Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

Molecular Engineering towards Safer Lithium-Ion Batteries: A Highly Stable and Compatible Redox Shuttle for Overcharge Protection

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Experiments:

1. Synthesis

1,4-di-*tert*-butyl-2,5-bis(2-methoxyethoxy)methoxybenzene (DBMOEB) and 1,4-bis(2-methoxyethoxy)-2,5-di-*tert*-butylbenzene (DBBB) are not commercially available and were synthesized in our lab according to the following procedure (**Figure S1**). 2,5-di-*tert*-butylhydroquinone (9 mmol) was dissolved in anhydrous THF (20 ml). Sodium hydride (27 mmol) and 2-methoxyethoxymethyl chloride or 2-chloroethyl methyl ether (18 mmol) was added to the solution. The reaction was stirred at room temperature for overnight.

After removal of the solvent, the residue was partitioned between dichloromethane (DCM) and $NaHCO_3$ (0.1 M). The organic portion was separated and dried over Na_2SO_4 before solvent was removed under vacuum. The crude product was chromatographed (silica, hexanes/DCM from 5:1 to 1:1) to afford oligo(ethylene glycol) functionalized compounds, which were further purified by crystallization from saturated dichloromethane solution under low temperature. For DBMOEB, the yield was 65% and it has been fully characterized by the following methods: ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.14 (s, 2H), 5.25 (s, 4H), 3.86 (t, J = 4.5 Hz, 4H), 3.60 (t, J = 4.5 Hz, 4H), 3.40 (s, 6H), 1.36 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 151.01, 137.00, 114.53, 94.37, 71.93, 67.53, 59.26, 34.80; Mass spectroscopy (EI^+): calcd. $(M+Na)^+$ 421.2561, found $(M+Na)^+$ 421.2562.

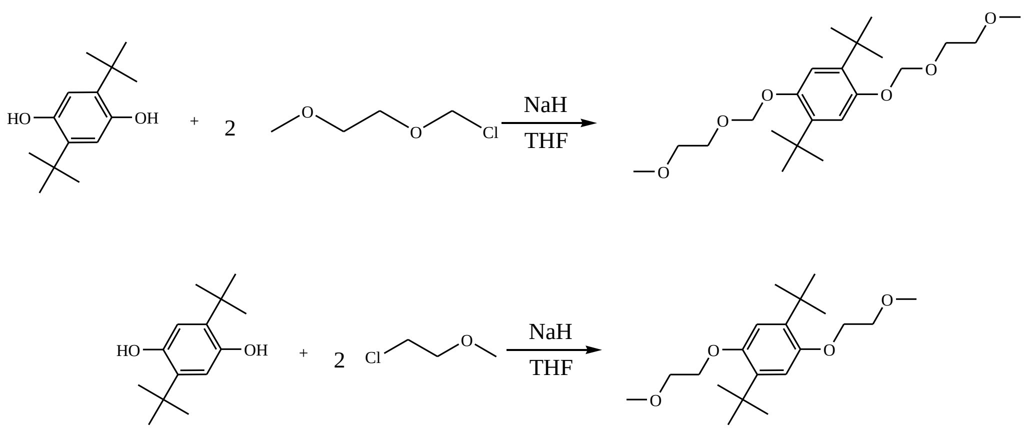

Figure S1. Synthesis routes of 1,4-di-*tert*-butyl-2,5-bis(2-methoxyethoxy)methoxybenzene (DBMOEB) and 1,4-bis(2-methoxyethoxy)-2,5-di-*tert*-butylbenzene (DBBB).

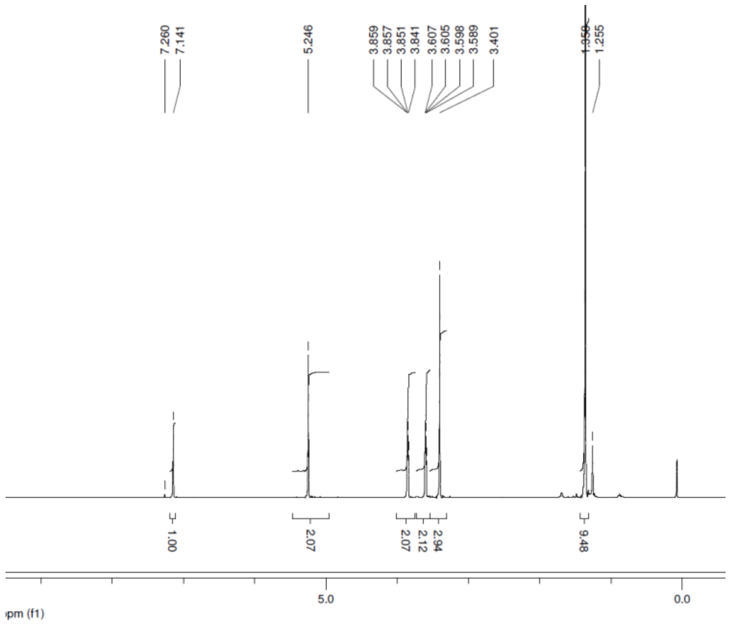

Figure S2. ^{1}H-NMR spectrum of the DBMOEB.

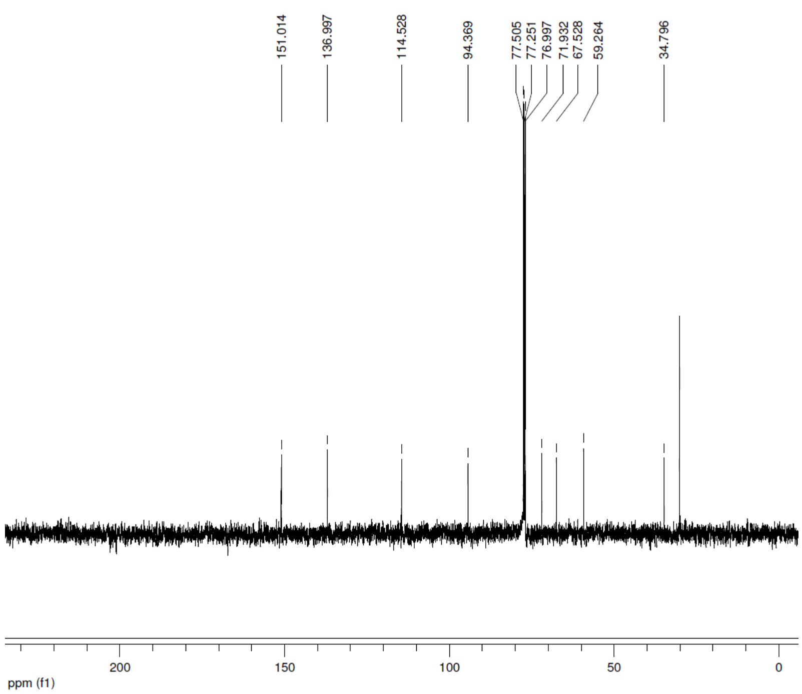

Figure S3. ^{13}C-NMR spectrum of the DBMOEB.

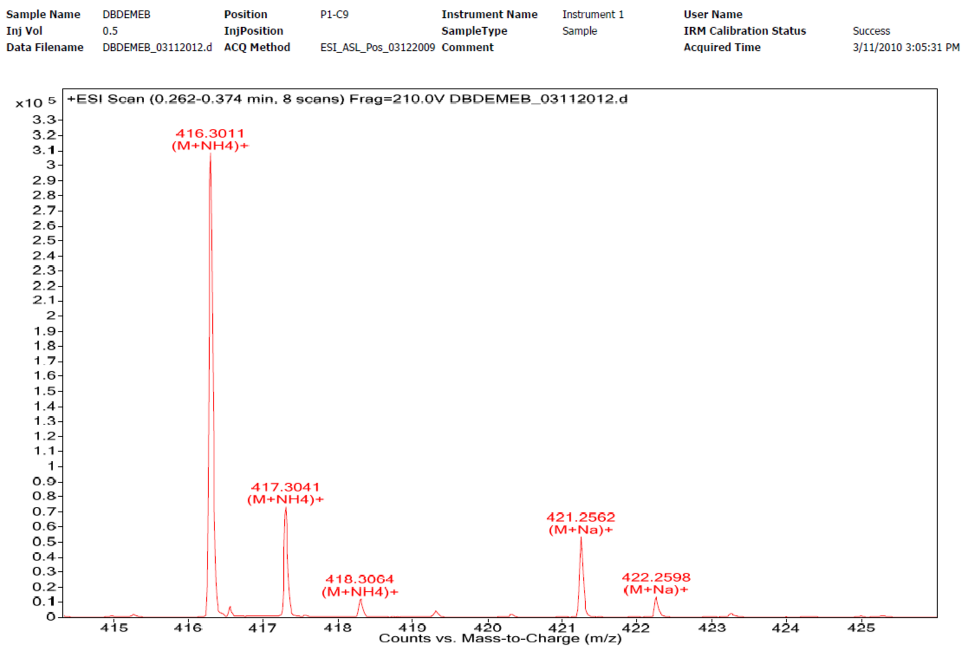

Figure S4. Mass spectrum of the DBMOEB.

For DBBB, the yield was 70% and it has been fully characterized by the following methods: ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 6.86 (s, 2H), 4.14 (t, J = 1.5 Hz, 4H), 3.79 (t, J = 1.5 Hz, 4H), 3.47 (s, 6H), 1.39 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 151.53, 136.76, 112.82, 71.89, 68.28, 59.41, 34.95; Melting point: 69.3-70.1^{o}C; Mass spectroscopy (EI^+): calcd. $(M+Na)^+$ 361.2364, found $(M+Na)^+$ 361.2365.

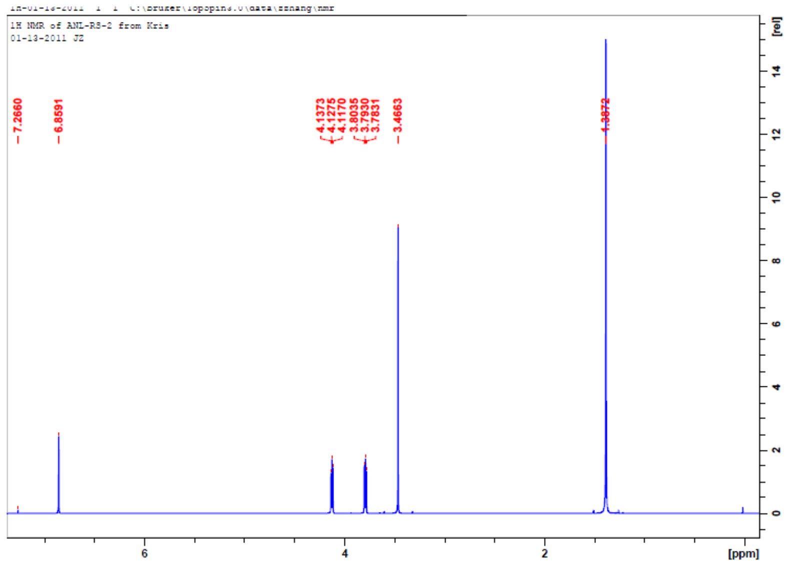

Figure S5. ^{1}H-NMR spectrum of the DBBB.

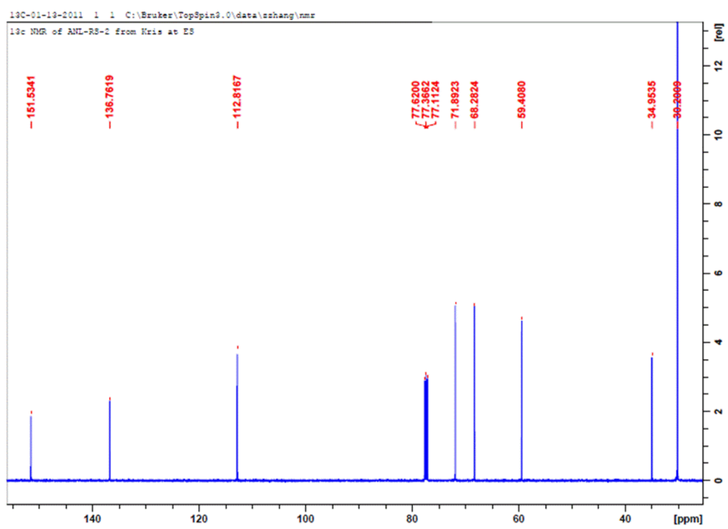

Figure S6. ^{13}C-NMR spectrum of the DBBB.

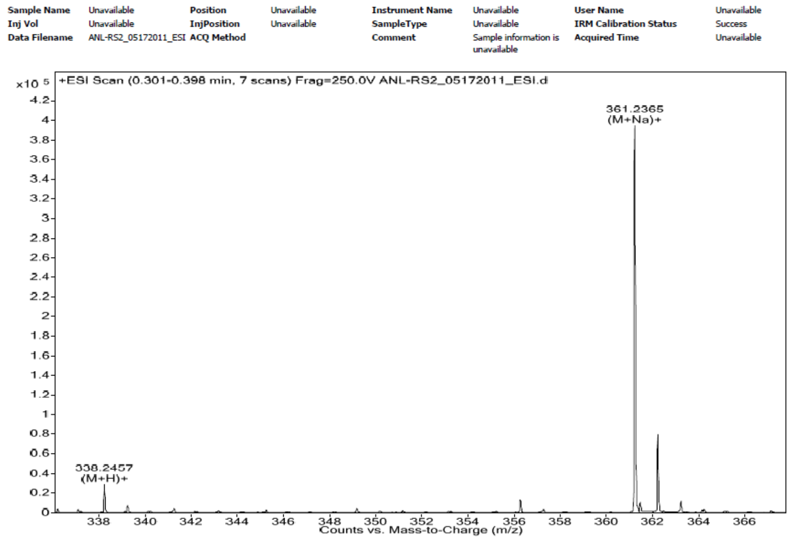

Figure S7. Mass spectrum of the DBBB.

2. Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed in custom-made three electrode cells with 1 mm diameter Pt working electrode, a Li metal reference electrode, and a Li counter electrode using Solartron Analytical 1470E system. The overcharge test was conducted by assembling $LiFePO_4$/graphite 2032 coin cells. Graphite electrode used is mesocarbon microbeads (MCMB). The lamination of $LiFePO_4$ electrode is composed of 80% $LiFePO_4$ active material, 12% acetylene carbon black and 8% PVDF as binder. The electrolyte used was 1.2 M $LiPF_6$ in EC/EMC in a weight ratio of 3:7 (Gen 2 electrolyte). The concentrations of the shuttle molecule varied from 0.1 M to 0.4 M. The cells were charged using a constant current to 200% capacity (100% overcharge ratio) or until a specific upper cutoff voltage was reached (normally 4.95V *vs* Li/Li^+), whichever occurred first. After the charging process, the cells were discharged to a normal cutoff voltage using the same constant current.

3. Computational Methods

B3LYP calculations were performed with Gaussian 03[1]. Free energies were calculated as follows. B3LYP/6-31G* optimization and frequency calculations were performed followed by PCM SCRF calculations at the B3LYP/6-31+G* level with modified water solvent. A dielectric constant of 55.725 was used to represent a typical 25% EC/25% ethyl methyl carbonate/50% PC electrolyte. B3LYP/6-311+g(3df,2p) energies were then calculated to account for the effects of a larger basis set.

4. Diffusion coefficient

Diffusion coefficient is an important parameter to evaluate the efficiency of the charge shunting process of redox shuttles. **Figure S9** plots the anodic peak current (I_p) versus the square root of the sweep rates ($v^{1/2}$). The resulting slope was then substituted into the Randles-Sevcik[2] equation (1) to calculate the diffusion coefficient, where I_p is the anodic peak current, *n* is the number of electrons involved in the redox process, *C* is the concentration of redox shuttle and *D* is the diffusion coefficient. The linear slope derived from **Figure S9** suggests diffusion-controlled redox chemistry. The calculated diffusion coefficient for DBBB is 9.26×10^{-7}cm/s.

$$i_p = (269{,}000)n^{3/2}AD^{1/2}Cv^{1/2} \qquad (1)$$

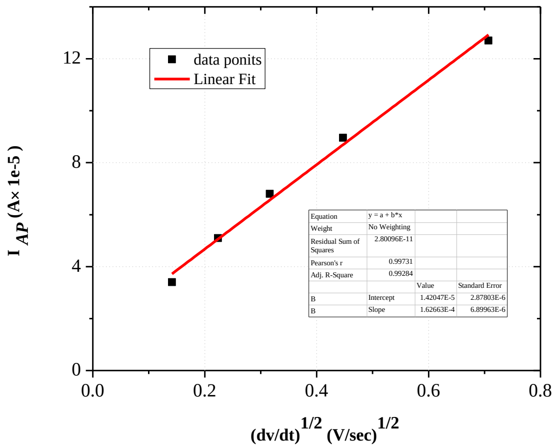

Figure S9. Plot of I_p vs. $v^{1/2}$ used for determination of diffusion constant.

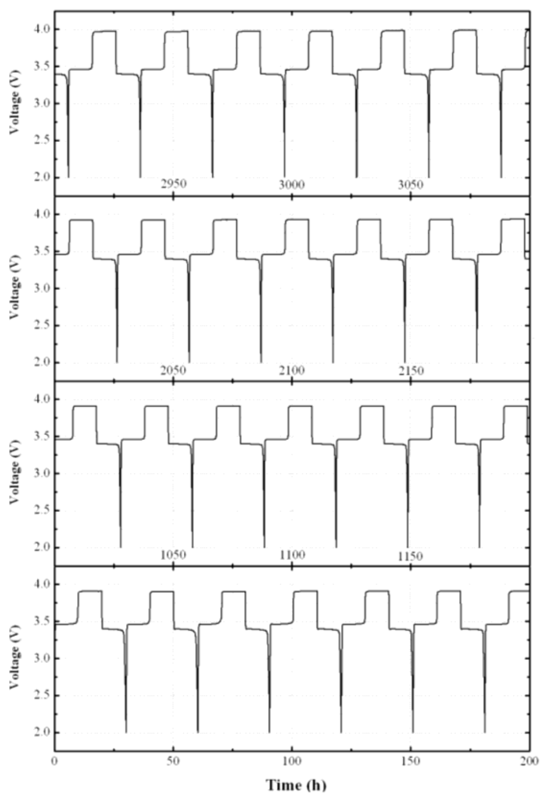

Figure S10. Voltage profiles of overcharge abuse tests using Li/$LiFePO_4$ coin cells containing 0.1 M DBBB in Gen 2 electrolyte during the course of 0-3000 h. Charging rate is C/10 and overcharge ratio is 100%.

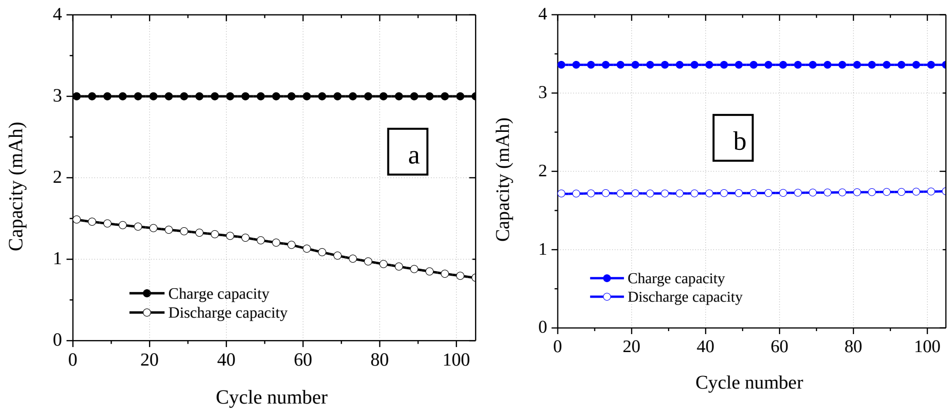

Figure S11. Capacity profiles of overcharge abuse tests using MCMB/ $LiFePO_4$ (a) and Li/$LiFePO_4$ (b) coin cells containing 0.1 M DBBB in Gen 2 electrolyte. Charging rate is C/10 and overcharge ratio is 100%. The difference of charge and discharge capacity comes from the electricity shunted by redox shuttle additive during overcharge.

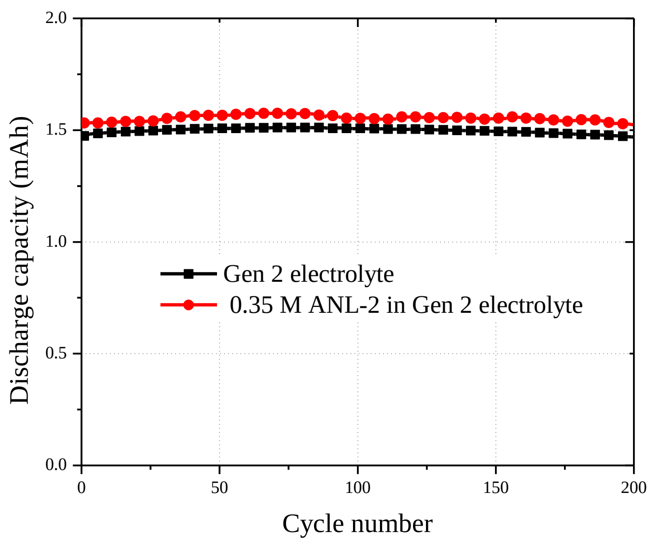

Figure S12. Capacity retention profiles of normal cycle tests using MCMB/$LiFePO_4$ coin cells containing none or 0.35 M DBBB in Gen 2 electrolyte. Charging rate is C/3 and cut off voltage is 2.3 ~3.6 V.

Reference:

(1) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004. 2003.

(2) Feng, J. K.; Ai, X. P.; Cao, Y. L.; Yang, H. X. *Electrochemistry Communications* **2007**, *9*, 25.