Supplementary Information (SI) for Chemical Science. This journal is © The Royal Society of Chemistry 2024



Scheme S1. Synthetic route for 1 and 4.



Figure S1. FTIR spectra of 2, 4 and 1.



Figure S2. ¹³C-NMR spectrum of **2**, **4** and **1** (1,1,2,2-tetrachloroethane- d_2 , 125 MHz, 298K).



Figure S3. Structure of the different [2+4], [3+6] and [4+8] cages that can be generated by the condensation of **2** and **3**.



Figure S4. a) UV-Vis and b) fluorescence spectrum (normalized) of **2**, **4** and **1** in chloroform having concentration $10^{-5}(M)$. c) and d) are the digital photographs of the chloroform solution of the **2**, **4** and **1** under visible and UV light respectively.



Figure S5. Thermal gravimetric analysis (TGA) of reference 4 and cage 1 under N₂ (10 °C/min)



Figure S6. PXRD profile of reference 4 and cage 1.



Figure S7. Different conformers and relative energies at the DFT M06-2X-6-31G(d,p) level in a chloroform continuum, top and side views.



Figure S8. Electronic density of the frontier orbitals computed at the B3LYP-6-31G(d,p)/M06-2X-6-31G(d,p)-chloroform level.



Figure S9. DFT derived point charges for 1 (bottom) and 4 (top).



Figure S10. DFT computed electrostatic potential projected on the molecular, solventexcluded surface, of **1** and **4.** The N_{sp}^2 atoms possess negative charges creating attractive electrostatic hot spots for Li⁺ adsorption rendered in red, while white and blue show neutral and positive electrostatic potentials, respectively.



Figure S11. Li adsorption sites on **4** computed with the GFN1-xTB tight binding model, see text for details, top and side views.



Figure S12. Possible different reduced states of 4 screened with DFT, top and side views.



Figure S13. Reduction potentials for **4** with corresponding geometries with respect to Li/Li^+ for sequential reductions computed with DFT.



Figure S14. (a) EIS curves of cage **1** and reference **4** used for diffusion coefficient analysis and (b) the corresponding equivalent circuit used to fit the EIS spectra



Figure S15. Voltage profile of Li | Cage **1** cell when cycled a various C-rate, ranging from 1C to 10C.



Figure S16. Specific capacity and columbic efficiency as a function of cycle number of Li | Cage **1** cell when cycled a various C-rate, ranging from 1C to 10C.



Figure S17. Long-term cycling of Li | Cage **1** cell at a C-rate of 4C: specific capacity and coulombic efficiency as a function of cycle number.



Figure S18. Long-term cycling of Li | Cage **1** cell at a C-rate of 10C: specific capacity and coulombic efficiency as a function of cycle number.

Table	S1.	Frontier	orbitals	eigenvalues	computed	at	the	B3LYP-6-31G(d,p)/M06-2X-6-
31G(d	,p)-cl	nloroform	level. <mark>L</mark>	JMOs, HOM	Os and gaps	. A	ll val	ues in eV.

						LUMO+1	LUMO	номо				GAP
4	-1.02	-1.03	-1.1	-1.44	-1.65	-2.26	-2.34	-5.69	-5.87	-5.98	-6.07	3.35
1	-1.63	-2.25	-2.25	-2.25	-2.33	-2.33	-2.33	-5.69	-5.69	-5.7	-5.86	3.36

General Procedures

Commercial chemicals and solvents were used as received. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck. Column chromatography was carried out using Silica gel 60 ($40-60 \mu m$) from Scharlab.

NMR spectra in solution were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer at 298 K using partially deuterated solvents as internal standards.

Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments MALDI-TOF) were recorded using DCTB and silver trifluoroacetate in ground steel plates on a Bruker REFLEX spectrometer in POLYMAT by Dra. Estíbaliz González de San Román Martín.

Absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer.

Fluorescence spectra were recorded on a LS55 Perkin-Elmer Fluorescence spectrometer.

Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600–4000 cm⁻¹ region or using a Diamond ATR (Golden Gate).

TA Instruments Discovery system was used to perform the thermogravimetric analysis (TGA) using a 10 °C min⁻¹ heating rate under a nitrogen flow.

The powder X-ray diffraction (PXRD) patterns were collected by using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta-theta configuration, secondary monochromator with Cu-K α radiation ($\lambda = 1.5418$ Å) and a PIXcel solid state detector (active length in 2 θ 3.347°).

A slurry of **4** or **1** based cathode was prepared by mixing active material powder, Super C65 (Timcal) and a styrene-ethylene/butylene-styrene binder (Sigma-Aldrich) (20:70:10 wt.%) in NMP using a Flacktek Speedmixer (DAC 330-100 SE) at 3000 rpm for 5 minutes. The prepared slurry was cast onto a carbon coated aluminum current collector (Gelon energy Co. Limited, Linyi, China, 11 μ m thick) using a doctor blade casting method (200 μ m) and the solvent was allowed to evaporate for 24 h. The cathode electrode was then further dried under high vacuum at 50 °C for 24 h, resulting in a **4** or **1** loading of 1.0 and 0.6 mg cm⁻².

Cyclic voltammetry (CV) measurement were recorded in a three-electrode cell inside an argonfilled glovebox using a multi-channel Potentiostat (Biologic, VMP3). A platinum wire and lithium metal strip were used as counter and reference electrode, respectively. Glassy carbon electrode coated with active materials slurry was used as working electrode. A slurry of **4** or **1** based cathode was prepared by mixing active material powder, Super C65 (Timcal) and a PVDF (Solef[®] 5130) (50:40:10 wt.%) in NMP. A solution of 1.0 M lithium hexafluorophosphate in ethylene carbonate and diethyl carbonate (EC/DEC, 50/50 v/v) (Solvionic) was used as electrode for both CV and lithium metal cell.

Lithium metal battery were assembled in an argon-filled glovebox, using an 11 mm diameter lithium metal electrode (Gelon energy Co. Limited, Linyi, China, 100 µm thick). Galvanostatic cycling of lithium metal battery was performed using a battery cycler (Neware).

Calculations

Tight Binding docking calculations of Li on 4 were performed with the automated Interaction Site Screening (aISS) procedure with as implemented in the XTB v6.70 software package.^{1, 2} This yielded 320 adsorption sites after optimization with the GFN1-xTB Hamiltonian. Based on these, we selected 16 unique adsorption sites which were initially explored with DFT at the M06-2X-6-31G(d,p) level with closed shell and doublet multiplicities, Figure S12. These calculations were refined by screening different ground state multiplicities at the improved M06-2X-6-31+G(d,p) level in an acetone continuum as previously proposed for battery electrodes.³ Interestingly, convergence problems were found in reduced molecules adsorbed on imine N_{sp}^{2} atoms, indicating that the reduction on these sites is not only thermodynamically unfavored but electronically hindered. The atomic charges presented were computed with the CM5 procedure based on Hirshfield charges computed at the M06-2X 6-31+G(d,p)choloroform level. As a check, we also computed these charges at the B3LYP-6-31G(d,p)choloroform/M06-2X 6-31G(d,p)-choloroform level obtaining fundamentally the same results. The depicted molecular electrostatic potential was computed at the B3LYP-6-31G(d,p)choloroform while the presented reduction potentials were computed at the M06-2X-6-31+G(d,p)-acetone level with the SMD solvent continuum approach. All DFT calculations were performed with the Gaussian 16 Software.⁴ In addition, the packages GaussSum⁵ and Jmol⁶ were used to analyse the results and produce images depicting molecular orbitals, adsorption sites, electrostatic potentials and charges.

Diffusion coefficient analysis

Figure S14 shows the EIS curves of both the cage1 and reference **4** that was used to calculate the lithium diffusion coefficient D_{Li^+} . First the Warburg factor (σ) was extrapolated from the EIS data by plotting the Z' vs. $\omega^{-0.5}$ (See Figure 3d in main manuscript), using the following equation:

$$Z_{re} = R_e + R_{ct} + \sigma \omega^{-0.5}$$

Then the lithium diffusion coefficient D_{Li^+} was calculated by the following equation:

$$D_{Li^+} = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma^2$$

Where *R* is the gas constant, *T* is the temperature, *A* is the electrode area, *n* is the number of electrons involved in the redox reaction per lithium, *F* is the Faraday constant, σ is the Warburg factor and C the lithium concentration.



Tetrabromo dibenzotetraazahexacene⁷ (2.5 g, 3.0 mmol), Pd(PPh₃)₄ (0.7 g, 0.6 mmol) and K₂CO₃ (1.24 g, 9 mmol) were added to a 500 mL round bottom flask. The reaction mixture was kept under vacuum for 1 hr. Separately, DMF (130 mL) and water (43 mL) were degassed by bubbling nitrogen for 30 mins. Thereafter, the degassed solvents were added to the reaction mixture under nitrogen and heated up to 80 °C. Thereafter, compound 4-formyl phenylbornicacid (4.5 g, 30 mmol) was added to the hot mixture under nitrogen atmosphere. The reaction temperature was then raised to 100 °C and the reaction was stirred for 48 hrs under the N₂ atmosphere. After being cooled to room temperature, the reaction mixture was extracted with chloroform, washed well with water. The organic phase was collected, dried with sodium sulphate and evaporated under reduced pressure. The solid residue was washed several times with methanol and ethyl acetate followed by chromatographed on silica, eluting with chloroform, to afford the desired product **2** (2.2 g, 78%) as a yellow powder. The spectroscopic data is consistent with that reported previously.⁷

¹**H-NMR** (1,1,2,2-tetrachloroethane-*d*₂, 500 MHz, 298K) δ (ppm) : 10.09 (s, 4H), 9.91 (s, 4H), 8.63 (s, 4H), 7.90 (d, *J* = 7.7 Hz, 8H), 7.60 (d, *J* = 7.8 Hz, 8H), 1.82 (s, 18H).

¹³**C-NMR** (1,1,2,2-tetrachloroethane-*d*₂, 125 MHz, 298K) δ (ppm) : 191.50, 151.56, 146.27, 144.06, 141.70, 141.63, 135.56, 131.21, 130.06, 129.51, 129.37, 126.11, 125.46, 120.38, 35.90, 31.83.

MS MALDI (m/z): [M+H]⁺ Calculated for C₆₄H₄₆N₄O₄ 935.359; found 935.353.



Figure S19. ¹H-NMR spectrum of **2** (1,1,2,2-tetrachloroethane-d₂, 500 MHz, 298K). Asterisks indicate solvent residual peaks.



Figure S20. ¹³C-NMR spectrum of **2** (1,1,2,2-tetrachloroethane-d₂, 125 MHz, 298K). Asterisks indicate solvent residual peaks.



Compound **2** (1 mmol, 0.93 g) was taken in a round bottom flask containing 150 ml of chloroform and subsequently, catalytic amount of trifluoroacetic acid (TFA) (1 drop) was added into it. The solution was followed by the addition of excess cyclohexyl amine (10 mmol, 1 g), solubilized in 30 ml of CHCl₃. Thereafter, the reaction mixture was allowed to stir overnight at RT, under N₂ atmosphere. The completion of the reaction was monitored by TLC. The reaction mixture was then concentrated by evaporation and hexane was added into it. Resulting precipitate was filtered off and washed several times with hexane, methanol and minimum volume of dichloromethane. The precipitate was then dried well under the vacuum to obtain the 4 as bright yellow powder (1.13 g, 90%).

¹**H-NMR** (1,1,2,2-tetrachloroethane-*d*₂, 400 MHz, 298K) δ (ppm): 9.82 (s, 4H), 8.53 (s, 4H), 8.35 (s, 4H), 7.72 (d, *J* = 7.9 Hz, 8H), 7.45 (d, *J* = 7.9 Hz, 8H), 3.29-3.19 (br. m, 4H), 1.90-1.82 (br. m, 8H), 1.77 (s, 18H), 1.73-1.67 (br. m, 8H), 1.59-1.53 (br. m, 8H), 1.46-1.27 (br. m, 16H).

¹³**C-NMR** (1,1,2,2-tetrachloroethane-*d*₂, 125 MHz, 298K) δ (ppm) : 157.87, 151.09, 143.52, 142.58, 142.33, 141.57, 135.87, 130.86, 130.68, 130.14, 128.77, 127.95, 125.76,124.9, 69.52, 35.87, 34.46, 31.88, 25.85, 24.87.

MS MALDI (m/z): [M+H]⁺ Calculated for C₈₈H₉₀N₈ 1259.737; found 1259.703.



Figure S21. ¹H-NMR spectrum of **4** (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 298K). Asterisks indicate solvent residual peaks.



Figure S22. ¹³C-NMR spectrum of **4** (1,1,2,2-tetrachloroethane- d_2 , 125 MHz, 298K). Asterisk indicate solvent residual peak.



Compound 2^7 (1.20 mmol, 1.12 g) was taken in an oven dried 500 ml round bottom flask containing 350 ml of anhydrous chloroform and subsequently, catalytic amount of TFA (2 drops) was added into it. The solution was followed by the slow addition of (1*R*, 2*R*) -1, 2-diamino cyclohexane (3) (2.52 mmol, 0.289 g), solubilized in 100 ml of anhydrous CHCl₃. Thereafter, the reaction mixture was allowed to stir for 5 days at RT, under N₂ atmosphere. After 5 days, the slightly opaque reaction mixture was filtered and concentrated by evaporation at RT. Thereafter, the concentrated solution was precipitated by adding anhydrous hexane into it. The resulting precipitate was then filtered off and further washed well with anhydrous hexane, dry methanol and minimum amount of anhydrous dichloromethane. The precipitate was then dried well under the vacuum to obtain the 1 as a yellowish orange powder (0.97 g, 77%).

¹**H-NMR** (1,1,2,2-tetrachloroethane-*d*₂, 500 MHz, 298K) δ (ppm) : 9.24-8.83 (br. m, 12H), 8.57-8.33 (br. m, 12H), 8.03-7.85 (br. m, 12H), 7.79-7.53 (br. m, 24H), 7.39-7.12 (br. m, 24H), 3.54-3.08 (br. m, 12H), 2.12-1.87 (br. m, 24H), 1.65 – 1.46 (br. m, 54H), 1.46-1.38 (br. m, 24H).

¹³**C-NMR** (1,1,2,2-tetrachloroethane- d_2 , 125 MHz, 298K) δ (ppm): Because of the limited solubility of cage **1**, the spectra show broad signals. Some of the signals are consistent with the formation of imines, see Figures S1 and S14.

MS MALDI (m/z): [M+Ag]⁺ Calculated for C₂₂₈H₁₉₈N₂₄ 3381.538; found 3381.585.



Compound **4** (0.04 mmol, 0.05 g) was taken in an oven dried 100 ml round bottom flask containing 30 ml of anhydrous chloroform and subsequently, catalytic amount of TFA (1 drop) was added into it. The solution was followed by the slow addition of (1*R*, 2*R*) -1, 2-diamino cyclohexane (**3**) (0.16 mmol, 0.02 g), solubilized in 12 ml of anhydrous CHCl₃. Thereafter, the reaction mixture was allowed to stir for 5 days at RT, under N₂ atmosphere. After 5 days, the slightly opaque reaction mixture was filtered and concentrated by evaporation at RT. Thereafter, the concentrated solution was precipitated by adding anhydrous hexane into it. The resulting precipitate was then filtered off and further washed well with anhydrous hexane, dry methanol and minimum amount of anhydrous dichloromethane. The precipitate was then dried well under the vacuum to obtain the **1** as a yellowish orange powder (0.03 g, 68%).



Figure 23. ¹H-NMR spectrum of **1** (1,1,2,2-tetrachloroethane- d_2 , 500 MHz, 298K). Asterisk indicate solvent residual peak.



Figure S24. ¹³C-NMR spectrum of **1** (1,1,2,2-tetrachloroethane- d_2 , 125 MHz, 298K). Asterisk indicate solvent residual peak.

References

- 1. P. Pracht, F. Bohle and S. Grimme, Automated exploration of the low-energy chemical space with fast quantum chemical methods, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169-7192.
- 2. C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher and S. Grimme, Extended tight-binding quantum chemistry methods, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2021, **11**, e1493.
- 3. O. Borodin, M. Olguin, C. E. Spear, K. W. Leiter and J. Knap, Towards high throughput screening of electrochemical stability of battery electrolytes, *Nanotechnology*, 2015, **26**, 354003.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.
- 5. N. M. O'boyle, A. L. Tenderholt and K. M. Langner, cclib: A library for packageindependent computational chemistry algorithms, *J. Comput. Chem.*, 2008, **29**, 839-845.
- 6. Jmol: an open-source Java viewer for chemical structures in 3D. <u>http://www.jmol.org/</u>
- E. De Bolòs, M. Martínez-Abadía, F. Hernández-Culebras, A. Haymaker, K. Swain, K. Strutyński, B. L. Weare, J. Castells-Gil, N. M. Padial, C. Martí-Gastaldo, A. N. Khlobystov, A. Saeki, M. Melle-Franco, B. L. Nannenga and A. Mateo-Alonso, A Crystalline 1D Dynamic Covalent Polymer, J. Am. Chem. Soc., 2022, 144, 15443-15450.