Supporting Information

Insights on Redox Properties of Sumanene Derivatives for High-Performance Organic Cathodes

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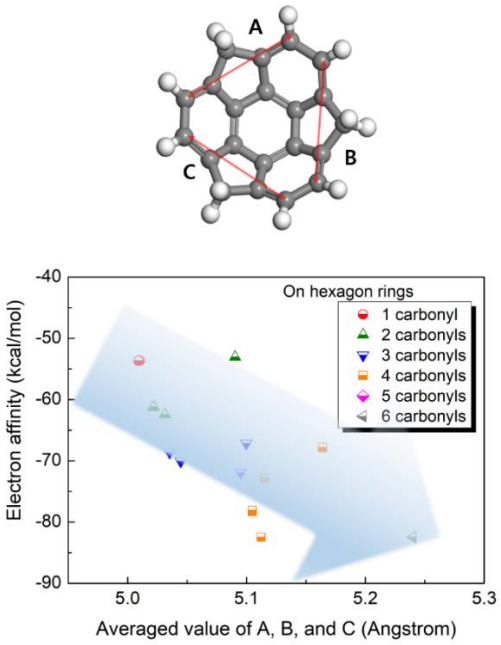


Figure S1. Correlation of electron affinity with the averaged value of A, B, and C for seventeen sumanene derivatives with different numbers (1 to 6) of carbonyls on hexagon ring(s) to indirectly assess their structural curvature. The carbon-carbon distances corresponding to A, B, and C are introduced to represent the degree of the symmetry of the structure. The atoms with the gray and white in color depict carbon and hydrogen, respectively.

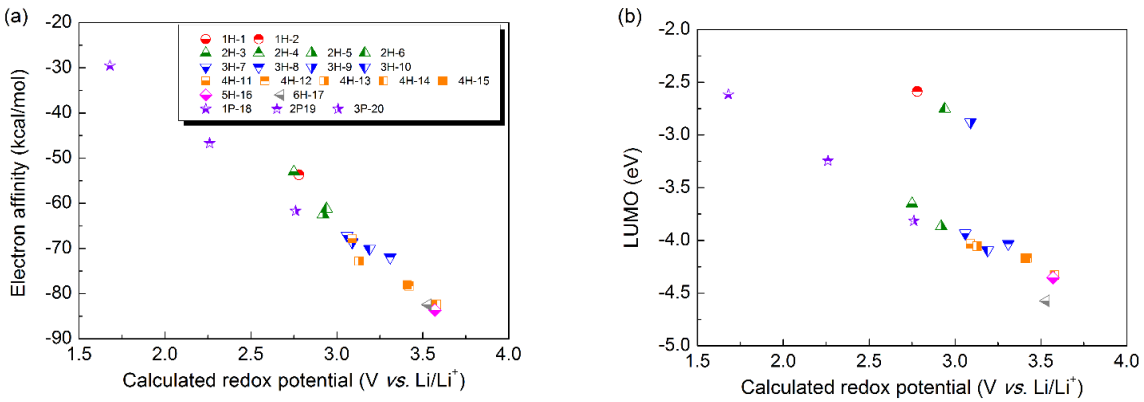


Figure S2. Correlations of redox potential with (a) electron affinity and (b) LUMO for the twenty sumanene derivatives (no Li bindings) described in Figure 1. In the legend, each symbol is named as defined in Figure 1.

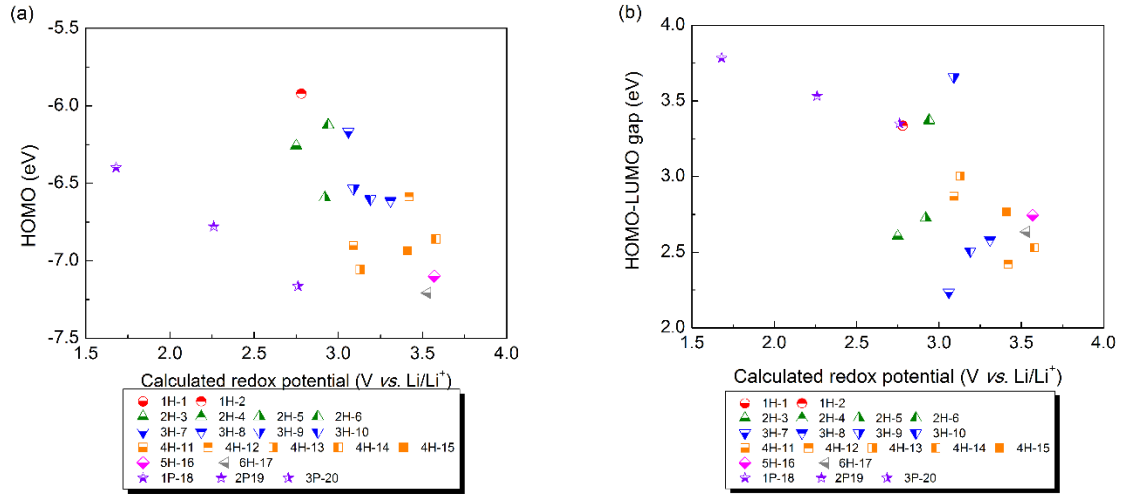


Figure S3. Correlations of redox potential with (a) HOMO and (b) HOMO-LUMO gap for the twenty sumanene derivatives (no Li bindings) described in Figure 1. In the legend, each symbol is named as defined in Figure 1.

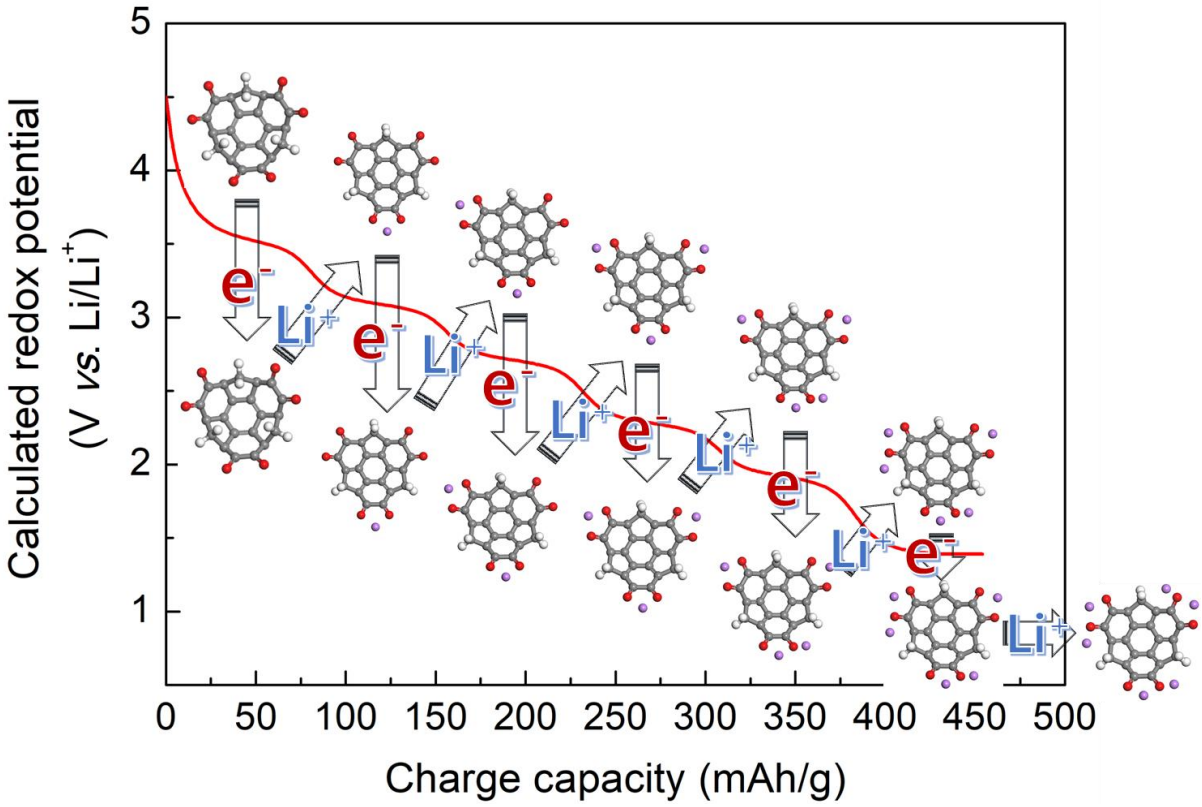


Figure S4. Li-storage mechanism of the sumanene with hexagon rings fully functionalized by six carbonyls during the discharging process. The sumanene derivative becomes cathodically inactive after storing six Li atoms.

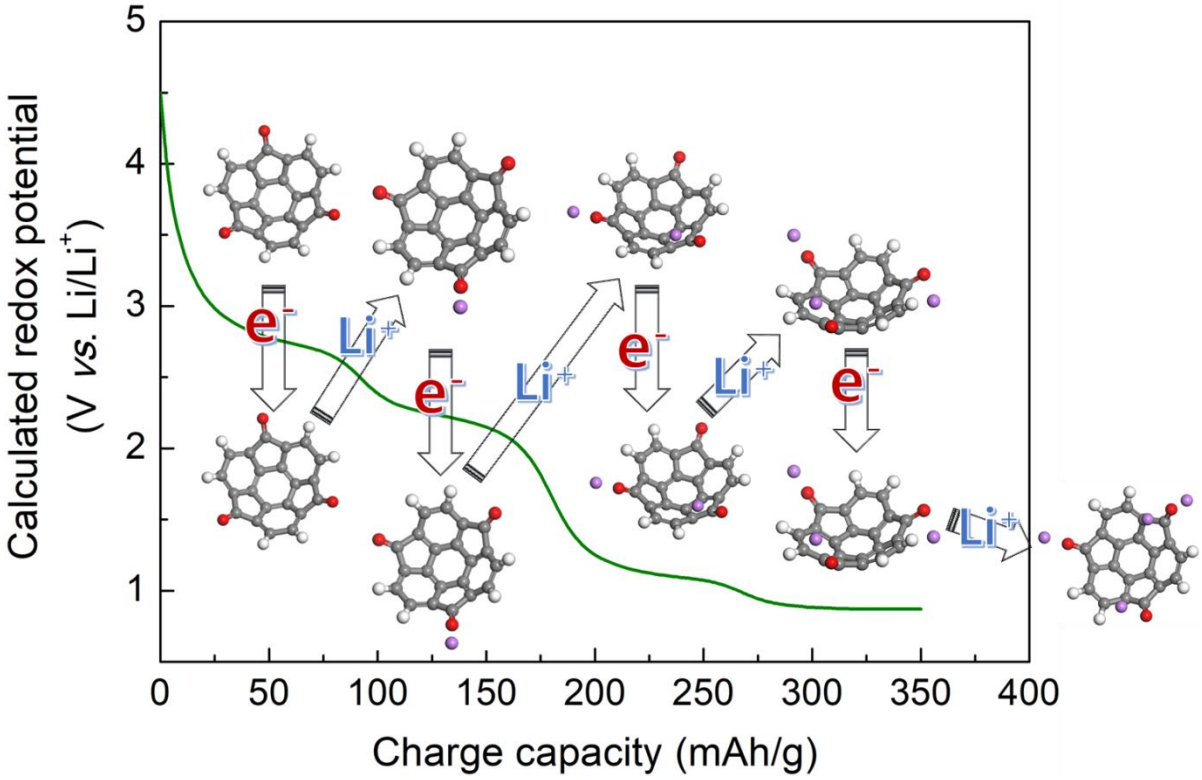


Figure S5. Li-storage mechanism of the sumanene with pentagon rings fully functionalized by three carbonyls during the discharging process. The sumanene derivative becomes cathodically inactive after storing four Li atoms.

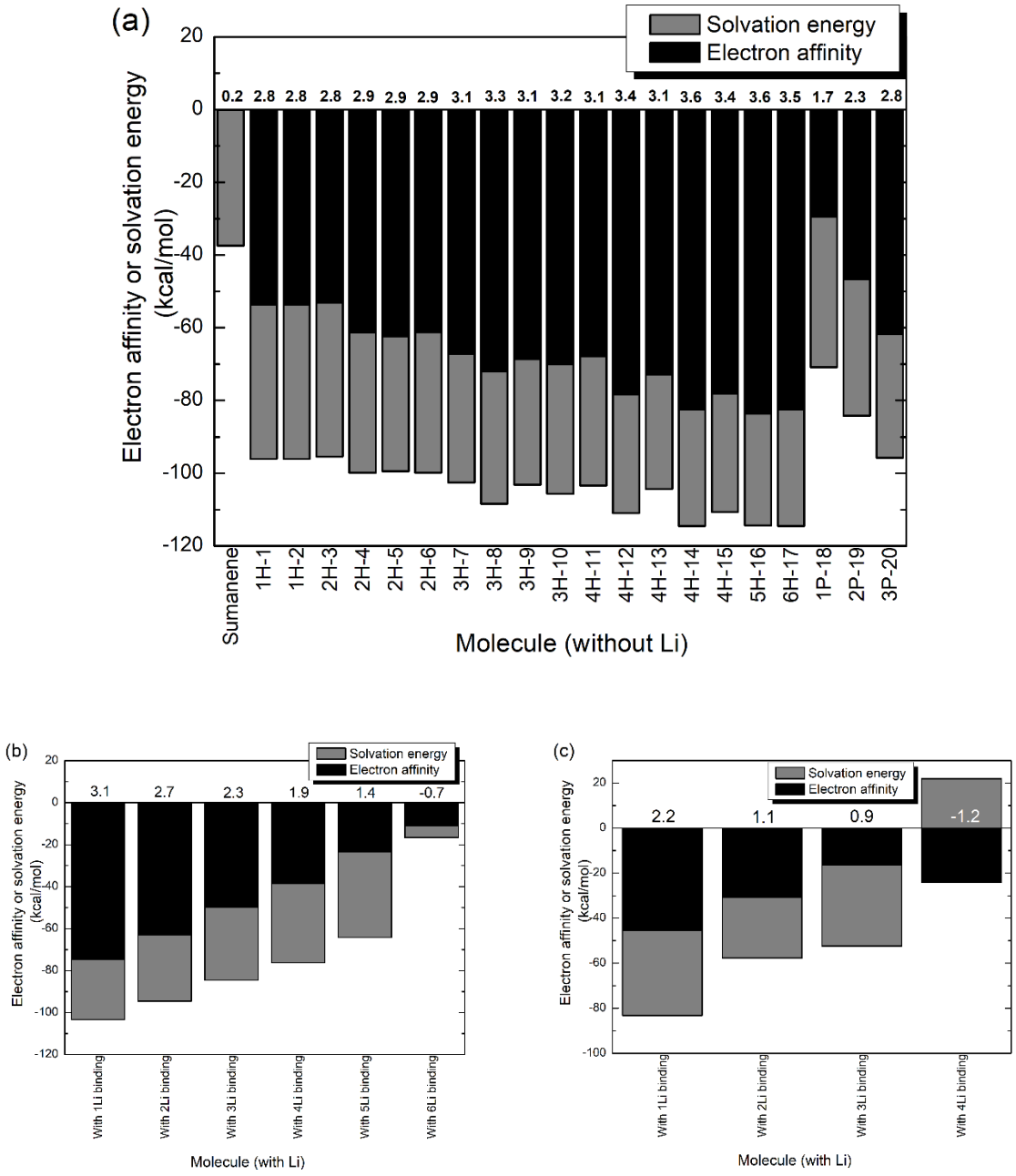


Figure S6. Contributions of electron affinity and solvation energy to redox potential for (a) the twenty sumanene derivatives (no Li binding) described in Figure 1 and (b-c) Li-bound complexes of 6H-17 and 3P-20, namely the two sumanene derivatives with either hexagon or pentagon rings fully functionalized by carbonyls. The redox potentials for the compounds are described in unit of V *vs.* Li/Li^+ in each figure.

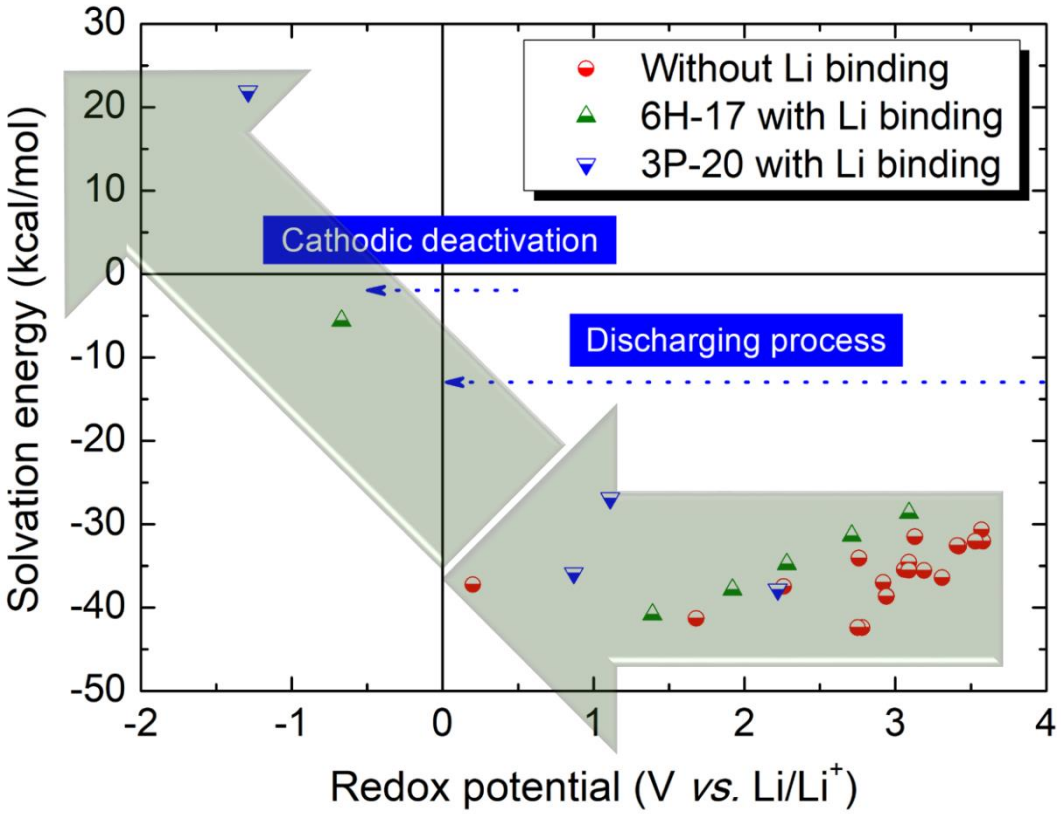


Figure S7. Correlation of redox potential with solvation energy for all the sumanene derivatives described in Figures 1 without and with bound Li atoms. The two big arrows describe the two-stage transition behavior of solvation energy as the redox potential decreases during the discharging process, highlighting the critical role of solvation energy in the cathodic deactivation.

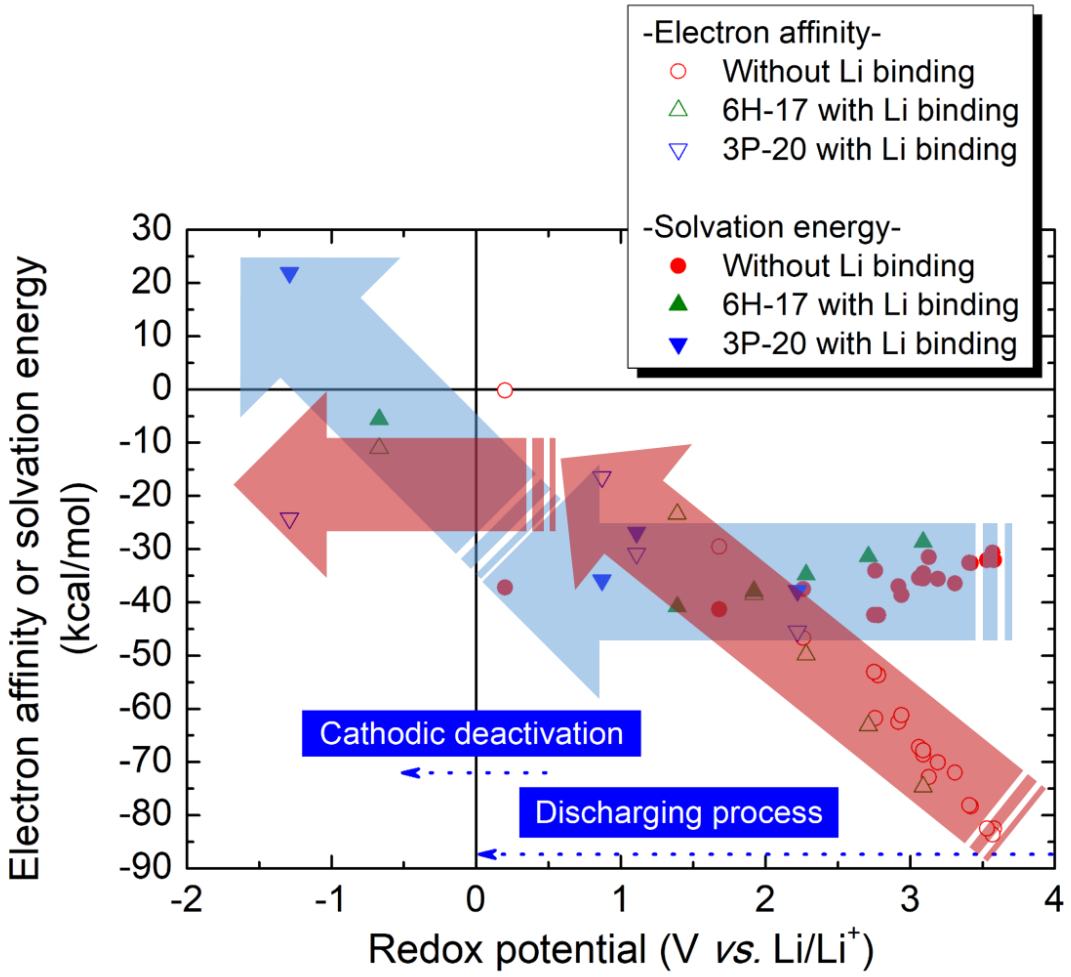
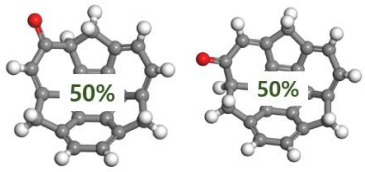
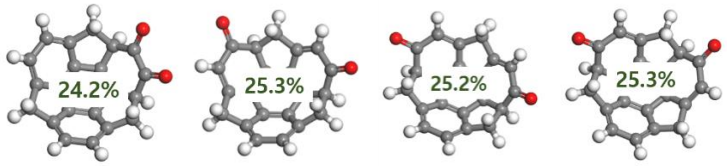
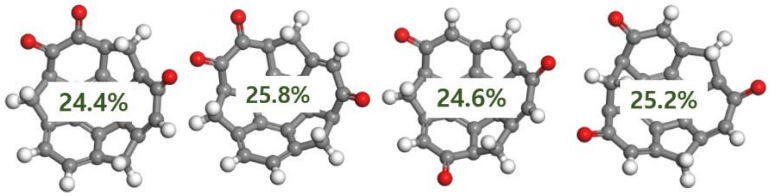


Figure S8. Correlations of redox potential with electron affinity and solvation energy for all the sumanene derivatives described in Figures 1 without and with bound Li atoms. The big arrows in red (blue) describe the two-stage transition behavior of electron affinity (solvation energy) as the redox potential decreases during the discharging process. This highlights that electron affinity would be the critical factor for the decrease in the redox potential during the discharging process (at the range of positive redox potentials) while the cathodic activity would be deactivated by solvation energy.

Table S1. Boltzmann factor-based thermodynamic probability for sumanene derivatives with the same number (1, 2, 3, or 4) of carbonyl functional groups on hexagon ring(s) in each set.

The number of carbonyls	Boltzmann factor-based thermodynamic probability
1	
2	
3	
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