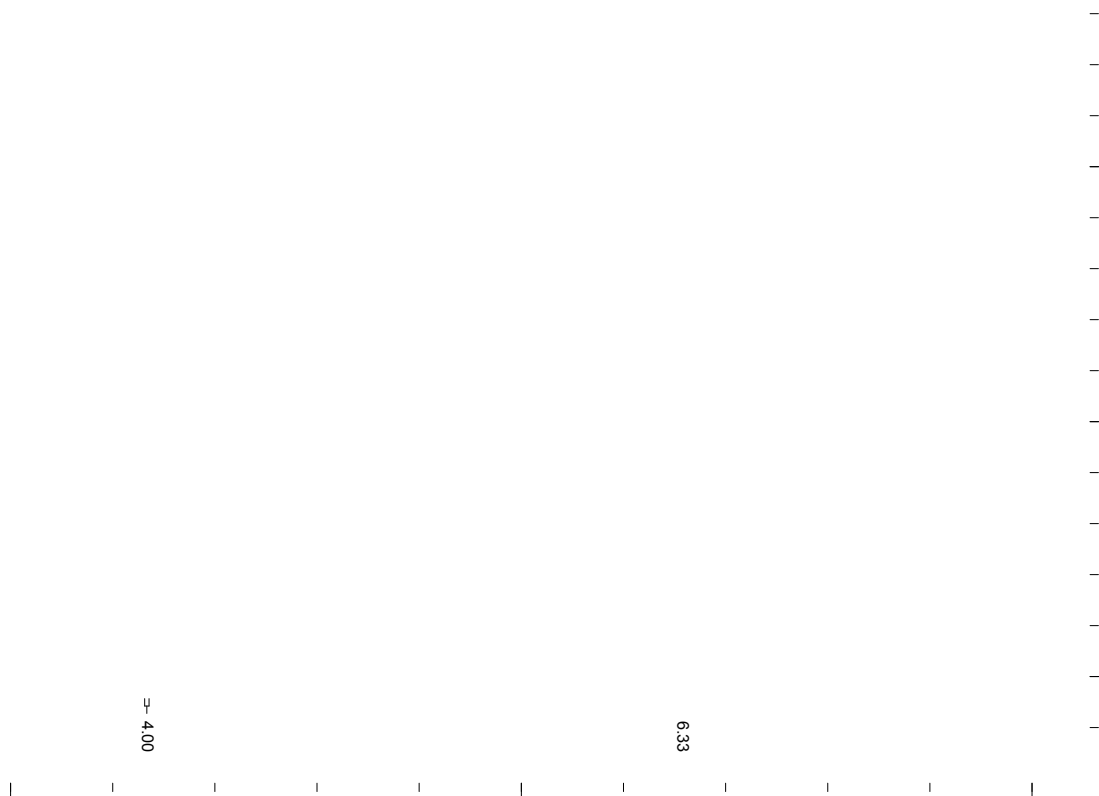
^1H NMR spectrum of NTCDA



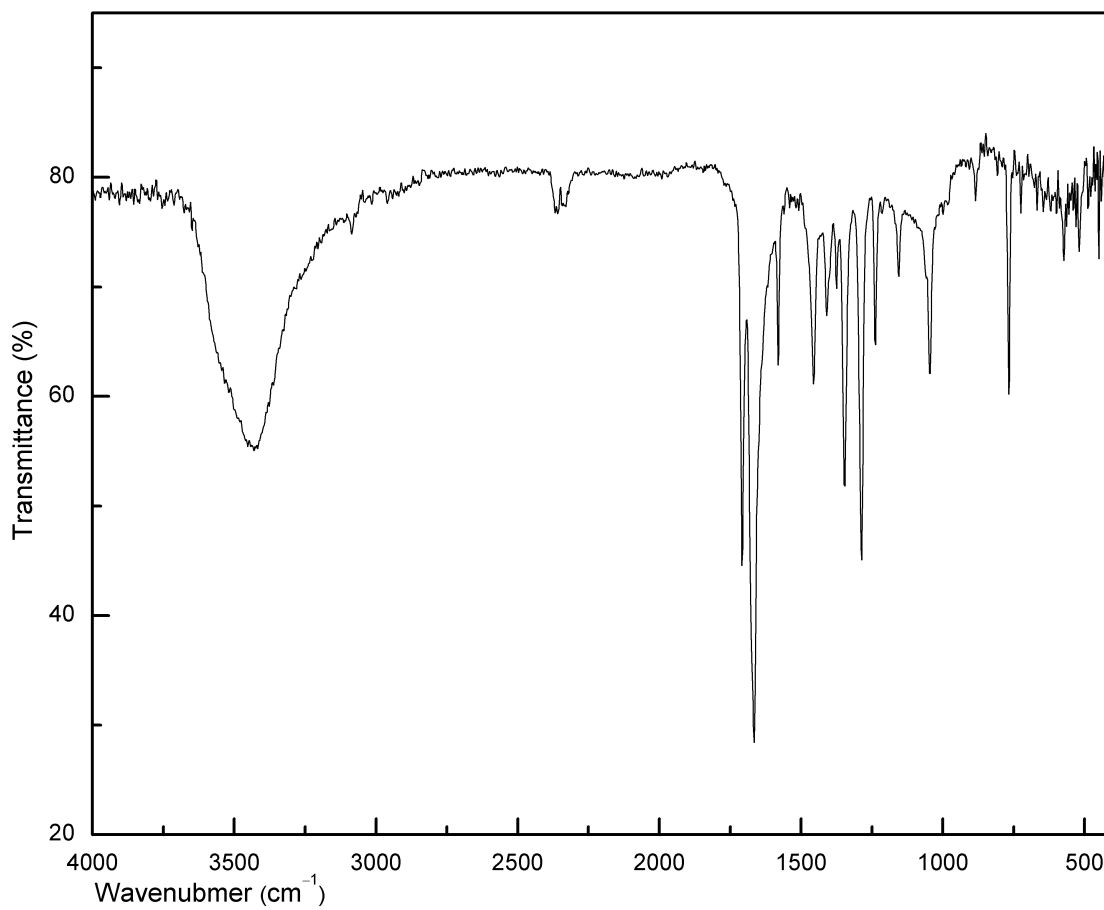
IR spectrum of NTCDA



^1H NMR spectrum of NTCDM



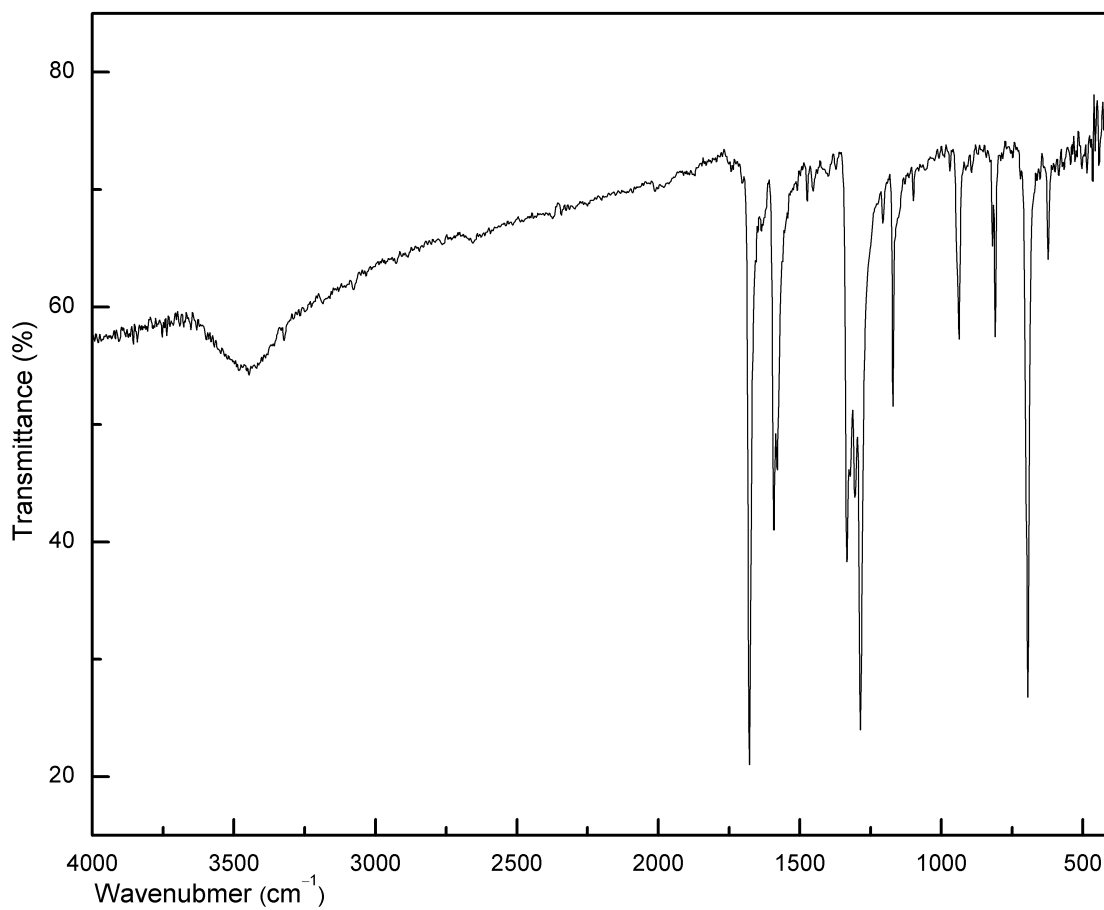
IR spectrum of NTCDM



^1H NMR spectrum of AQ



IR spectrum of AQ



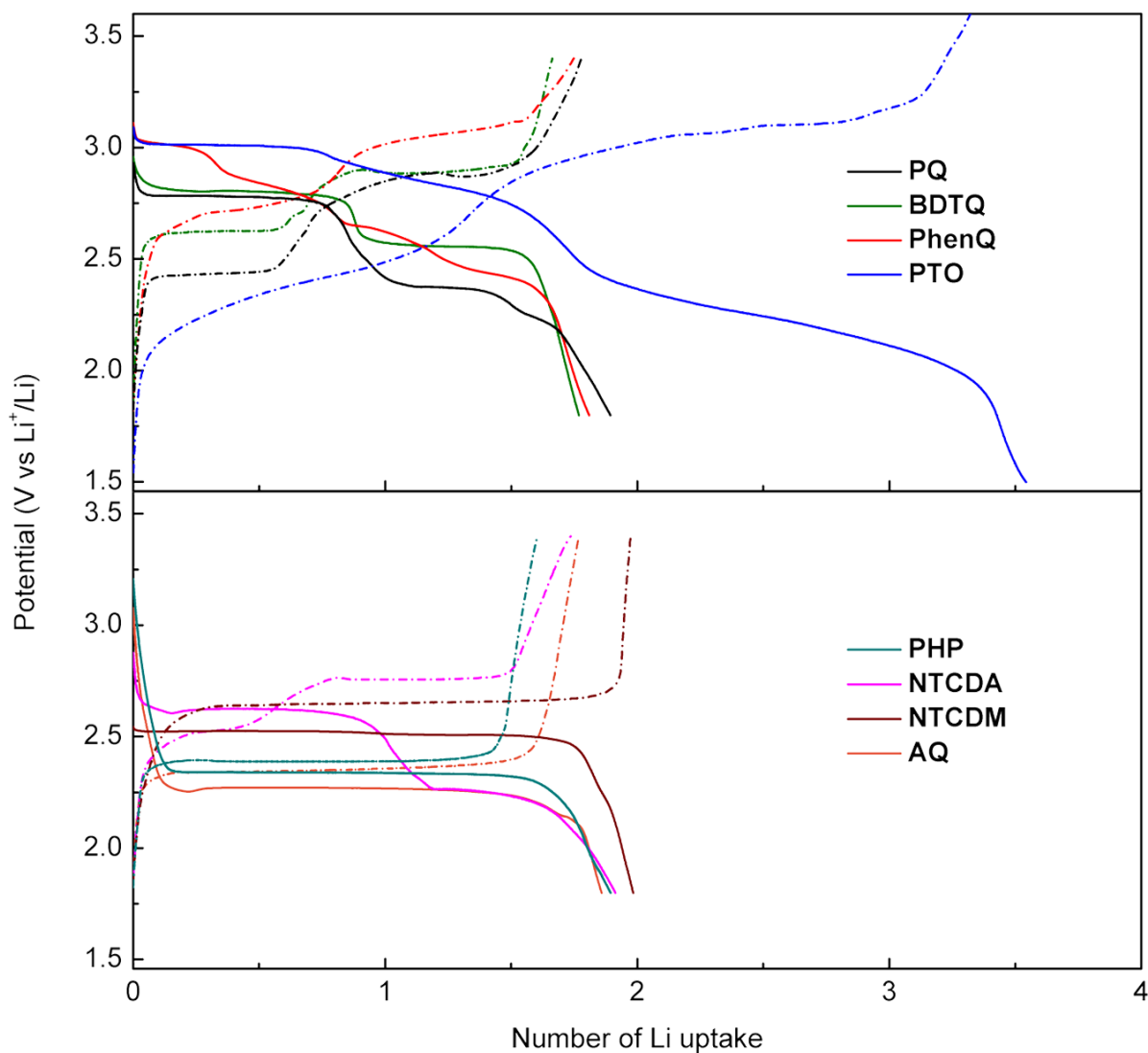


Fig. S1 Discharge–charge curves of the cathode molecules. Cells using the four molecules reported herein and the four control molecules as cathodes are discharged–charged galvanostatically at 0.1C rate for the first cycle. All compounds bearing two carbonyls (PQ, BDTQ, PhenQ, and AQ) undergo two-lithium uptake. Among those bearing four carbonyls, only the type III PTO accommodates four lithiums, while type I/II compounds PHP, NTCDA, and NTCDM accommodate only two, corresponding to low carbonyl utilizations of no more than 50%.

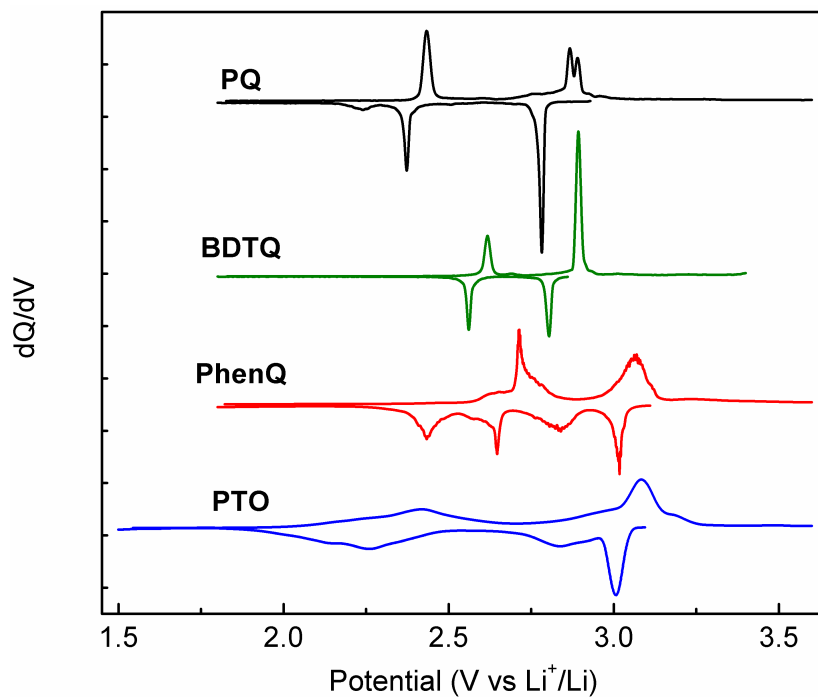


Fig. S2 Differential capacity vs potential of PQ, BDTQ, PhenQ, and PTO cathodes derived from the galvanostatic discharge–charge curves at 0.1C rate for the first cycle.

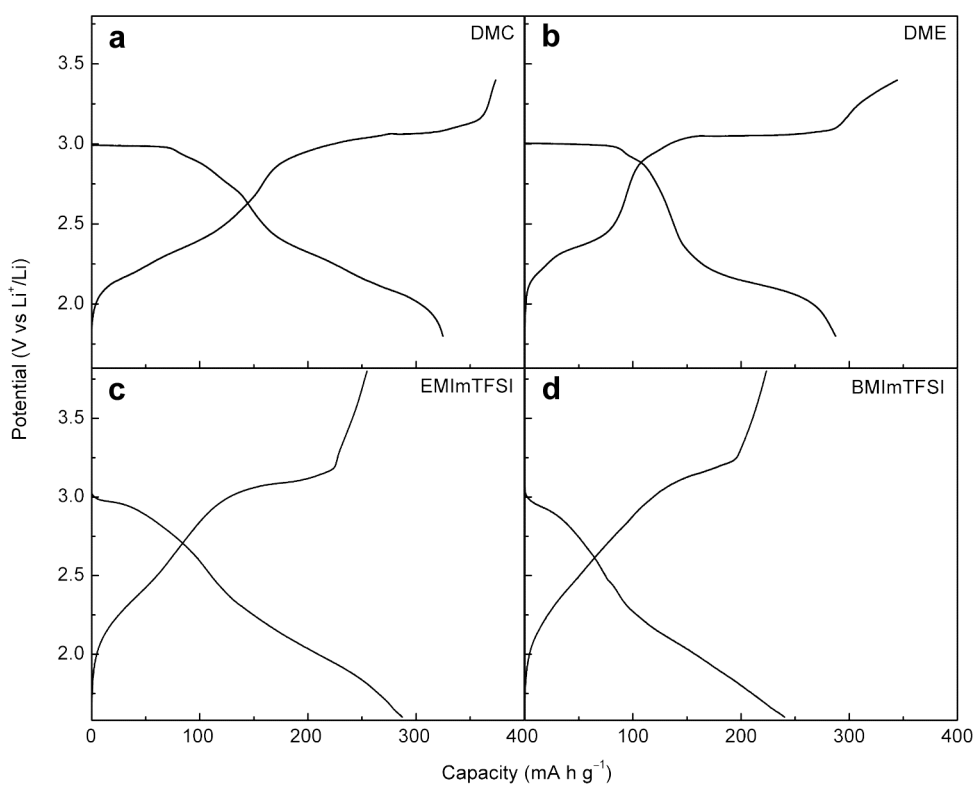


Fig. S3 Discharge–charge curves of PTO electrode (PTO–conductive carbon–PVDF, 3:5:2) in electrolytes composed of 1 M LiTFSI in (a) DMC, (b) DME, (c) EMImTFSI, and (d) BMImTFSI. The curves at the first cycle.

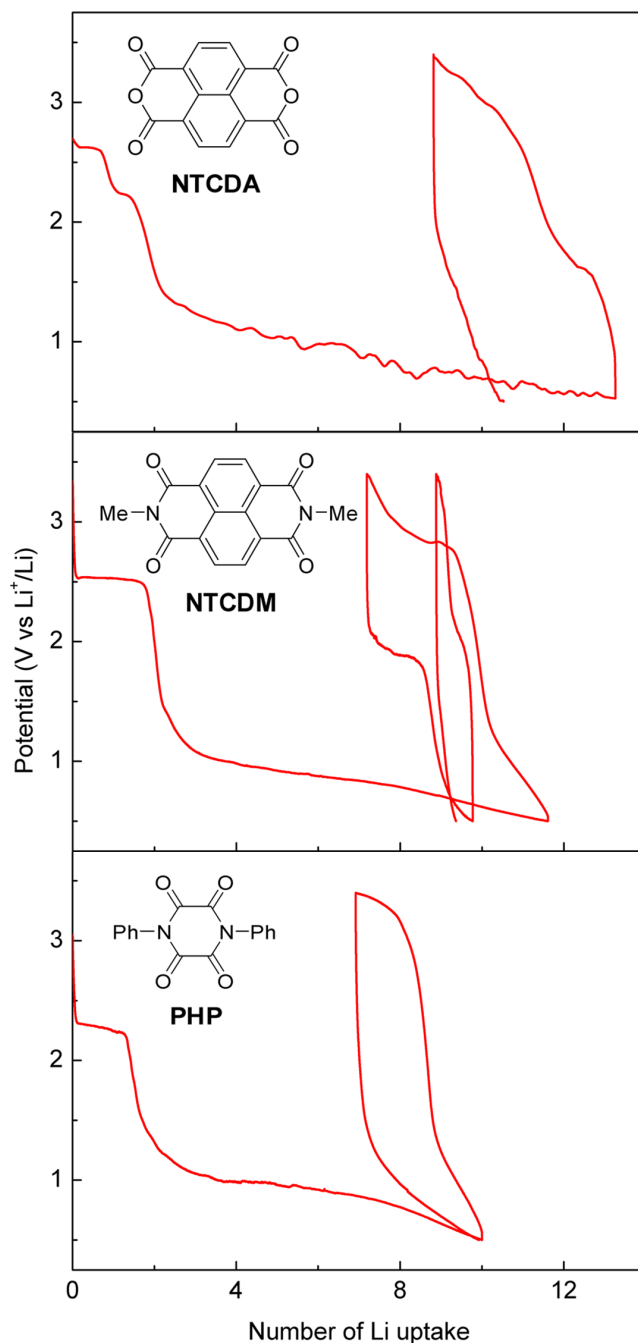


Fig. S4 Deep discharge–charge curves of selected cathode molecules. Cells employing type I/II compounds **PHP**, **NTCDA**, and **NTCDM** as cathodes are deeply discharged–charged galvanostatically at 0.1C rate. Even with a much lower cut-off voltage of 0.5 V instead of 1.8 V, reversible lithiation of the other two carbonyls does not occur. The irreversible discharge slopes at 1.4–0.5 V could have come from catalytic electrolyte decomposition, solid electrolyte interface formation, or reductive destruction of the molecular structure.

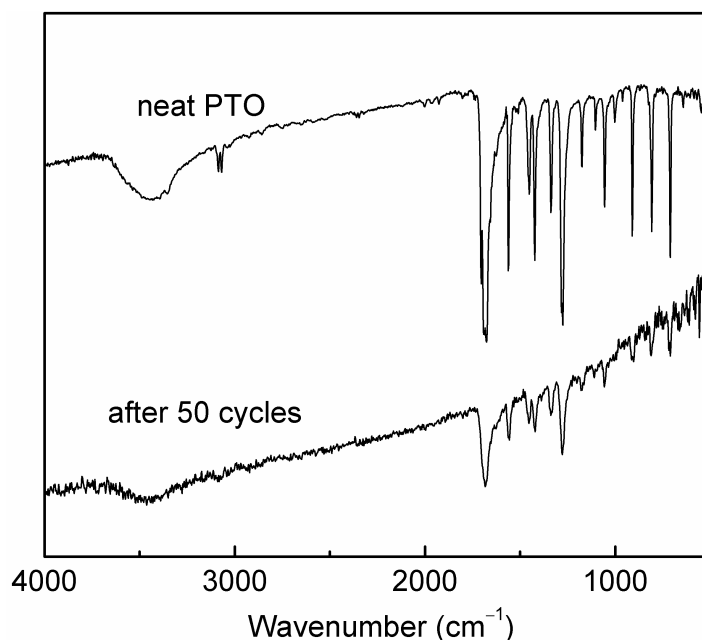


Fig. S5 IR spectra of (upper) neat PTO and (lower) a binder-free PTO electrode (PTO–conductive carbon, 3:7) after 50 discharge–charge cycles (electrolyte: 1 M LiClO₄ in BMImTFSI). The largely identical spectra indicate the chemical integrity of PTO during the electrochemical tests.

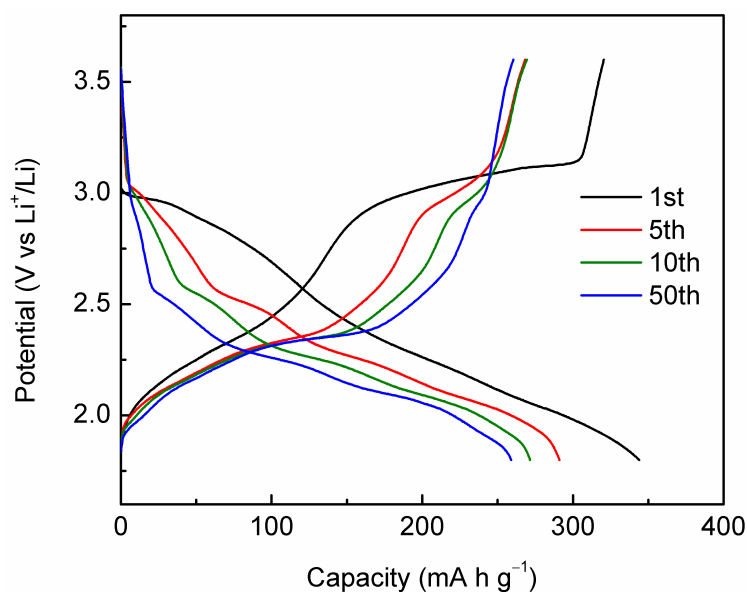


Fig. S6 Discharge–charge curves of PTO electrodes (PTO–conductive carbon–Al₂O₃, 3:6:1) in the LiClO₄–BMImTFSI electrolyte at the first and twentieth cycle.

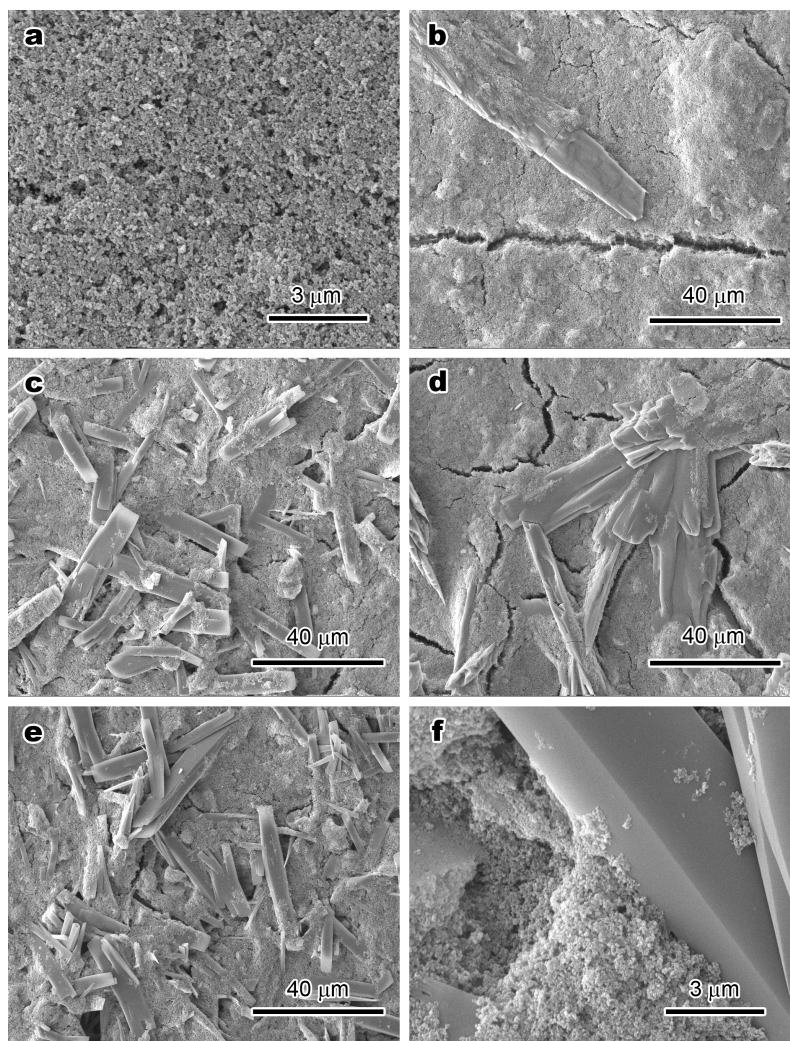


Fig. S7 Morphology of the cathode blends. Scanning electronic microscopy images of cathode blends including (a) carbon-only control, (b) PQ, (c) BDTQ, (d) PhenQ, and (e, f) PTO are displayed. The ratio of active material, carbon, and polyvinylidene is 3:5:2 (in the blank control, the ratio is 0:8:2). The morphology of blends rather than the neat cathode compounds are shown because some of these compounds undergo dissolution–precipitation during the *N*-methyl-2-pyrrolidinone-involved mixing process. All the compounds exist as cuboid crystals which are several tens of micrometers in length and several micrometers in width/height. PQ and PhenQ form partially interpenetrating structures with carbon, while the PTO crystals are largely separated from carbon.

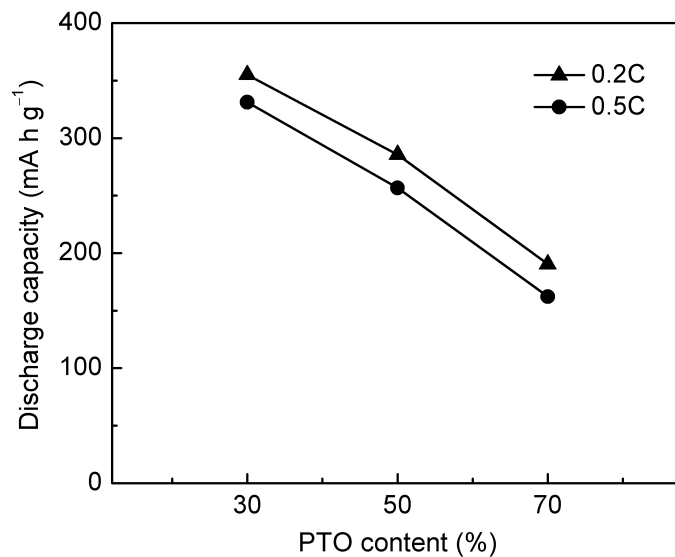


Fig. S8 Capacity dependence of binder-free PTO electrodes on the ratio of PTO–conductive carbon (3:7, 5:5, and 7:3) at 0.2C and 0.5C rates. The electrolyte is 1 M LiPF₆ in EC/DMC.

References

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