

Electronic Supplementary Information (ESI)

Lithiated Polycalix[4]arenes for Efficient Adsorption of Iodine from Solution and Vapor Phases

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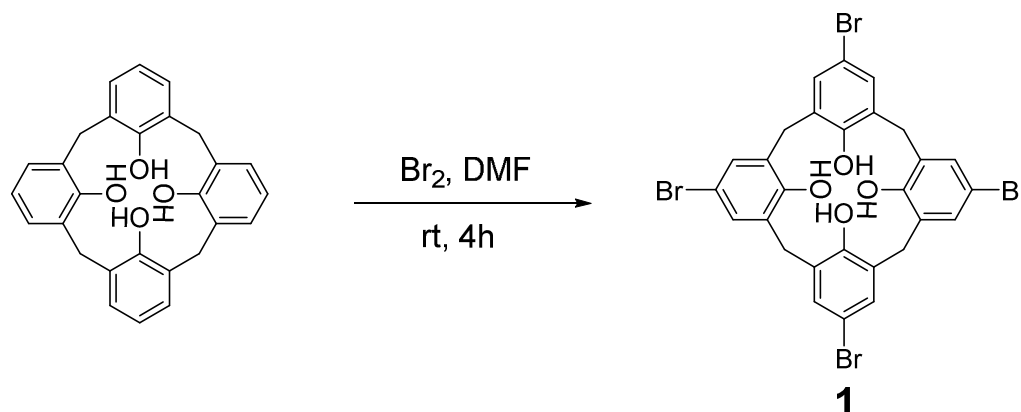
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General. All the chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Deionized water was used from Millipore Gradient Milli-Q water purification system. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). The plates were inspected with UV light. Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance spectrometer, with working frequencies of 500 MHz for ^1H , and 125.7 MHz for ^{13}C nuclei, respectively. All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent (DMSO-d_6 : $\delta = 2.50$ ppm).

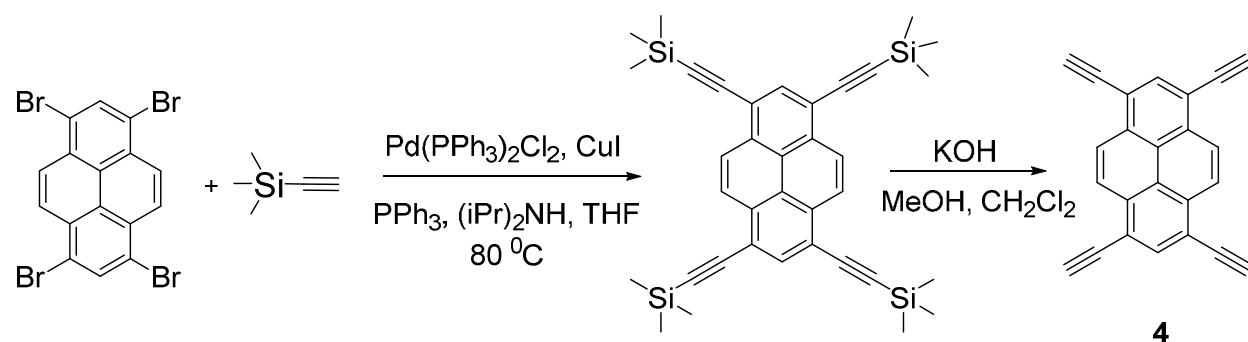
Materials characterization. FTIR studies were carried out on Agilent 670-IR spectrometer. TGA experiments were performed on a TA SDT Q600. SEM images were obtained from FEI Quanta 450FEG. TEM images were obtained from a FEI-Titan 300. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra of the polymers were recorded on a Bruker Avance 500 Wide Bore (500MHz) NMR spectrometer at ambient temperature with a magic angle spinning rate of 18.0 kHz. Solid-state magic angle spinning ^7Li -MAS NMR spectra of the polymers were recorded on a Bruker Avance-I (300MHz) NMR spectrometer at resonance frequency 107.7 MHz. We used a MAS double resonance probe designed for 4 mm o.d. zirconia spinners, and all the sample were spun at 10 kHz, at room temperature. UV-Vis studies were carried out on Cary 5000 UV-Vis-NIR spectrophotometer. All UV-Vis spectra were recorded at room temperature using a quartz cell with 10 mm or 1 mm path length over the range 200–800 nm and corrected against an appropriate background spectrum. Surface area measurements were conducted on a Micromeritics 3Flex gas sorption analyzer. Samples (50–150 mg) were degassed at 85 °C for 24 h and then backfilled with N_2 . Adsorption isotherms were generated by incremental exposure to ultrahigh-purity nitrogen up to 1 atm in a liquid nitrogen bath, and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). The elemental information and oxidation states of Li in the solid samples were analyzed using X-ray Photoelectron spectroscopy (XPS, Kratos AXIS UltraDLD). High resolution of I 3d and Li 1s XPS spectra was collected using monochromatic Al K α (1486 eV) X-ray source at 40 eV or 20 eV of pass energy with 4 sweeps and then calibrated with 483.5 eV

of C 1s XPS spectra, while a wide survey scan of the solid samples was collected at pass energy of 80 eV with 2 sweeps for identification of the all elemental information.

Synthesis of 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydrocalix[4]arene (**1**).¹



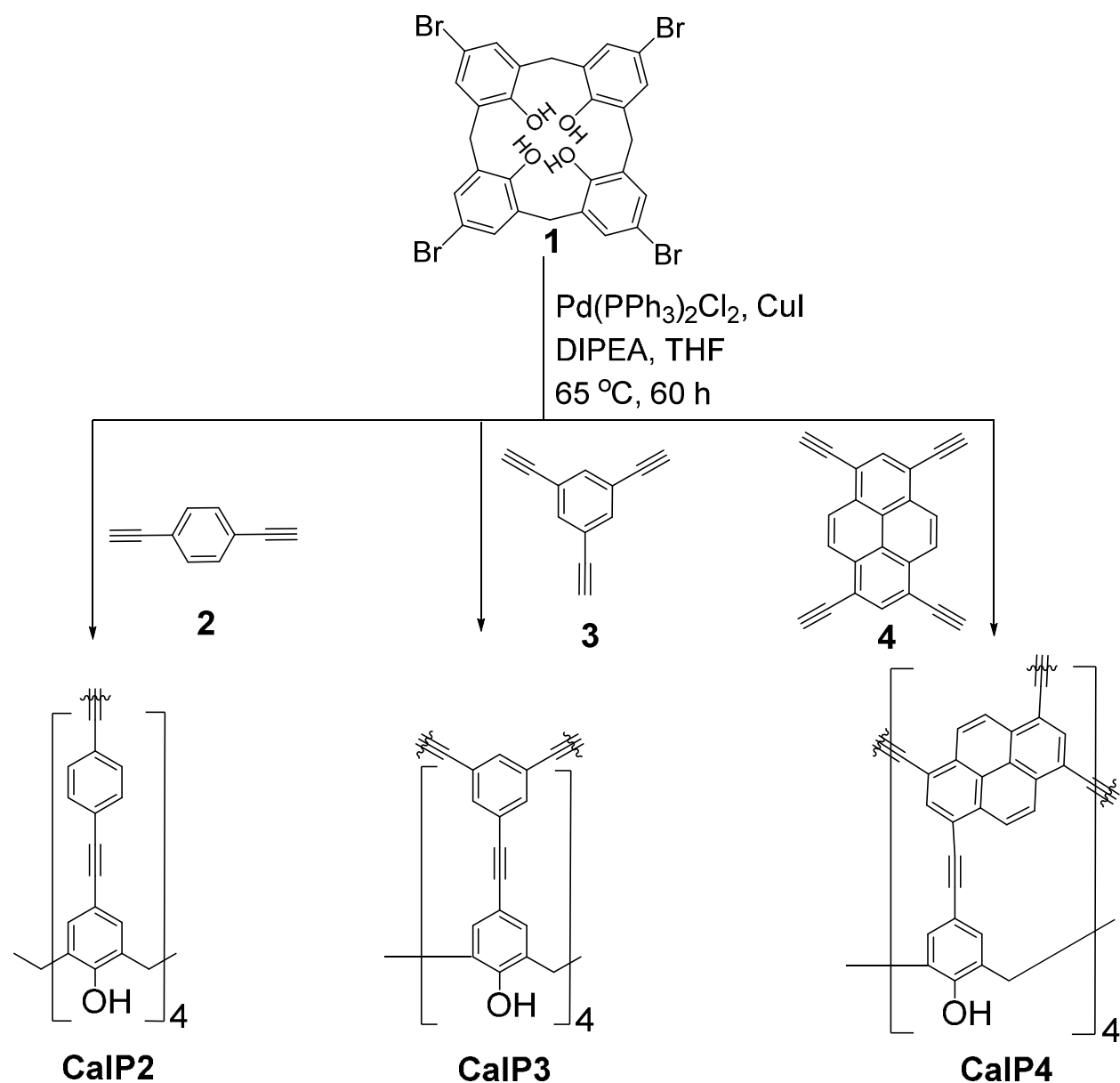
Bromine (0.4 mL, 7.84 mol) in DMF (5 mL) was added dropwise with stirring to a solution of calix[4]arene (0.5 g, 1.18 mmol) in DMF (20 mL). The solution was stirred for 4 h. A precipitate began to form after about 0.5 h. After the 4 h of reaction, methanol (20 mL) was added, and the mixture was left to stir for an additional 0.5 h. The precipitate was filtered off and washed with methanol to yield the brominated product, **1** (0.75 g, 87%) as a white solid. ^1H NMR ($[\text{D}_6]\text{DMSO}$, 25 °C, 500 MHz): δ = 7.34 (s, 8H), 3.81 ppm (br s, 8H). ^{13}C NMR ($[\text{D}_6]\text{DMSO}$, 25 °C, 125.7 MHz): δ_{c} = 151.8, 131.98, 131.08, 110.89, 30.94 ppm.



1,3,6,8-Tetrakis(trimethylsilyl)ethynylpyrene.² Compound 1,3,6,8-Tetrabromopyrene (1.0 g, 1.93 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (67 mg, 0.096 mmol), CuI (18 mg, 0.096 mmol), PPh_3 (50 mg, 0.193

mmol), and the terminal alkyne (11.6 mmol) were added to a degassed solution of diisopropylamine (20 mL) and THF (20 mL) under argon. The resulting mixture was stirred at 70 °C for 48 h. The reaction mixture was then cooled to room temperature and solvent was removed to give the crude reaction mixture. Column chromatographic purification of the crude product on silica gel with hexane as the eluent yielded a red orange solid (0.72 g, 66%). ¹H NMR (CDCl₃, 25 °C, 500 MHz): δ = 8.51 (s, 4 H), 8.26 (s, 2 H), 0.37 (s, 36 H) ppm. ¹³C NMR (CDCl₃, 25 °C, 125.7 MHz): δ = 134.5, 131.9, 126.8, 123.4, 118.5, 102.8, 101.3, 0.1 ppm.

1,3,6,8-Tetraethynylpyrene (4). To remove the silyl-protection groups, the filtrate was dissolved in ethanol (500 mL) in the presence of KOH (5 g), and stirred overnight. Two-thirds of solvent was removed by evaporation, and gradual addition of water gave a pale brownish precipitate. It was extracted using methylene chloride several times. Removal of the solvent gave the product **1** ¹H NMR ([D₈]THF, 25 °C, 500 MHz): δ = 8.68 (s, 4 H), 8.34 (s, 2 H), 4.28 (s, 4 H) ppm. ¹³C NMR ([D₈]THF, 25 °C, 125.7 MHz): δ = 135.7, 132.6, 127.3, 123.5, 119.1, 86.3, 81.9 ppm.



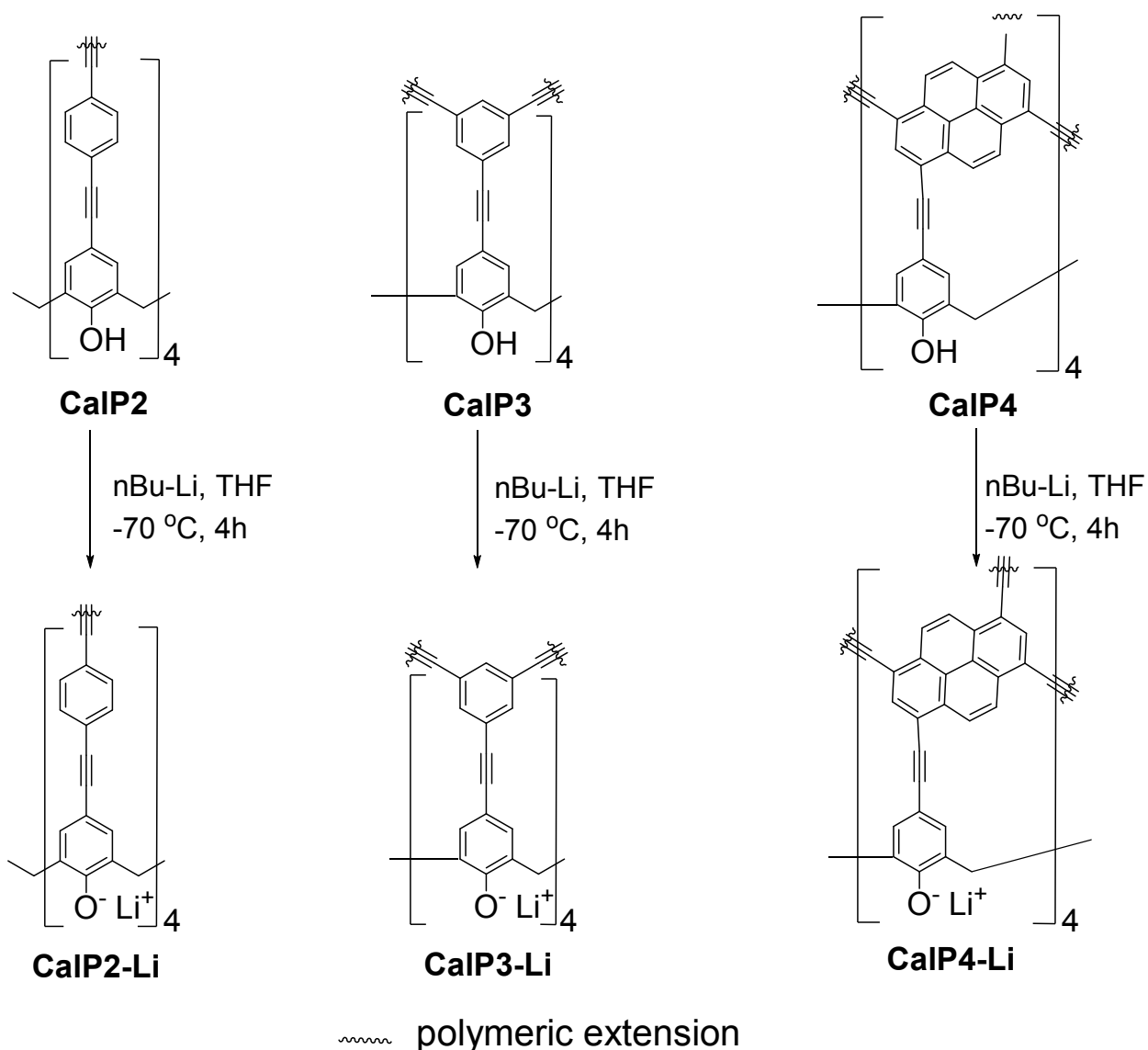
General procedure for the synthesis of polymer. A solution of 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene, bis(triphenylphosphine)palladium(II) chloride, and copper(I) iodide in anhydrous THF were placed in a 250 mL two-neck round-bottom flask equipped with a condenser. Diisopropylamine and alkyne were loaded into a separate 50 mL flask. Both solutions were purged with argon for at least 15 min. The ethynyl-compound solution was then added dropwise over 5 min to the calixarene solution with stirring to afford a dark brown reaction mixture after 5 min. The reaction was heated at 65°C under argon for 60 h. After cooling to room temperature, the solid product was centrifuged and washed with excess

(cold and hot) THF, DMA, CHCl₃, EtOH, and (cold and hot) H₂O to remove any unreacted monomers and metal catalyst residues. The final products were dried under a vacuum for 16 h at 60 °C.

CalP2: 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (1.0 g, 1.36 mmol), 1,4-diethynylbenzene (0.34 g, 2.72 mmol), bis(triphenylphosphine)palladium(II) chloride (0.285 g, 0.45 mmol), copper(I) iodide (0.13 g, 0.68 mmol), Diisopropylamine (1 mL), and tetrahydrofuran (100 mL).

CalP3: 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (1.0 g, 1.36 mmol), 1,3,5-triethynylbenzene (0.275 g, 1.8 mmol), bis(triphenylphosphine)palladium(II) chloride (0.285 g, 0.45 mmol), copper(I) iodide (0.13 g, 0.68 mmol), Diisopropylamine (1 mL), and tetrahydrofuran (100 mL).

CalP4: 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (1.0 g, 1.36 mmol), 1,3,6,8-Tetraethynylpyrene (0.405 g, 1.36 mmol), bis(triphenylphosphine)palladium(II) chloride (0.285 g, 0.45 mmol), copper(I) iodide (0.13 g, 0.68 mmol), Diisopropylamine (1 mL), and tetrahydrofuran (160 mL).



General procedure for the synthesis of lithiated-polymer. 0.2 g of each polymer (CalP2, CalP3, or CalP4) was immersed in anhydrous THF under argon atmosphere. The reaction mixture was stirred vigorously and cooled to -70 °C. 3 mL of 2.0 M n-butyl lithium in cyclohexene was introduced slowly to the reaction flask while maintaining the temperature at -78 °C and continued stirring at same temperature for 4h. After bringing the reaction flasks to room temperature, solid polymer was centrifuged and washed with anhydrous THF for 5 times. The resulting solid was dried under inert atmosphere and heated to 120 °C for 16 h to remove the trapped impurities.

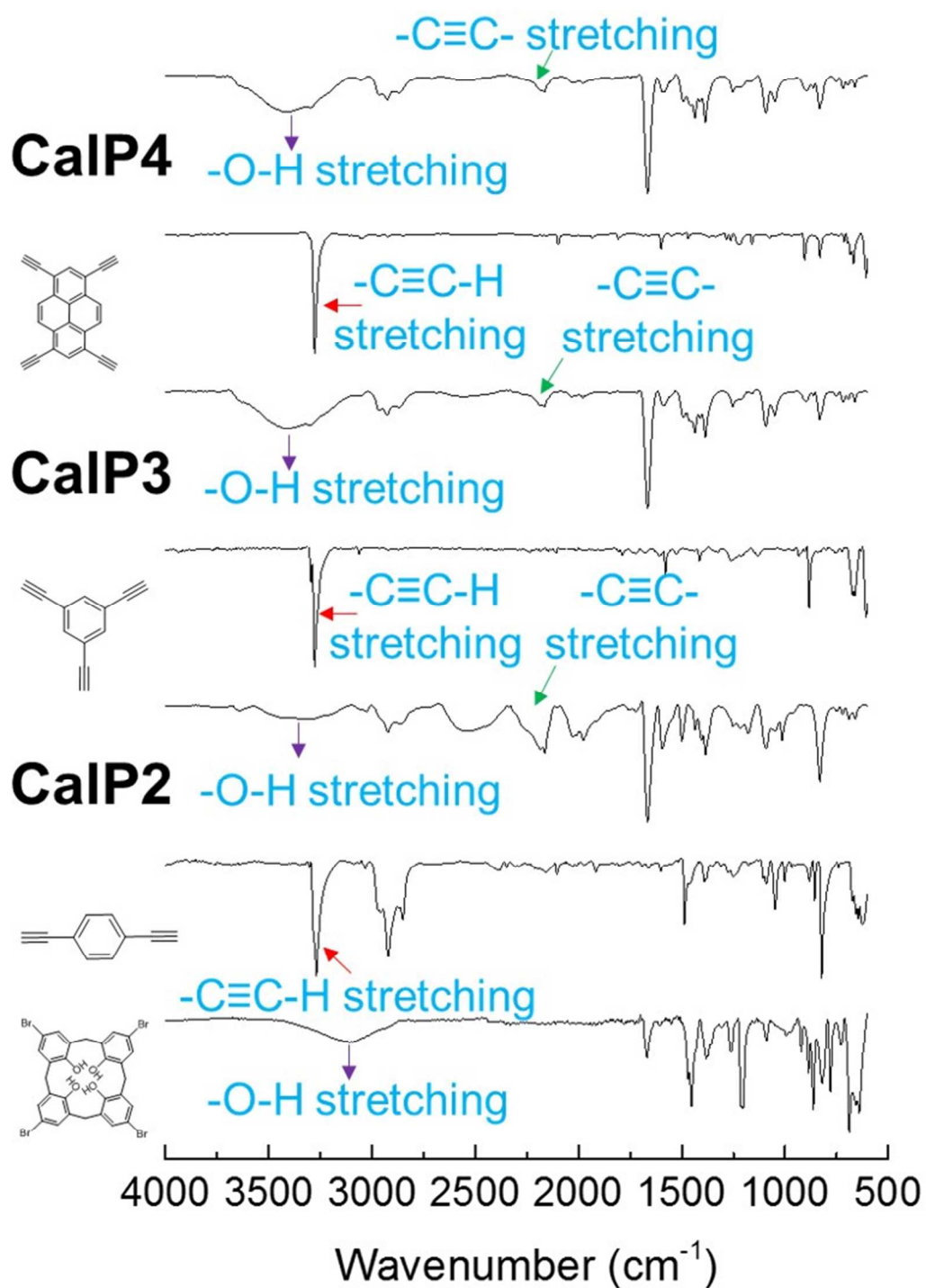


Figure S1. FTIR spectra of CalP2, CalP3, CalP4, and corresponding monomers.

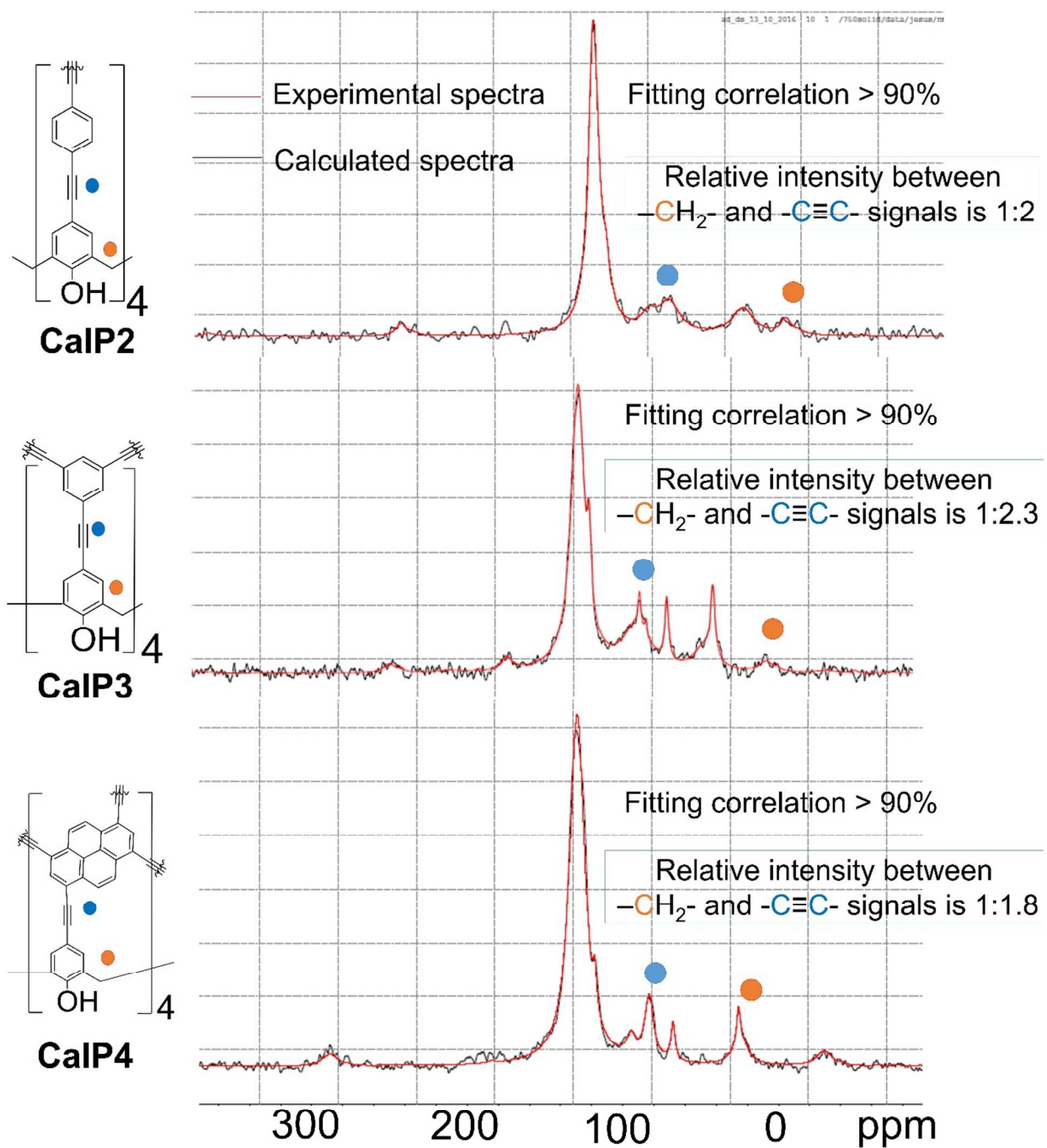


Figure S2. ^{13}C DP/MAS NMR spectrum of **CalP n** ($n = 2-4$). Experimental spectra and calculated fitting with solid-state NMR parameters that shows over 90% overlap during the interpretation of NMR signals indicate the relative peak intensity between methylene ($-\text{CH}_2-$, orange) carbons of calix[4]arene and acetylene carbons ($-\text{C}\equiv\text{C}-$, blue) conjugated to the macrocycle is $\sim 1:2$.

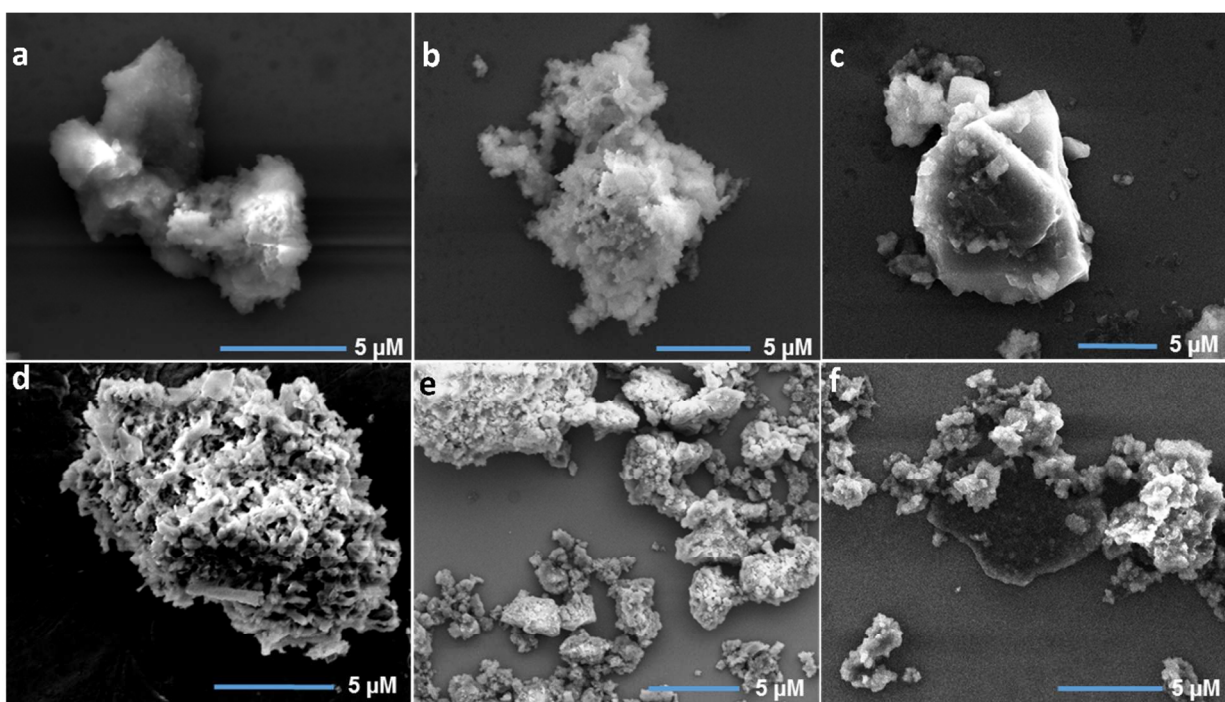


Figure S3. Low-magnification SEM images of **CalP2** (a), **CalP3** (b), and **CalP4** (c), **CalP2-Li** (d), **CalP3-Li** (e), and **CalP4-Li** (f); scale bar = 5 μm . High-resolution.

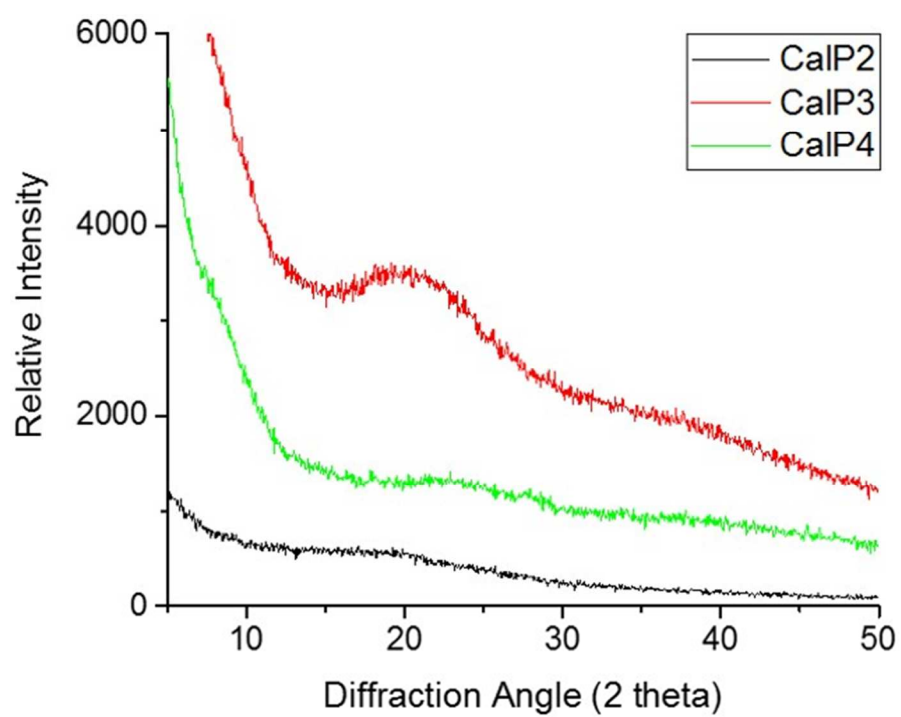


Figure S4. Powder X-ray diffraction (PXRD) pattern of **CalP2** (black), **CalP3** (red), and **CalP4** (green).

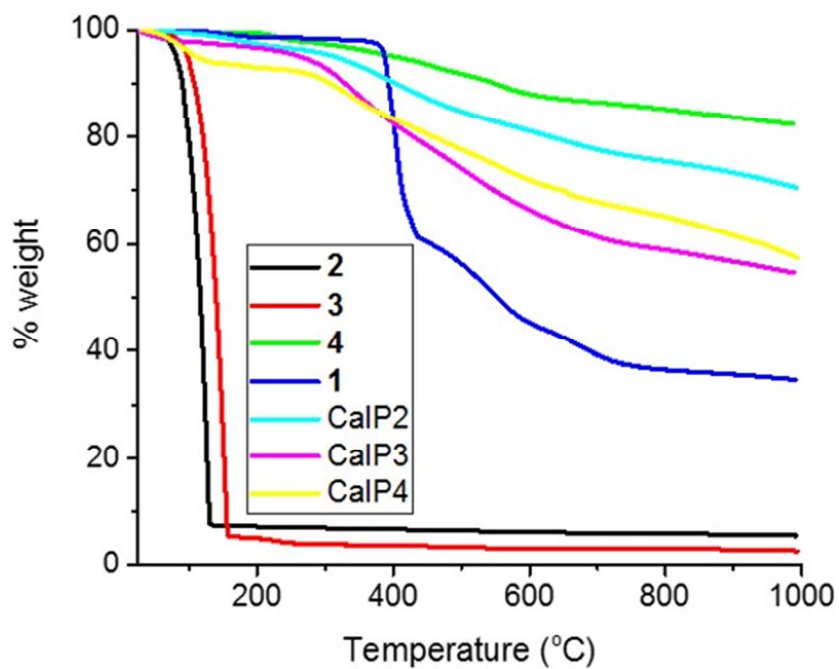


Figure S5. TGA plots for **CalP2** (green), **CalP3** (pink), **CalP4** (yellow), 1,4-diethynylbenzene (**2**, black), 1, 3, 5-triethynylbenzene (**3**, red), 1,3,6,8-Tetraethynylpyrene (**4**, green) and tetrabromocalix[4]arene (**1**, blue).

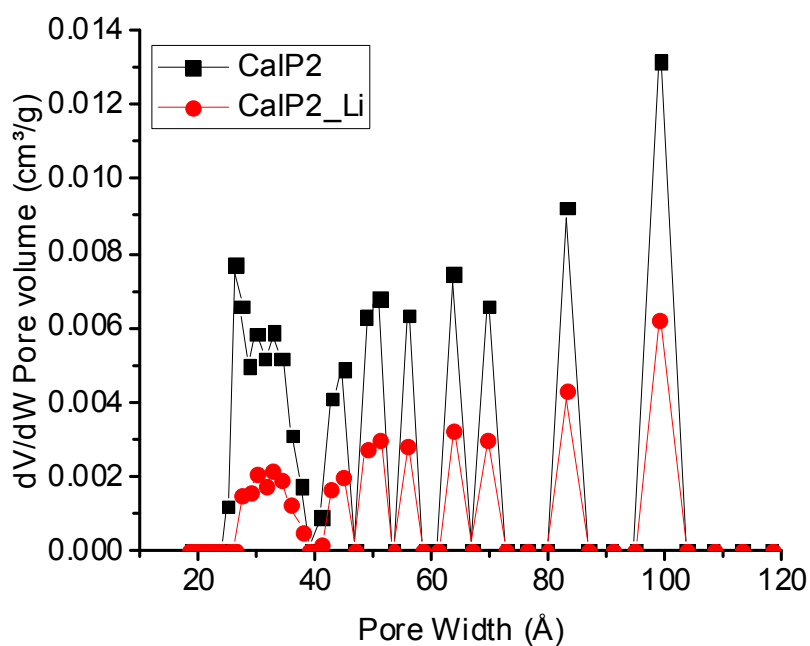


Figure S6. NLDT pore size distribution for **CalP2** and **CalP2-Li** determined from N₂ adsorption/desorption isotherms.

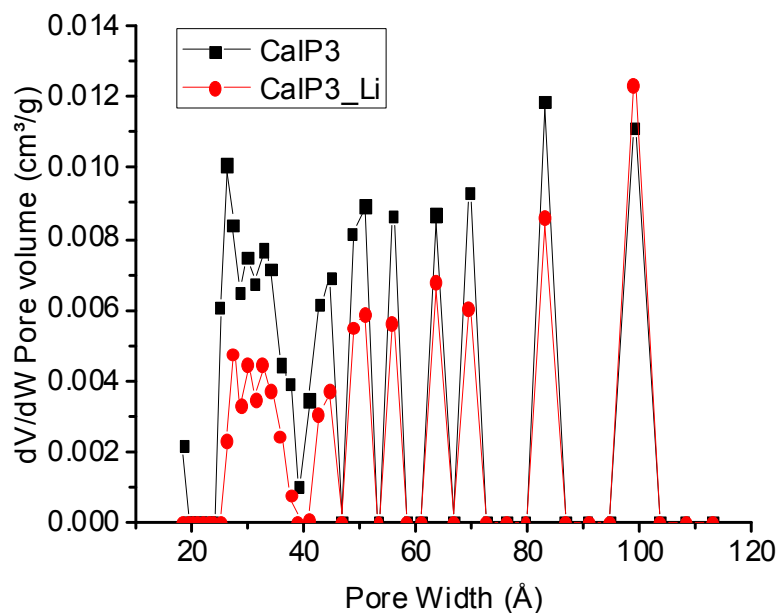


Figure S7. NLDT pore size distribution for **CalP3** and **CalP3-Li** determined from N₂ adsorption/desorption isotherms.

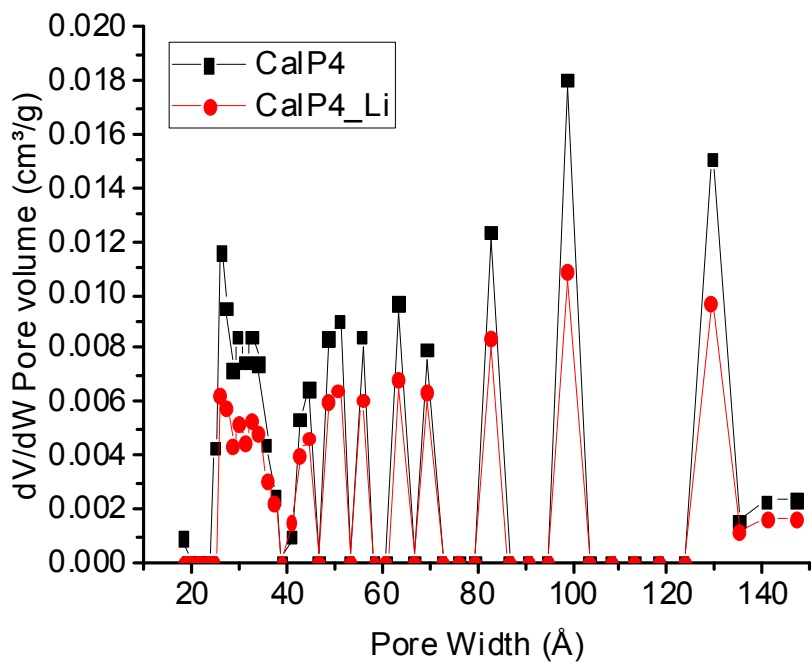


Figure S8. NLDFT pore size distribution for **CalP3** and **CalP3-Li** determined from N₂ adsorption/desorption isotherms.

Iodine capture and recycling measurement. Samples were prepared as follows: 25 mg of polymeric powder was placed in glass petri which was placed in a sealed glass chamber containing solid iodine flakes which were placed below the top level of the petri dish. The chamber with sample was placed on pre-heated (348 K) sand bath at ambient pressure and continued heating at same temperature. After adsorption of the iodine vapor over (for 0-24 h), the I₂-loaded powder was cooled to room temperature and weighed. Iodine uptake capacity was calculated as follows: $C_u = (W_2 - W_1)/W_1 \times 100$ wt %, with C_u being the iodine uptake capacity and W_1 and W_2 being mass of the polymer before and after adsorption, respectively. Recycling of the polymer was performed by washing the I₂-loaded polymer repeatedly with 10 mL aliquots of EtOH. Iodine release was monitored by UV-visible analysis of the EtOH solution. After complete release of I₂, the recovered polymer was dried and used again for iodine adsorption.

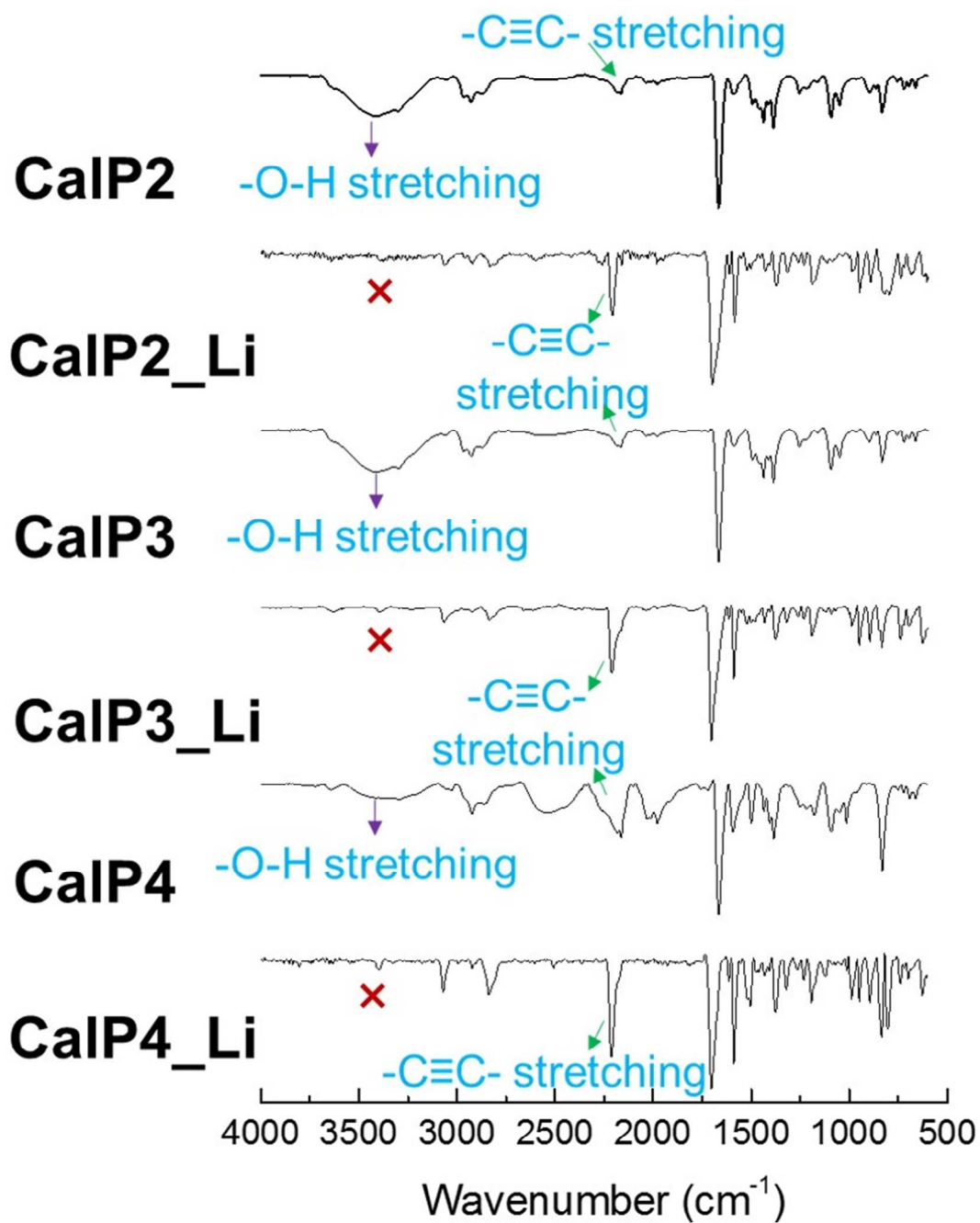


Figure S9. FTIR spectra of CalP2, CalP3, CalP4, and their corresponding lithiated polymers (CalP2-Li, CalP3-Li, and CalP4-Li).

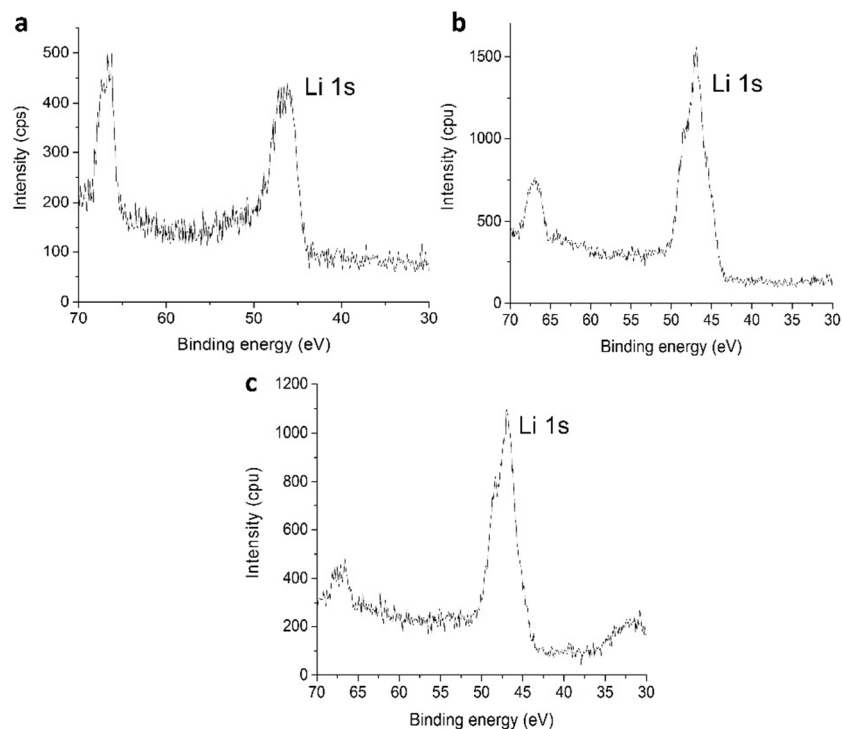


Figure S10. XPS spectrum of CalP2-Li (a), CalP3-Li (b) and CalP4-Li (c)

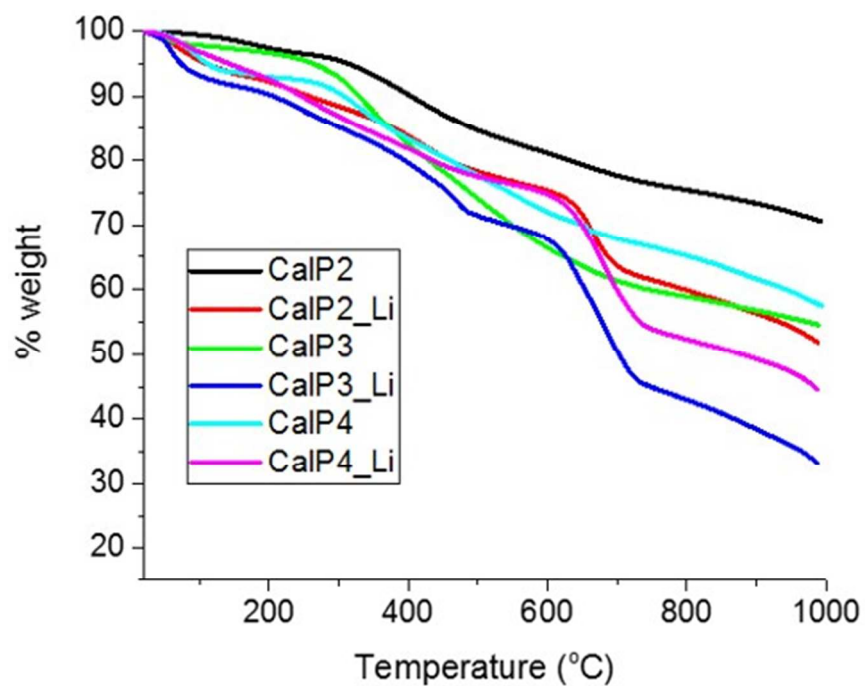


Figure S11. TGA plots for CalP2 (black), CalP2-Li (red), CalP3 (green), CalP3-Li (blue), CalP4 (magenta) and CalP4-Li (pink).

Table S1: Comparison of iodine uptake capacities of our materials with those of other reported materials.

Material	Sorption method	Adsorption time	Temp. (K)	I ₂ vapor uptake (wt %)	Reference
PAF-1	Fixed vapor pressure	10 h (In n-hexane)	333	74.2	<i>J. Mater. Chem. A</i> , 2014 , 2, 7179-7187
JUC-Z2	Vacuum swing adsorption	10 h (In nhexane)	298	59.0	<i>J. Mater. Chem. A</i> , 2014 , 2, 7179-7187
JUC-Z2	Fixed vapor pressure	10 h (In nhexane)	333	80.4	<i>J. Mater. Chem. A</i> , 2014 , 2, 7179-7187
{[Zn ₃ (DLlac) ₂ (pybz) ₂]·2.5DMF} _n	Vapor adsorption/Cyclohexane	90min(Vapor) 48h(Cyclohexane)	-	82.6	<i>J. Am. Chem. Soc.</i> 2010 , 132, 2561–2563
PAF-24	Vapor adsorption/Cyclohexane	48h(Vapor) 72h (cyclohexane)	348	276	<i>Angew. Chem. Int. Ed.</i> 2015 , 54, 12733 – 12737
Azo-Trip	Vapor adsorption/Cyclohexane	48h (Vapor) 36h(cyclohexane)	350	233	<i>Polym. Chem.</i> , 2016 , 7, 643–647
NiP-CMP	Vapor adsorption/Cyclohexane	48h (Vapor) 24h (cyclohexane)	350	202	<i>Chem. Commun.</i> , 2014 , 50, 8495-8498
[Mo ₃ S ₁₃]	Vapor	24 h	333	100	<i>J. Am. Chem. Soc.</i> 2015 , 137, 13943–13948
Sb ₄ Sn ₃ S ₁₂ , Zn ₂ Sn ₂ S ₆ , and K _{0.16} CoS _x	Vapor	48h	348	225	<i>Chem. Mater.</i> 2015 , 27, 2619–2626
(BEA) ₂ [PbBr ₄]	Vapor	4-72h	313	43	<i>Angew. Chem. Int. Ed.</i> 2014 , 53, 1039–1042
SCMP-II	Vapor	60 min	353	345	<i>Chem. Commun.</i> 2016 , 52, 9797-9800
HCMP-3	Vapor	40 min	358	336	<i>Macromolecules</i> 2016 , 49, 6322-6333
COP-Series	Vapor/Cyclohexane	3-5 min	333	195-380	<i>J. Mater. Chem. A</i> , 2016 , 4, 15361-15369
TTPB	Vapor	12 h	350	443	<i>J. Mater. Chem. A</i> , 2017 , 5, 7612-7617
CalP2	Vapor/hexane	8h	343	88	<i>This work</i>
CalP3	Vapor/hexane	8h	343	196	<i>This work</i>
CalP4	Vapor/hexane	8h	343	220	<i>This work</i>
CalP2_Li	Vapor/hexane	6h	343	108	<i>This work</i>
CalP3_Li	Vapor/hexane	2h	343	248	<i>This work</i>

CalP4_Li	Vapor/hexane	30 min	343	312	<i>This work</i>
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N.B: Equilibrium uptake in weight (%) $\alpha = (m_2 - m_1)/m_1 \times 100$ wt%, m_1 = Sample mass and m_2 = (Sample + iodine) mass.

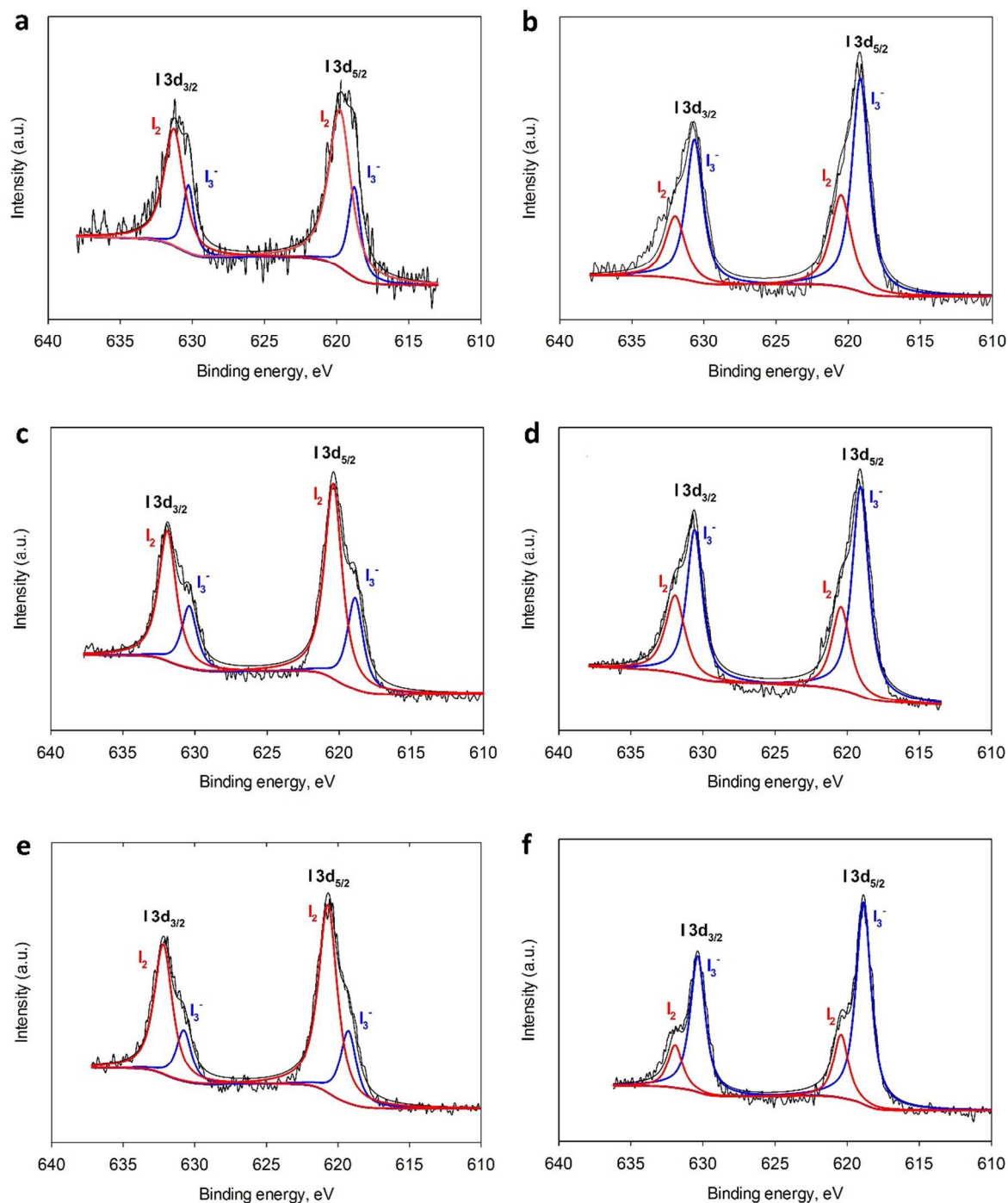


Figure S12. Deconvoluted XPS spectra of I₂-loaded **CalP2** (a), **CalP2-Li** (a), **CalP3** (c), **CalP3-Li** (d), **CalP4** (e) and **CalP4-Li** (f). Region of interest is iodine potential.

Sample	S.O.S [*]	O.S.I ^{**}	B.E. (eV)	FWHM ^{***}	Area	% Area	I ₂ /I ₃ ⁻
CalP2-Li	I 3d _{3/2}	I ₂	631.9	1.67	3028	13.7	0.52
		I ₃ ⁻	630.7	1.40	5809	26.3	
	I 3d _{5/2}	I ₂	620.5	1.70	4542	20.6	
		I ₃ ⁻	619.2	1.40	8715	39.4	
CalP3-Li	I 3d _{3/2}	I ₂	631.9	1.58	4789	17.0	0.51
		I ₃ ⁻	630.6	1.29	7428	26.4	
	I 3d _{5/2}	I ₂	620.4	1.48	4788	17.0	
		I ₃ ⁻	619.1	1.37	11143	39.6	
CalP4-Li	I 3d _{3/2}	I ₂	631.9	1.19	1762	9.30	0.30
		I ₃ ⁻	630.4	1.25	5799	30.8	
	I 3d _{5/2}	I ₂	620.4	1.22	2644	13.9	
		I ₃ ⁻	618.8	1.26	8699	46.0	
CalP2	I 3d _{3/2}	I ₂	631.3	1.64	1867	30.3	3.13
		I ₃ ⁻	630.3	0.9	597	9.69	
	I 3d _{5/2}	I ₂	619.8	1.82	2802	45.5	
		I ₃ ⁻	618.8	1.02	896	14.5	
CalP3	I 3d _{3/2}	I ₂	631.9	1.45	7362	28.2	2.39
		I ₃ ⁻	630.4	1.27	3097	11.8	
	I 3d _{5/2}	I ₂	620.4	1.46	11044	42.3	
		I ₃ ⁻	618.9	1.31	4646	17.7	
CalP4	I 3d _{3/2}	I ₂	632.2	1.50	5764	29.9	2.96
		I ₃ ⁻	630.8	1.27	1929	10.1	
	I 3d _{5/2}	I ₂	620.7	1.56	8647	44.9	
		I ₃ ⁻	619.3	1.35	2894	15.1	

*S.O.S = Spin-orbit splitting

**O.S.I = Oxidation states of iodine

***FWHM = Full width at half-maximum of a peak

Table S2. Summary of I 3d XPS spectra of solid samples

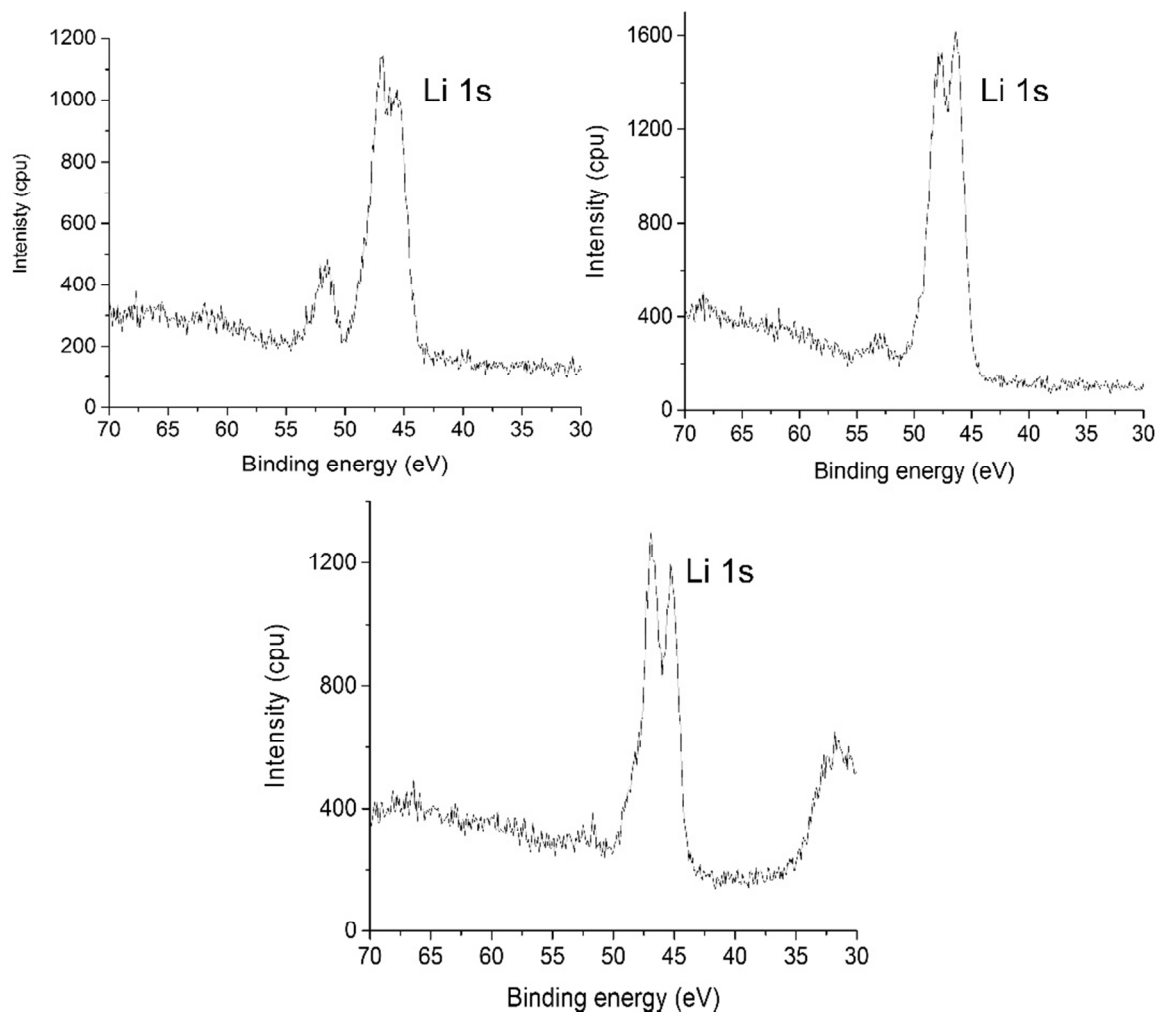


Figure S13. XPS spectrum of I₂-loaded **CalP2** (a), **CalP2-Li** (a), **CalP3** (c), **CalP3-Li** (d), **CalP4** (e) and **CalP4-Li** (f). Region of interest is lithium potential.

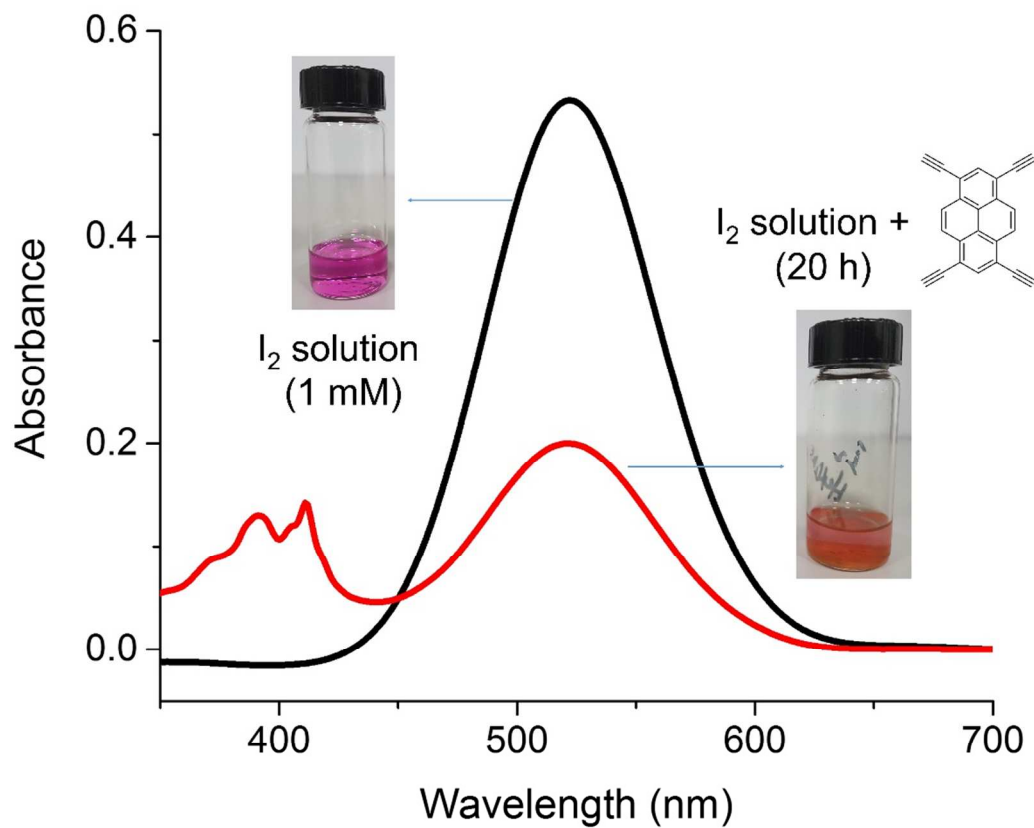


Figure S14. UV-visible absorption spectra of I_2 stock solution (1 mM in hexane) before and after treating with **4**. UV-intensity of the I_2 solution soaked with **4** was decreased mainly due to the interactions between pi-surface of **4** and I_2 molecules.

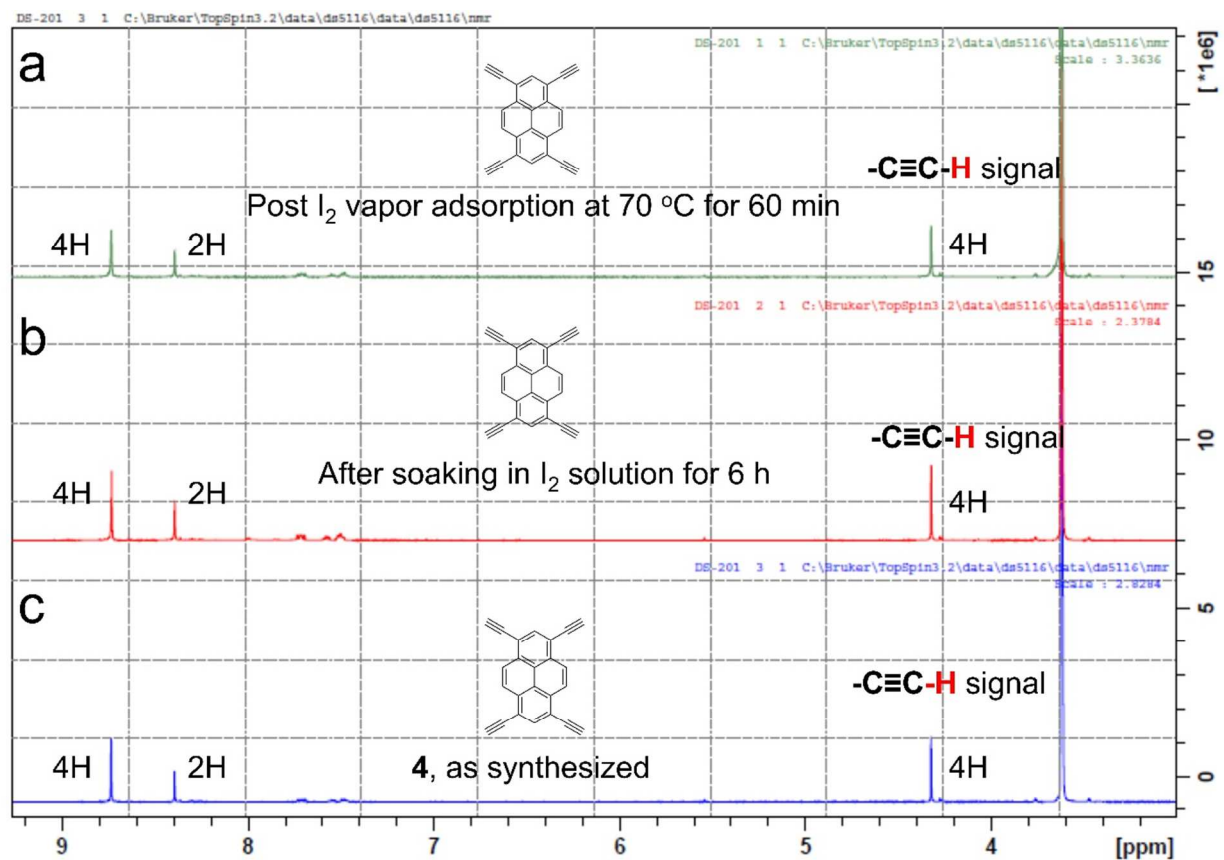


Figure S15. ^1H NMR spectra (500 MHz, THF-d_8) of (a) **4** after I_2 vapor adsorption at 70°C for 60 min, (b) **4** after soaking in high concentration I_2 solution in hexane, and (c) **4** as synthesized recorded at 298 K, respectively. There is no bond formation between acetylene bonds of **4** and I_2 , which was indicated by intact $-\text{C}\equiv\text{C}-\text{H}$ proton signals.

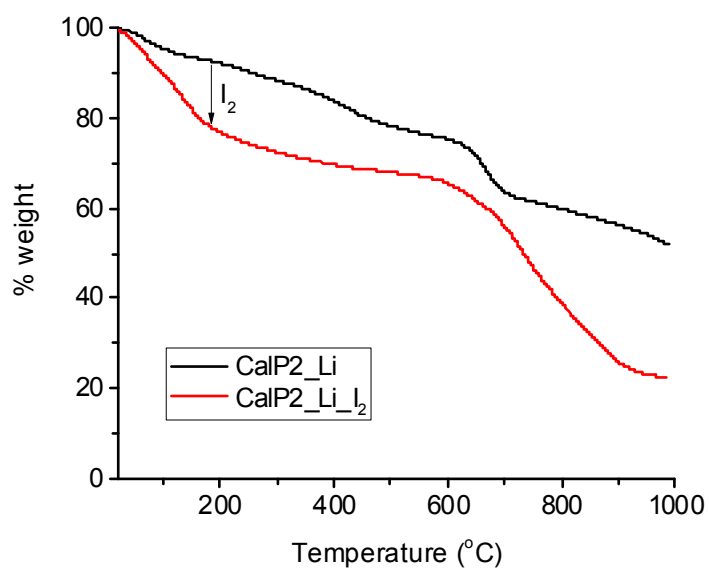


Figure S16. TGA plots for **CalP2-Li** before (black) and after (red) I₂ adsorption.

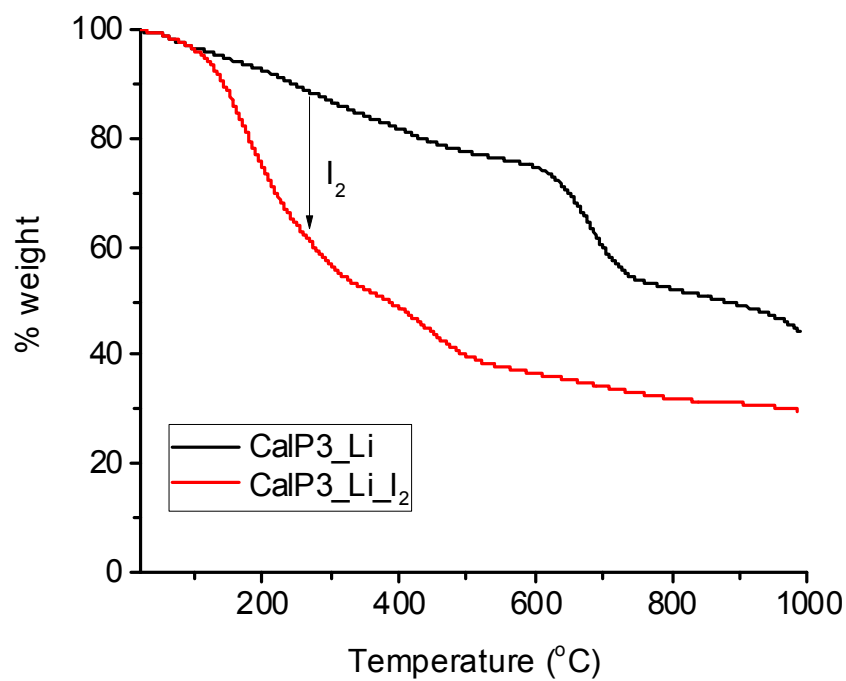


Figure S17. TGA plots for **CalP3-Li** before (black) and after (red) I₂ adsorption.

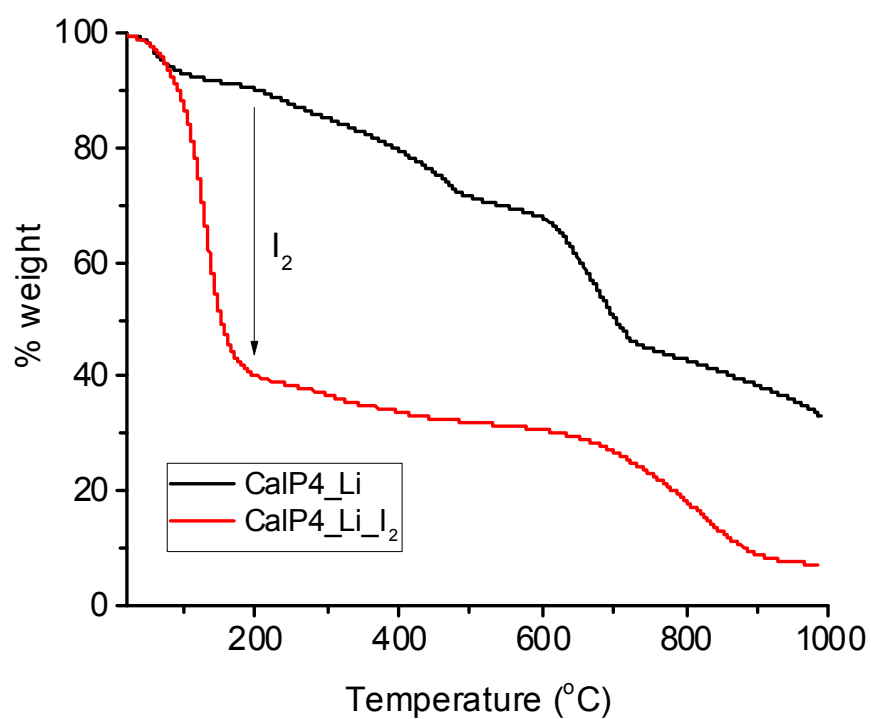


Figure S18. TGA plots for **CalP4-Li** before (black) and after (red) I₂ adsorption.

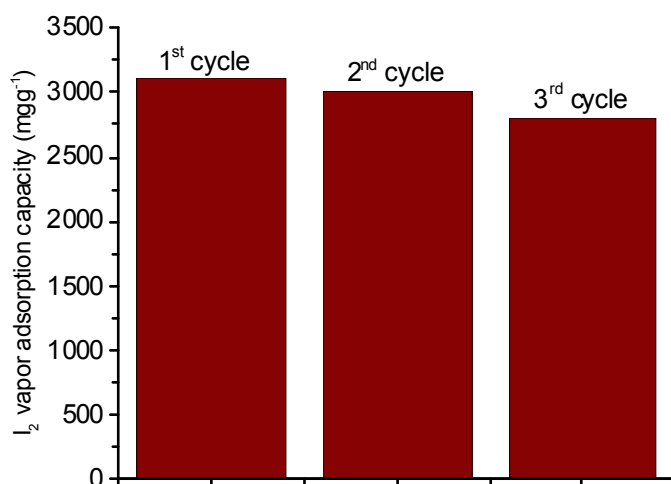


Figure S19. Recycling efficiency of **CalP4-Li** for I₂ vapor adsorption

References

1. Clark, T. E.; Makha, M.; Sobolev, A. N.; Rohrs, H.; Atwood, J. L.; Raston, C. L., Engineering nanorrafts of calixarene polyphosphonates. *Chem. Eur. J.* **2008**, 14, (13), 3931-3938.
2. Venkataramana, G.; Sankararaman, S., Synthesis, Absorption, and Fluorescence-Emission Properties of 1, 3, 6, 8-Tetraethynylpyrene and Its Derivatives. *Eur. J. Org. Chem.* **2005**, (19), 4162-4166.