Electronic Supplementary Information

Concave Binding of Cationic Li to Quadrannulene

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Computational methods

All calculations are performed with the GAUSSIAN 09 program.[1] The M06-2X density functional including Grimme's D3 dispersion in conjunction with the basis set of cc-pVDZ are employed for structural optimizations. Vibrational frequency analyses are carried out at the same level of theory to confirm the optimized saddle points and the zero-point energy (ZPE) correction is taken into account for each relevant structure to evaluate to barriers (energy difference between transition states and reactants) and reaction energies (energy difference between products and reactants). To verify the influence of computational methods on results, the binding energies between Li^+ and quadrannulene are re-calculated at the levels of wB97xD/cc-pVDZ, PW6B95D3/cc-pVDZ, and M06-2X-D3/aug-cc-pVTZ (listed in Table S1-S3). The binding energies are corrected using BSSE (basis set superposition error) approach. Kinetically, based on the transition state theory (TST), the reaction rates is obtained by Arrhenius formula: $v\exp(-G^{\ddagger}/k_BT)$, where v is the attempt frequency, T is the reaction temperature, $G^{\ddagger}$ is the computed activation barrier under reaction temperature, and k_B is the Boltzmann constant.

1. Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S1 Binding energies (kcal mol^{-1}) of Li$^+$@quadrannulene complexes (wB97xD/cc-pVDZ)

Complex	E_{BE}[a]	E_{BE}+BSSE	G_{BE}[b]	G_{BE}+BSSE
Li$^+$@QUA-η^4	39.7	38.8	33.9	33.1
Li$^+$@QUA-η^6	40.6	39.5	34.4	33.3
Li$^+$@QUA-η^8	**45.0**	**43.2**	**38.7**	**36.9**

a. E_{BE}: electronic energy with ZPE correction. b. G_{BE}: Gibbs free energy at room temperature.

Table S2 Binding energies (kcal mol^{-1}) of Li$^+$@quadrannulene complexes (PW6B95D3/cc-pVDZ)

Complex	E_{BE}[a]	E_{BE}+BSSE	G_{BE}[b]	G_{BE}+BSSE
Li$^+$@QUA-η^4	43.0	42.0	36.7	35.7
Li$^+$@QUA-η^6	43.1	41.8	36.9	35.5
Li$^+$@QUA-η^8	**45.1**	**43.0**	**38.5**	**36.4**

a. E_{BE}: electronic energy with ZPE correction. b. G_{BE}: Gibbs free energy at room temperature.

Table S3 Binding energies (kcal mol^{-1}) of Li$^+$@quadrannulene complexes (M06-2X-D3/aug-cc-pVTZ)

Complex	E_{BE}[a]	E_{BE}+BSSE	G_{BE}[b]	G_{BE}+BSSE
Li$^+$@QUA-η^4	41.0	40.7	34.7	34.4
Li$^+$@QUA-η^6	41.5	41.3	35.2	34.9
Li$^+$@QUA-η^8	**41.8**	**41.4**	**35.4**	**35.0**

a. E_{BE}: electronic energy with ZPE correction. b. G_{BE}: Gibbs free energy at room temperature.

Table S4 Reaction barriers ($E^{\ddagger}$, kcal mol^{-1}), distortion energies[a] (E_{dis}, kcal mol^{-1}) of cyclopentadiene (CP) and buckybowls (QUA and Li$^+$@QUA), and interactions[b] between cyclopentadiene and buckybowls (E_{int}).

Reaction	$E^{\ddagger}$	E_{dis}-CP	E_{dis}-QUA/ E_{dis}-Li$^+$@QUA	E_{int}
CP + QUA-spoke	11.3	11.2	4.0	3.9
CP + Li$^+$@QUA-spoke	3.5	7.0	4.4	7.9

a. defined as the single-point energy difference between transition states and intermediates.

b $E_{int} = \sum E_{dis} - E^{\ddagger}$

Table S5 POAV (°) of buckybowls (QUA and Li+@QUA-η^8)

Buckybowl	POAV-C_{hub}	POAV-C_{spoke}	POAV-C_{rim}
QUA	17.71	7.41	2.53
Li$^+$@QUA-η^8	17.67	7.57	2.22

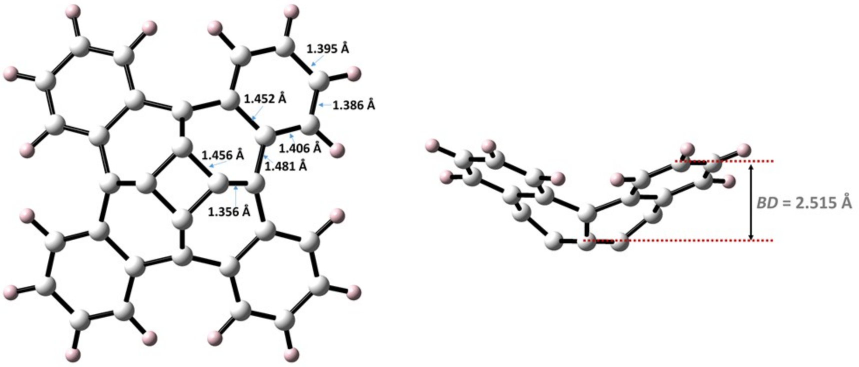
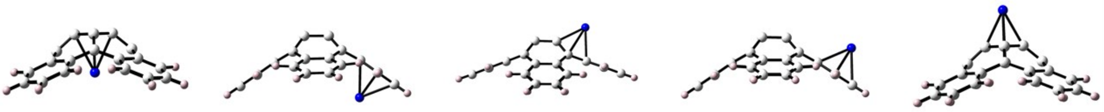


Fig. S1. Structure and bowl-depth (*BD*) of tetrabenzoquadrannulene (TBQ).



(a) Li$^+$@TBQ-concave-η^8 *BE* = 47.4 kcal mol^{-1} (b) Li$^+$@TBQ-concave-η^6 *BE* = 45.9 kcal mol^{-1} (c) Li$^+$@TBQ-convex-η^6-a *BE* = 45.2 kcal mol^{-1} (d) Li$^+$@TBQ-convex-η^6-b *BE* = 45.1 kcal mol^{-1} (e) Li$^+$@TBQ-convex-η^4 *BE* = 43.2 kcal mol^{-1}

Fig. S2. Structures of Li$^+$-bound tetrabenzoquadrannulene (TBQ)

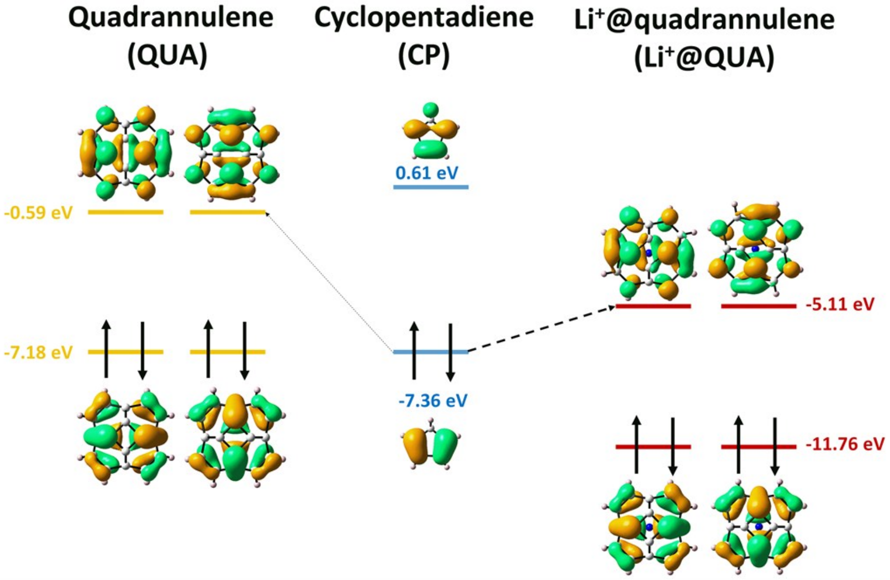


Fig. S3. Frontier orbital diagrams of quadrannulene (QUA), Li$^+$@QUA, and cyclopentadiene (CP).

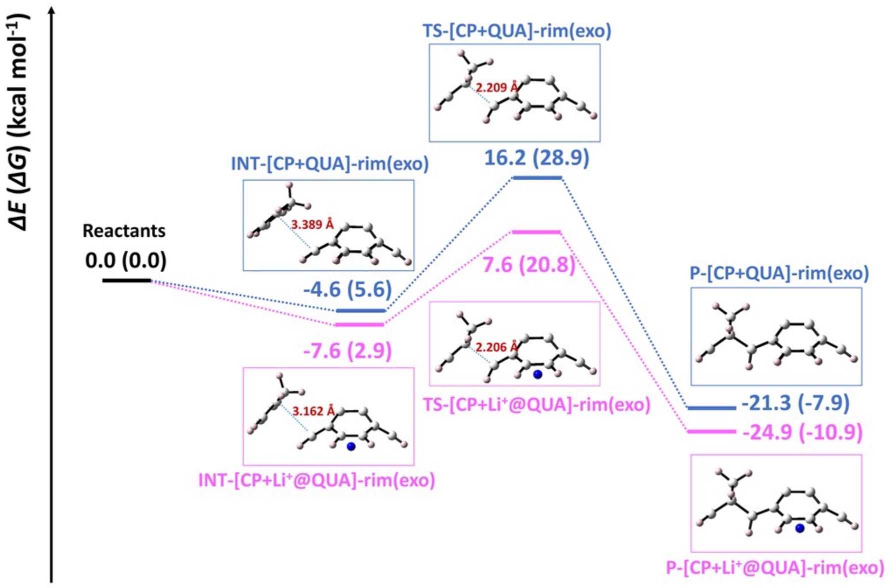


Fig. S4. Energy profiles (0 K and 298.15 K (in parentheses)) of Diels-Alder reactions between cyclopentadiene and the rim bonds of quadrannulene (QUA) or Li^+@QUA from an exo approach.

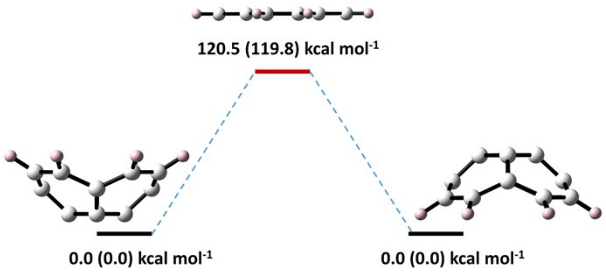


Fig. S5. Bowl inversion process of quadrannulene at 0 K and 298.15 K (in parentheses).

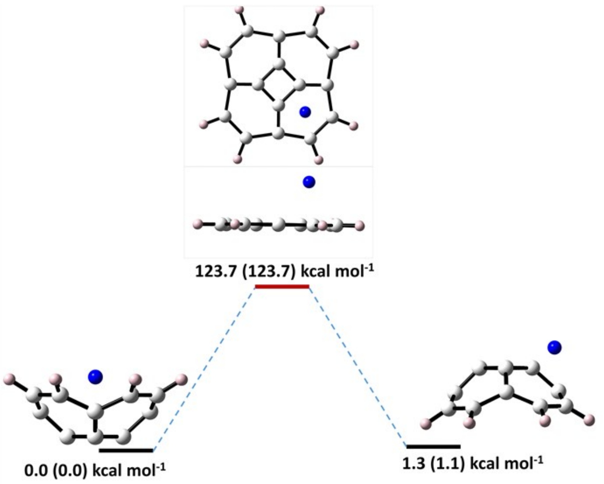


Fig. S6. Bowl inversion process of Li^+-bound quadrannulene at 0 K and 298.15 K (in parentheses).