Electronic Supplementary Material (ESI) for ChemComm.

Phosphonium salt incorporated hypercrosslinked porous polymer for CO_2 capture and conversion

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Supporting information

1. General information

The phosphonium salts, benzene, 1, 2-dichloroethane, polystyrene resin and iron chloride were purchased from Sigma-Aldrich. The epoxides were purchased from the VWR international. GC-MS were measured on SHIMADZU-QP2010. GC analyses were performed on an Agilent GC-6890 using a flame ionization detector. NMR spectra were recorded on a Bruker 400. N_2 sorption analysis and CO_2 sorption analysis were performed on a Micromeritics Tristar 3000 (77 and 273 K, respectively). TEM experiments were conducted on a FEI Tecnai G^2 F20 electron microscope (200 kV). TGA was performed on a Perkin–Elmer Pyris-1 thermogravimetric analyzer. Elemental analysis (CHNS) was performed on an Elementarvario MICRO cube. FT-IR experiments were performed on a Perkin Elmer Spectrum 100. ^{13}C CP-MAS NMR spectra were recorded on a Bruker 400 spectrometer equipped with an ultrashield widebore magnet and a 4 mm multinuclear double-bearing MAS probehead at room temperature at a frequency of 100.62 MHz, using 4 mm zirconia rotors and a sample spinning rate of 12 kHz. Adamantine (40.48 ppm for the downfield resonance) was used as external reference to obtain the chemical shift. ^{31}P CP-MAS NMR spectra were recorded on the same Bruker 400 spectrometer at room temperature at a frequency of 161.97 MHz, using 4 mm zirconia rotors and a sample spinning rate of 12 kHz. 85% H_3PO_4 solution (0 ppm) was used as external reference to obtain the chemical shift.

The calculations were carried out by performing DFT by use of the B3PW91functional with the 6-31++G (d, p) basis set (iodide using DGDZVP) as implemented in Gaussian 09 program package. The solvent effect uses the Conductor Polarizable Continuum Model (CPCM) in each case. Vibrational frequency calculations, from which the zero-point energies were derived, have been performed for each optimized stucture at the same level to identify the natures of all the stationary points. All the bond lengths are in angstroms (Å). Structures were generated using CYLview.[1]

1 CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).

2. *Experimental details*

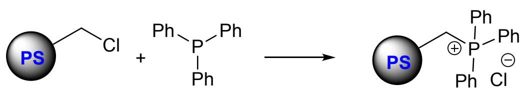
2.1 *Synthesis of phosphonium salt incorporated hypercrosslinked porous polymers*

Typically, iron (III) chloride (8 mmol) was added to a solution of methyl triphenyl phosphonium bromide (1 mmol), benzene (1 mmol) and FDA (8 mmol) in anhydrous dichloroethane (10 mL). The resulting mixture was heated at 80 °C for 20 h. After reaction, the solid product was centrifuged and washed with methanol (3×10 mL). The product was then further purified by Soxhlet extraction in methanol for 20 h and dried *in vacuo* at 60 °C for 12 h. The polymers were obtained as dark brown colored. The elemental results were presented in the Table S2.

2.2 *Synthesis of phosphonium salt and triphenylphosphane incorporated hypercrosslinked porous polymers*

Typically, iron (III) chloride (8 mmol) was added to a solution of methyl triphenyl phosphonium bromide (0.5 mmol), triphenylphosphane (0.5 mmol), benzene (1 mmol) and FDA (8 mmol) in anhydrous dichloroethane (10 mL). The resulting mixture was heated at 80 °C for 20 h. After reaction, the solid product was centrifuged and washed with methanol (3×10 mL). The product was then further purified by Soxhlet extraction in methanol for 20 h and dried *in vacuo* at 60 °C for 12 h. The polymers were obtained as dark brown colored.

2.3 *Synthesis of polystyrene resin supported phosphonium salts*



A mixture of chloromethyl polystyrene (1.0 g, 5.5 mmol Cl content), PPh_3 (16.5 mmol) and toluene (10 mL) was heated at 80 °C for 24 h in a 25 mL flask with vigorous stirring. After cooled down to room temperature, the solid residue was collected by filtration and washed with methanol(3×5 mL). Then, the solid was dried under vacuum at 60 °C for 12 h and polystyrene resin supported phosphonium salt was obtained. The loading of imidazolium salt attached on the PS was 4 mmol/g determined by nitrogen content from elementary analysis.

2.4 CO_2 capture

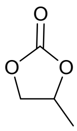
phosphonium salt incorporated hypercrosslinked porous polymers were subjected to the following gas capture and cycling experiment at 25 °C: CO_2 (99.8%) gas flow at 20 ml/min for 30 min, followed by N_2 (99.9995%) gas flow at 20 ml/min for 45 min. Changes in weight were recorded by TGA. Prior to the cyclic treatment, the sample was first purged under N_2 gas flow at

100 ^{o}C for 60 min, followed by cooling to room temperature. Change in buoyancy effects arising from the switching of gases was recorded by using an empty sample pan, and the buoyancy effects were corrected for in the TGA results.

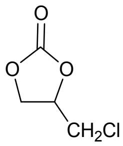
2.5 *CO_2 conversion*

CO_2 conversion reactions were conducted in a 25 ml stainless steel reactor equipped with a magnetic stirrer and automatic temperature control system. Typically, an appropriate volume of CO_2 (1.0 MPa) was added to a mixture of PO (0.1 ml), DMF (2 mL), phosphonium salt incorporated hypercrosslinked porous polymers (1 mmol% based on contents of the phosphonium salt) in the reactor at room temperature. The temperature was then raised to 130 ^{o}C. After the reaction was preceded for 4 h, the reactor was cooled to 0 ^{o}C in an ice water bath, and the remaining CO_2 was slowly removed. The product was then analyzed by GC and NMR. The phosphonium salt incorporated hypercrosslinked porous polymers could be easily separated by centrifugation, and used in the next run without further purification.

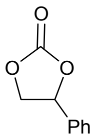
3. Characterization of cyclic carbonates



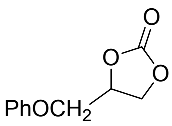
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 4.86-4.94 (m, 1H), 4.60 (t, *J*=8.0 Hz, 1H), 4.05 (t, *J*=8.8 Hz, 1H), 1.49 (d, *J*=6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): δ 154.95 (C=O), 73.51, 70.46, 18.95.



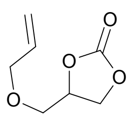
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 4.98 (m, 1H), 4.58 (t, 1H, *J*=8.4 Hz), 4.39 (dd, 1H, *J*=6.0 Hz), 3.80 (dd, 1H, *J*=5.2 Hz), 3.71 (dd, 1H, *J*=3.2 Hz); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): δ 154.95 (C=O), 73.51, 70.46, 43.83.



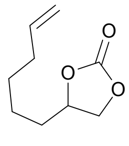
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.35-7.44 (m, 5H), 5.68 (t, 1H, *J*=8.0 Hz), 4.80 (t, 1H, *J*=8.4 Hz), 4.34 (t, 1H, *J*=8.4 Hz); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): δ 154.81 (C=O), 135.70, 129.63, 129.12, 125.81, 77.92, 71.10.



1H NMR ($CDCl_3$, 400 MHz): δ 7.31 (t, ^{3}J= 8.0 Hz, 2H), 7.02 (t, ^{3}J = 7.4 Hz, 1H), 6.91 [d, ^{3}J= 8.0 Hz, 2H], 5.03 [m, 1H], 4.62 [t, ^{3}J= 8.4 Hz, 1H], 4.55 (dd, ^{3}J= 8.4 Hz), 4.24 (dd, ^{3}J = 3.6 Hz, 1H), 4.15 (dd, ^{3}J = 4.4 Hz, 1H), ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): δ 157.71. 154.65, 129.62, 121.92, 114.57, 74.11, 68.84, 66.17.

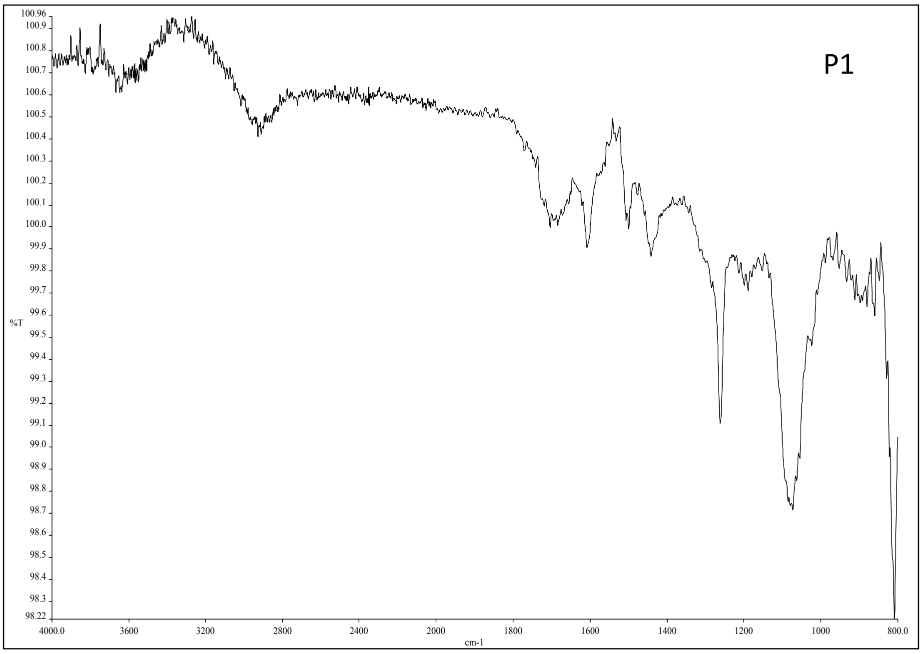


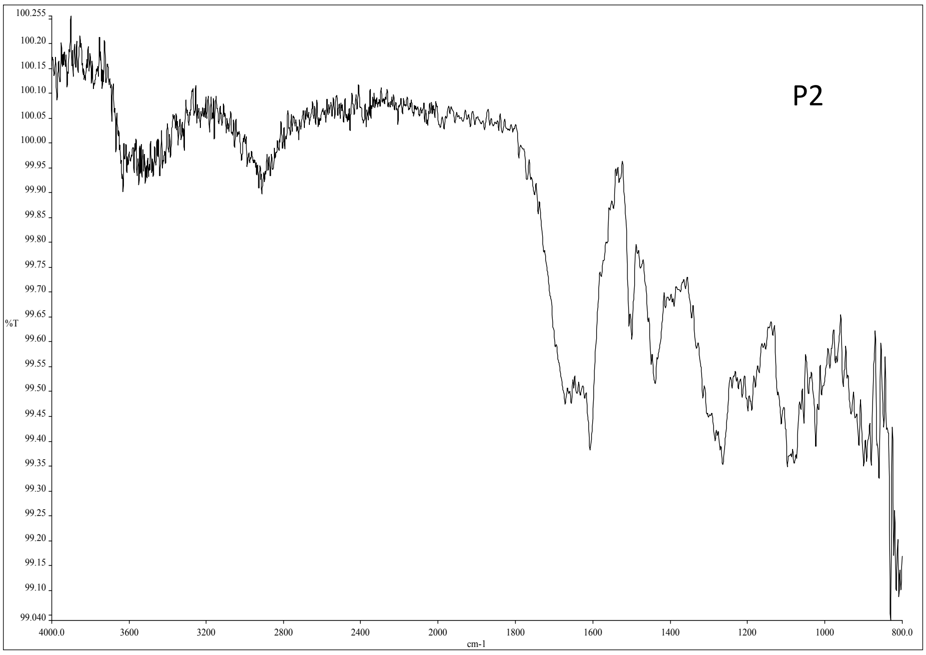
^{1}H NMR ($CDCl_3$, 400MHz): δ 5.8 – 6.0 (t, 1H), 5.0-5.2 (d, 2H), 4.4-4.7 (3H), 4.0-4.1 (m, 2H), 3.5-3.8 (d, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): δ 155.90, 133.88, 117.47, 72.05, 72.30, 68.92, 66.24.

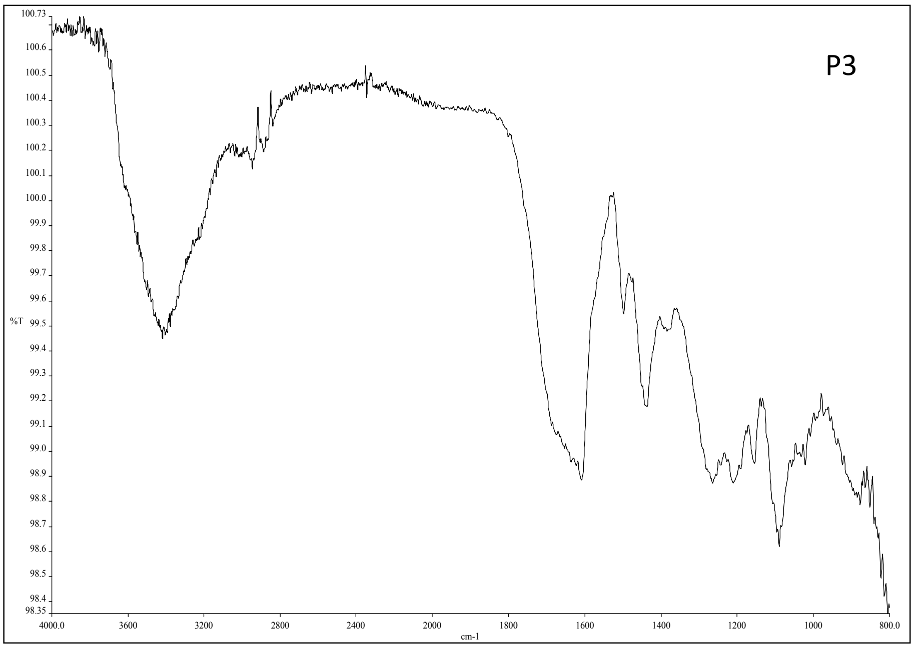


^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ δ 5.8 – 6.0 (t, 1H), 5.0-5.2 (d, 2H), 4.7 (m, 1H), 4.5 (dd, 1H), 4.04 (dd, 1H, *J*=8.4 Hz), 2.4-2.7 (m, 2H), 2.1 (m, 2H), 1.43-1.55 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): δ 155.2 (C=O), 139.2,115.6, 70.4, 66.3, 36.5, 33.8, 29.6, 25.3.

4. Supported Figures



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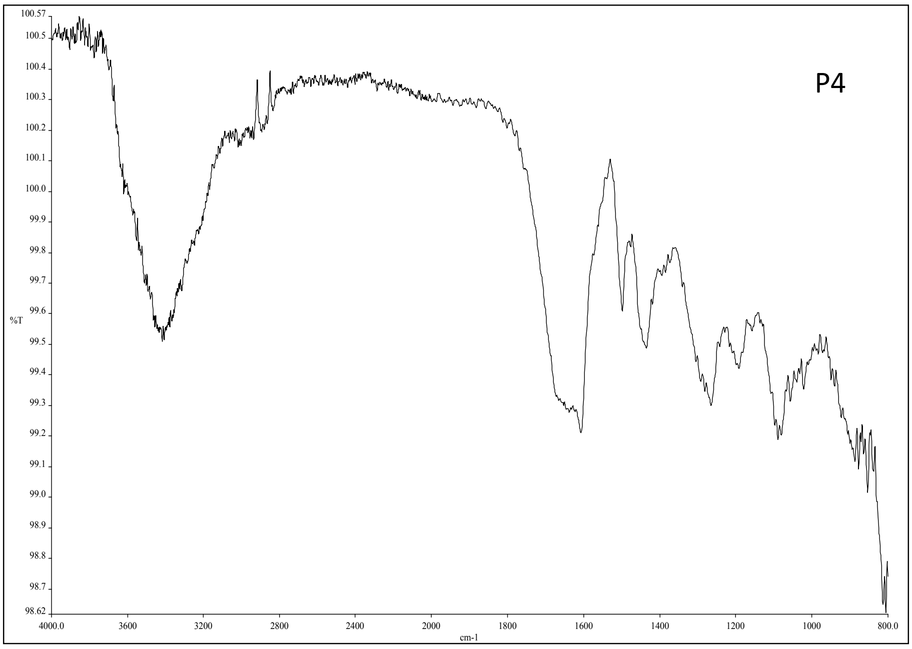
1000
800.0
100.73
98.35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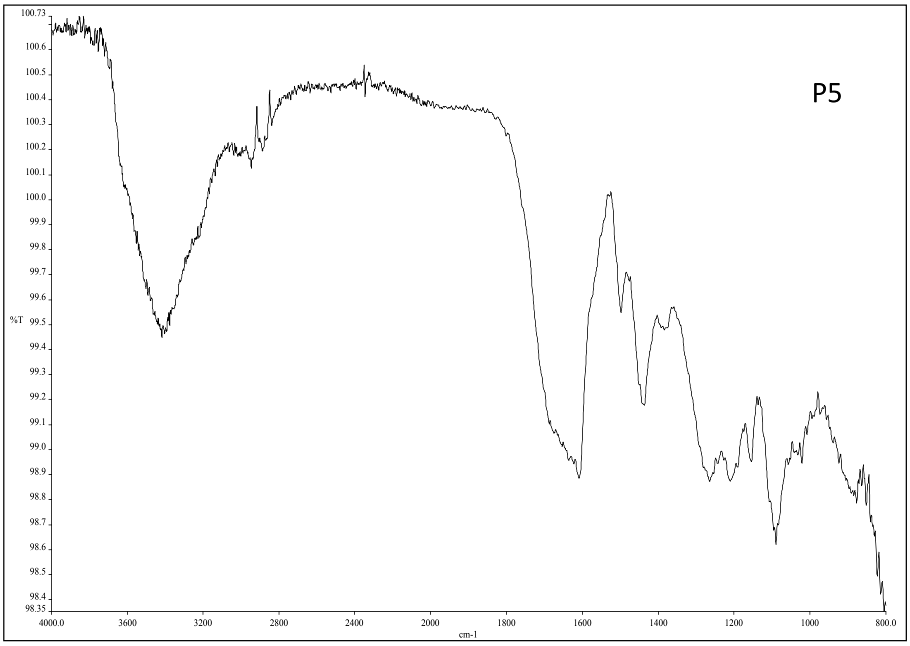


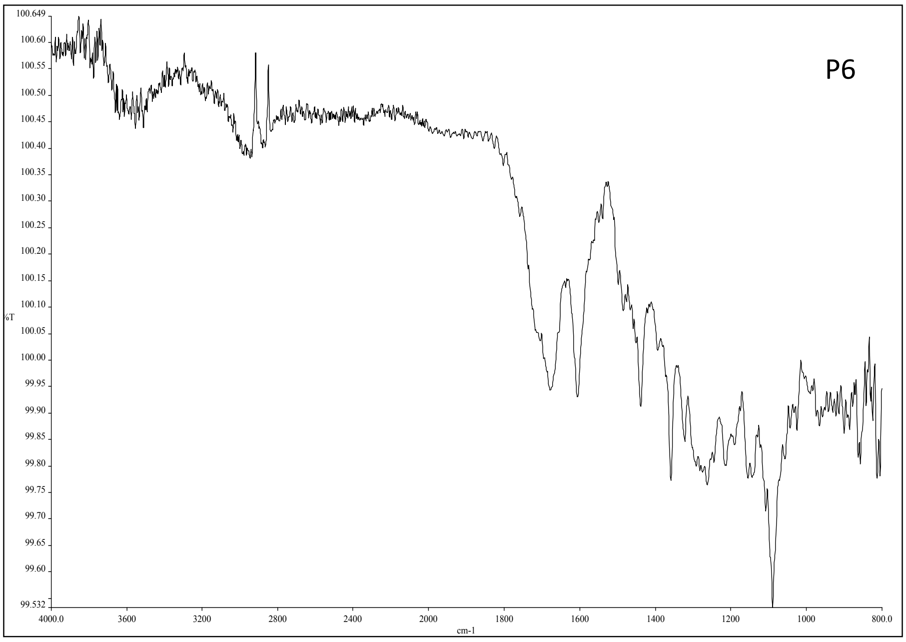
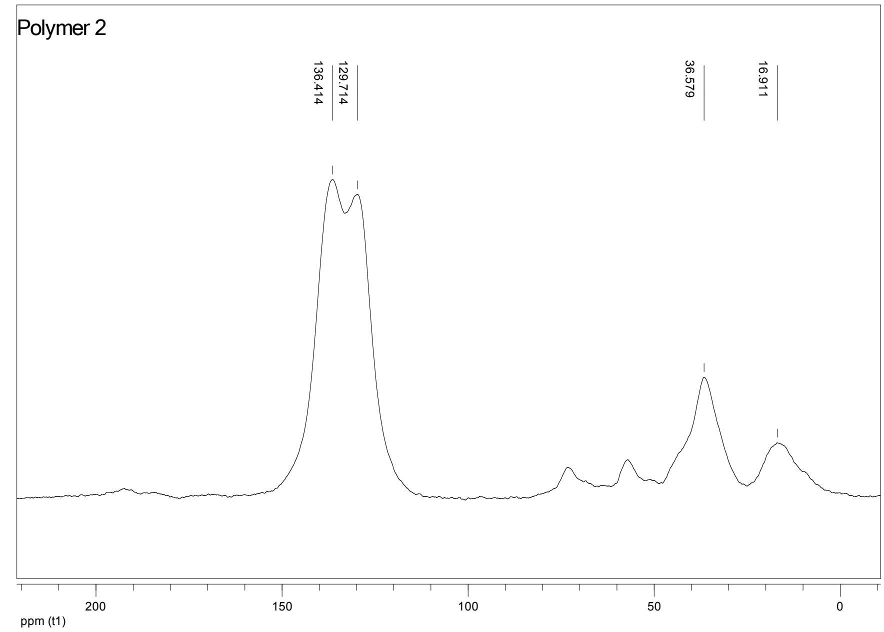


Fig. S1 FT-IR spectra



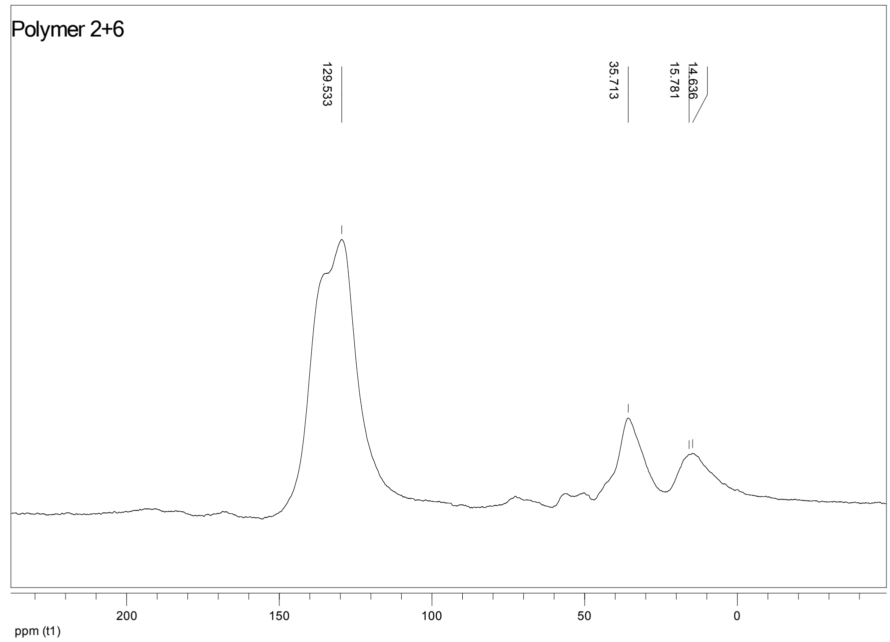


Fig. S2 Solid-^{13}C NMR spectra

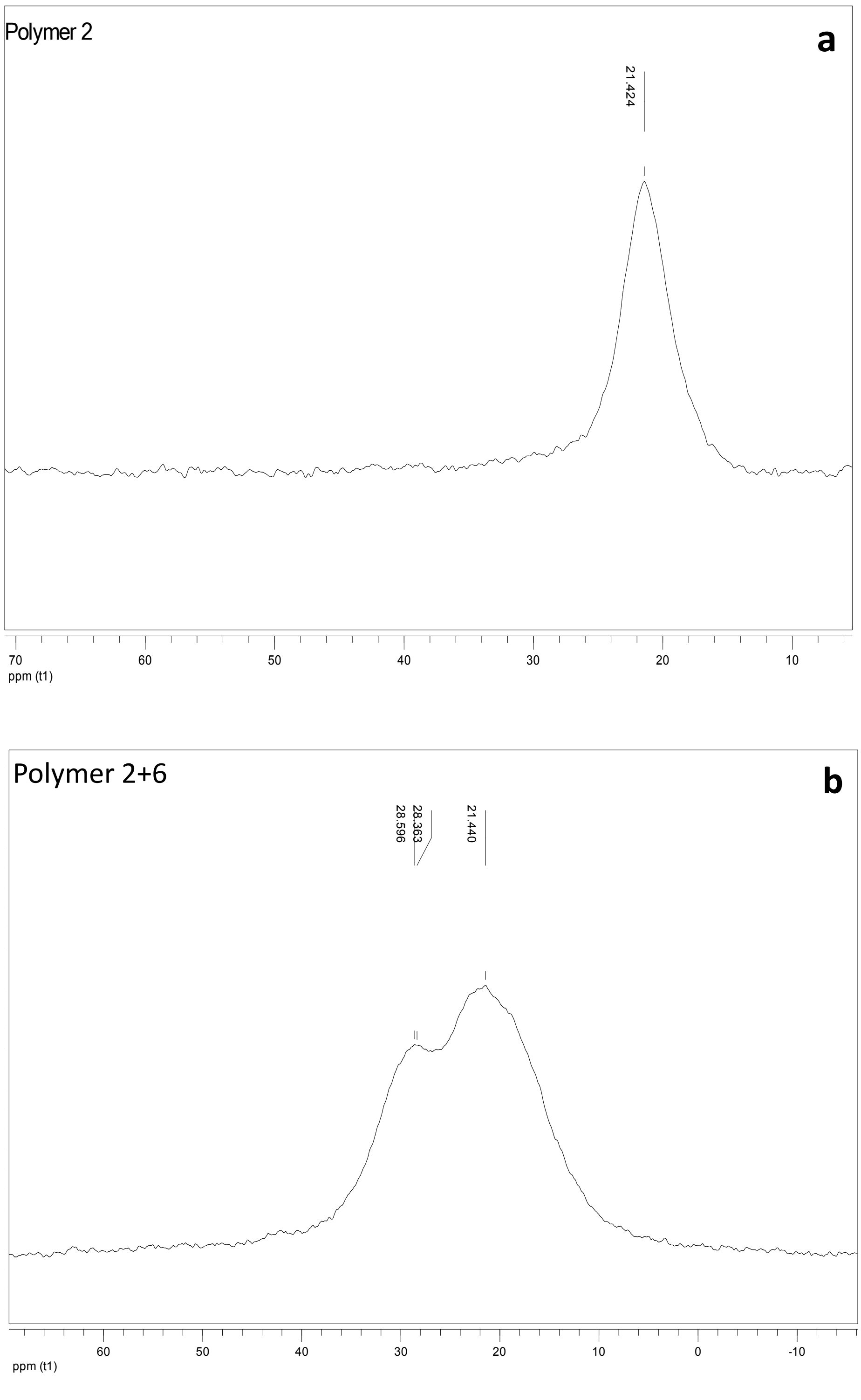


Fig. S3 Solid-^{31}P NMR spectra

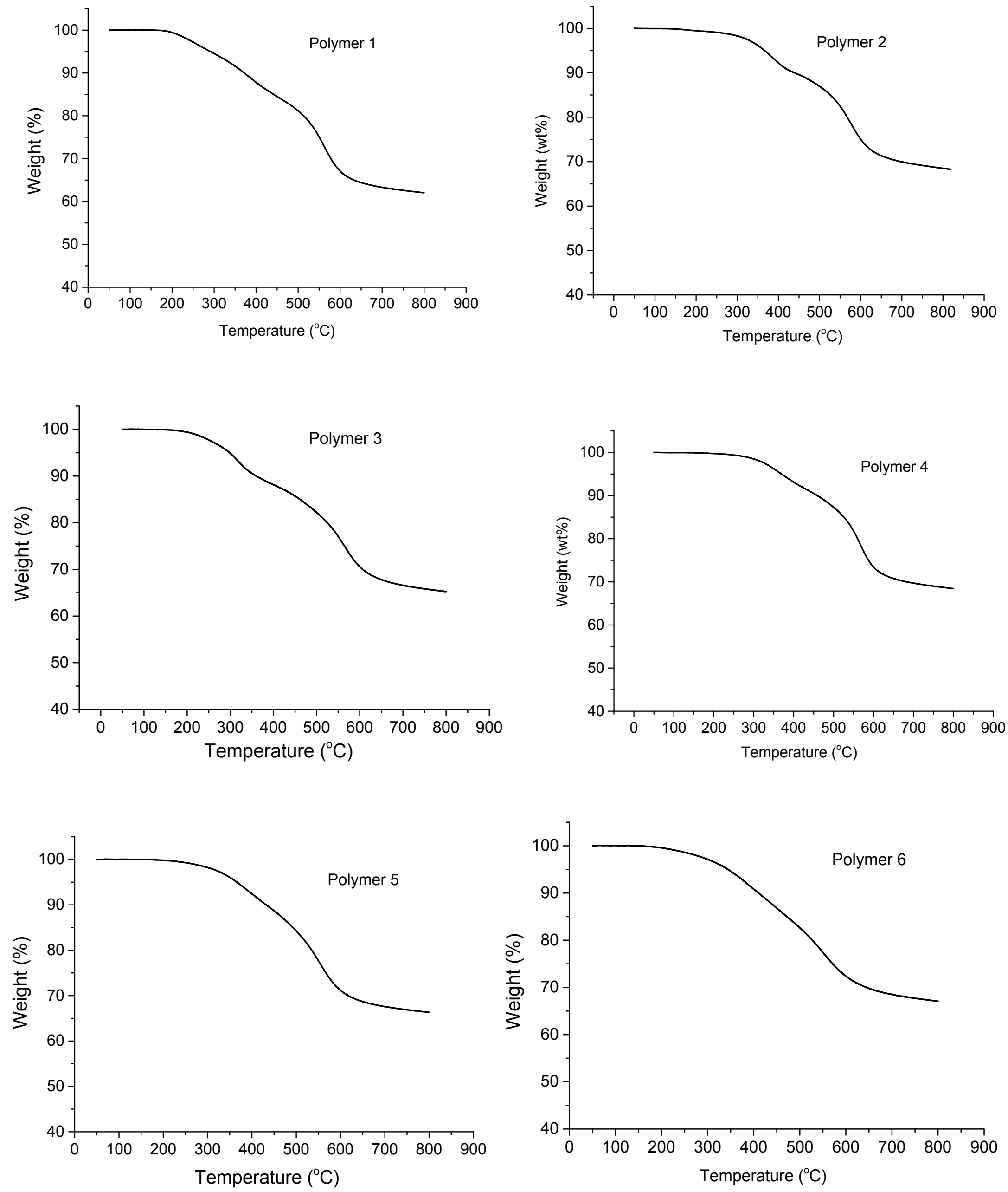


Fig. S4 TGA results

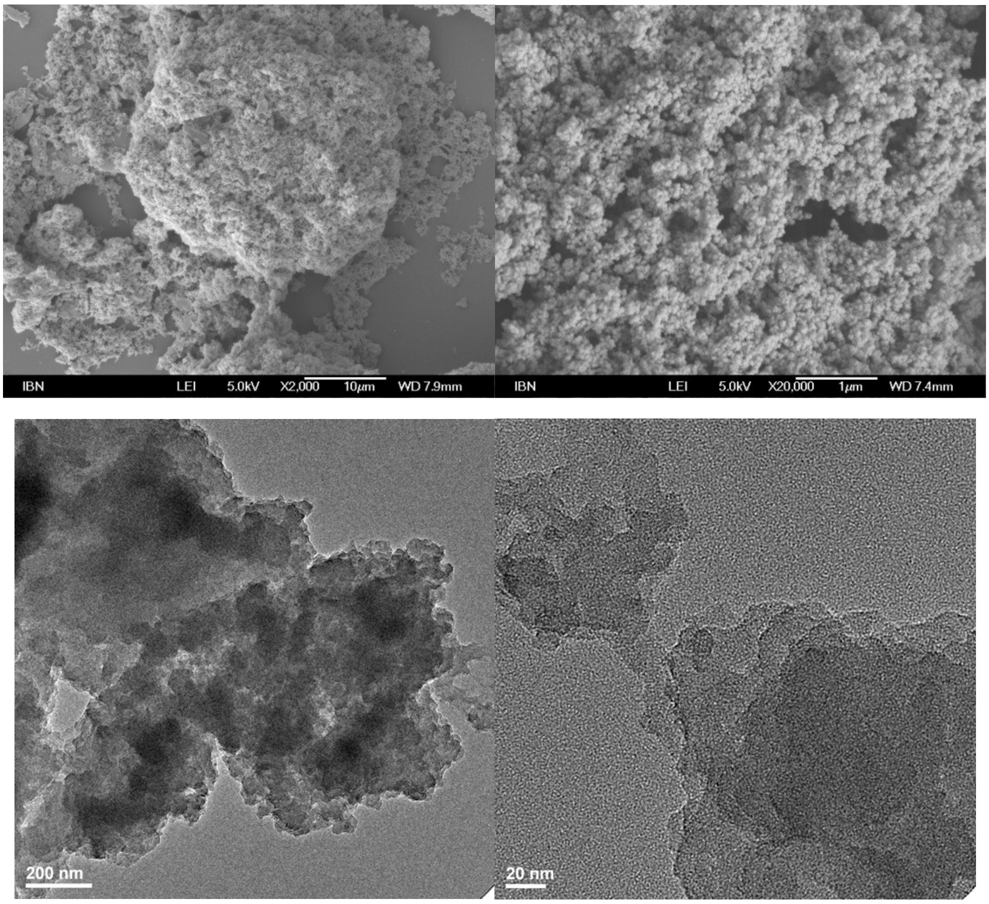


Fig. S5 TEM and SEM images of Polymer 2

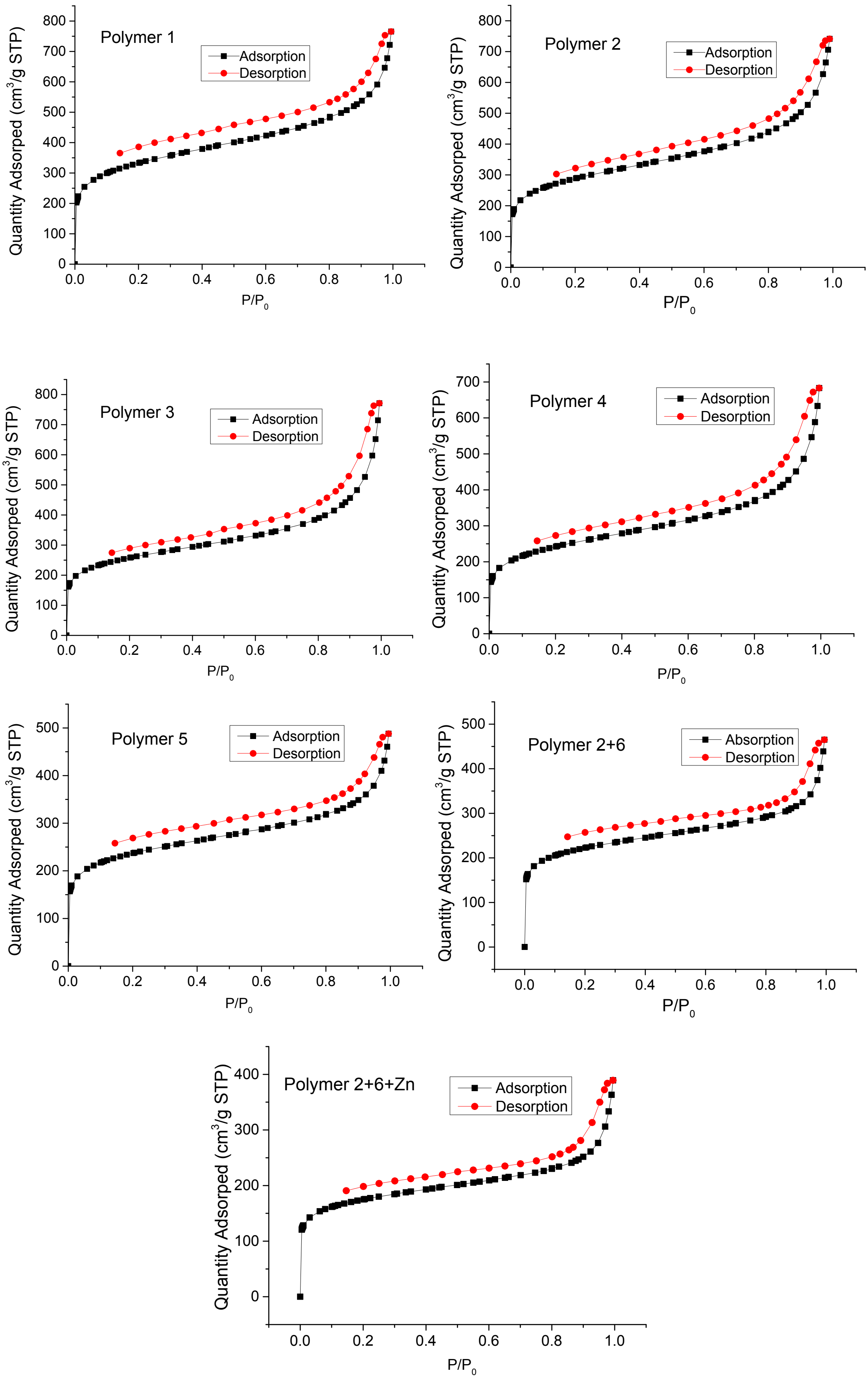


Fig. S6 N_2 adsorption-desorption isotherms

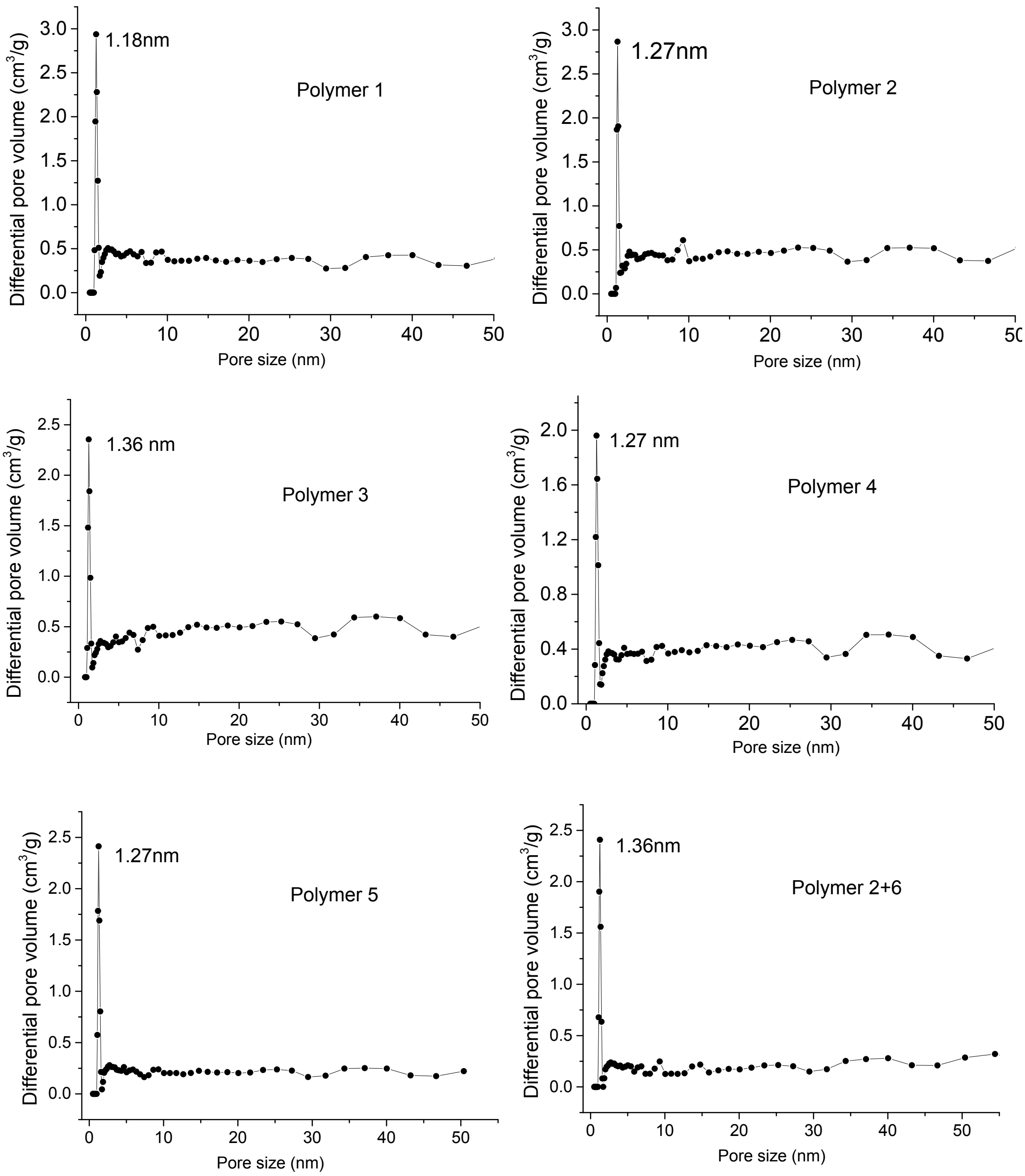


Fig. S7 Pore size distributions

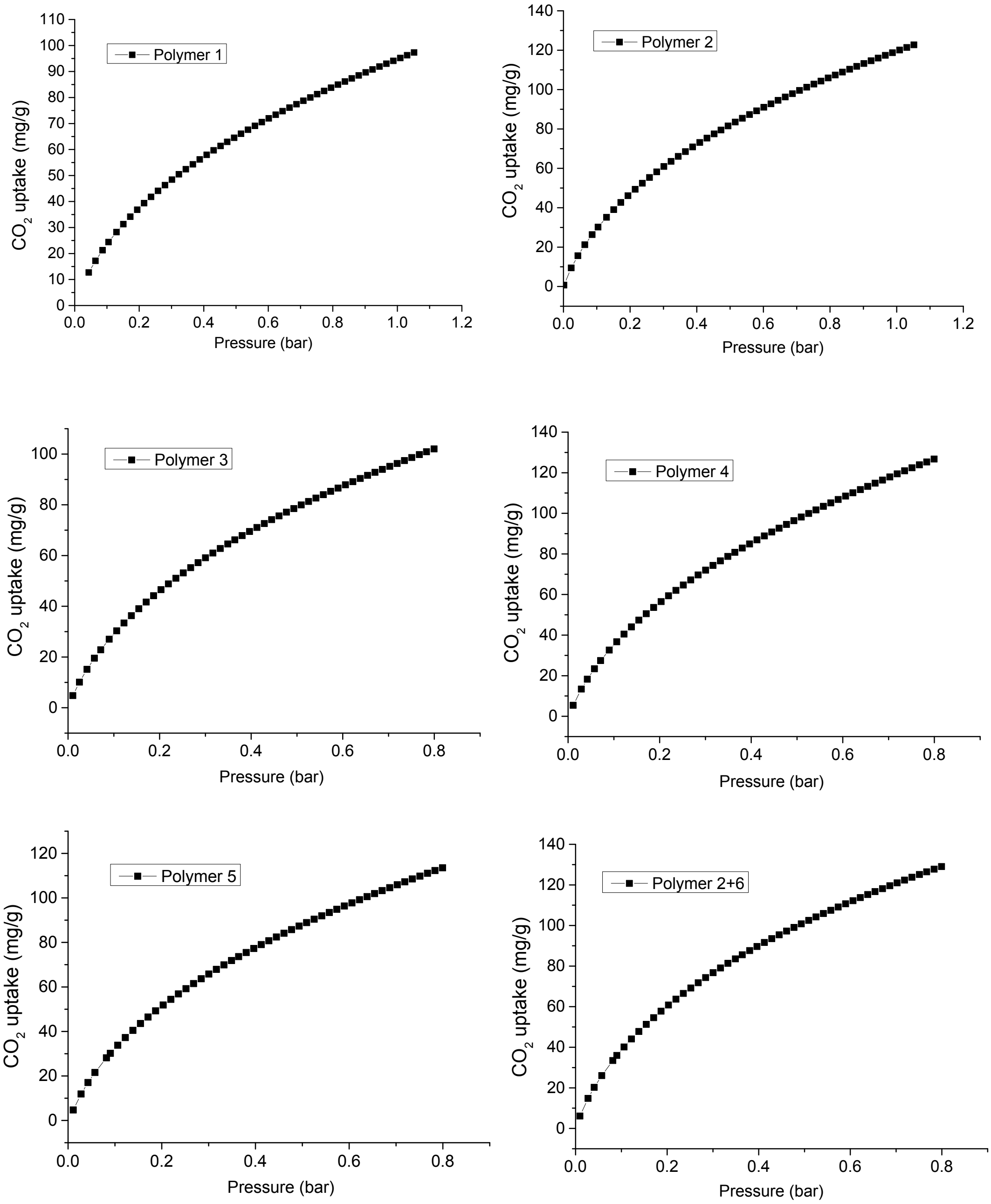


Fig. S8 CO_2 capacities at 273K

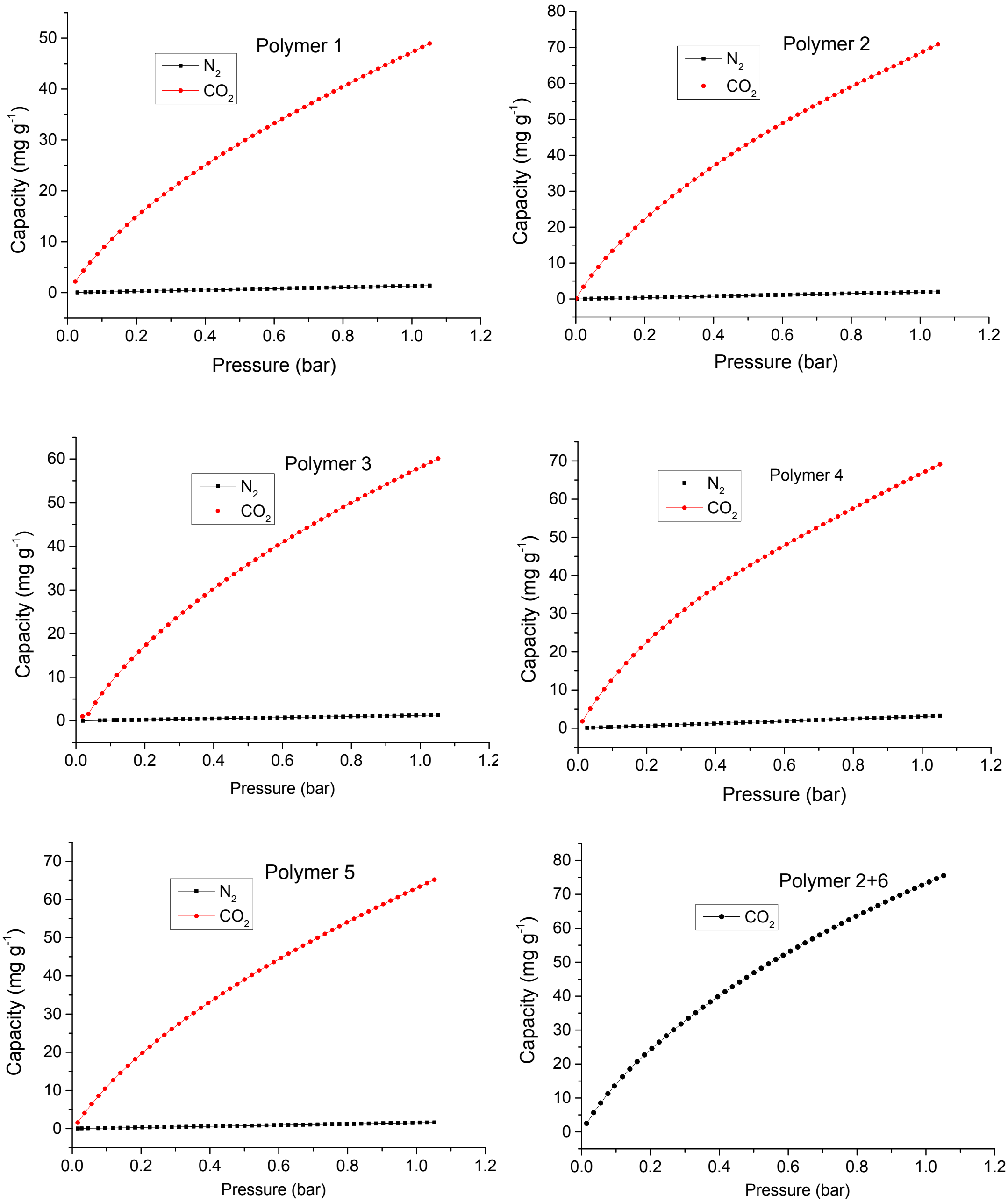
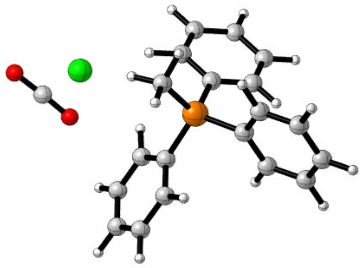
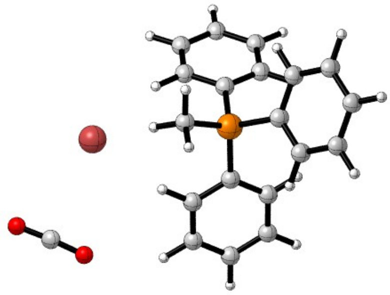


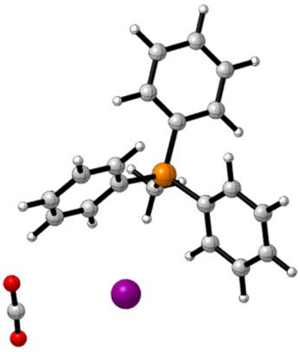
Fig. S9 CO_2 and N_2 capacities at 298K



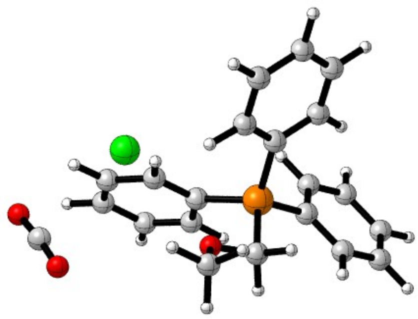
1 and CO_2



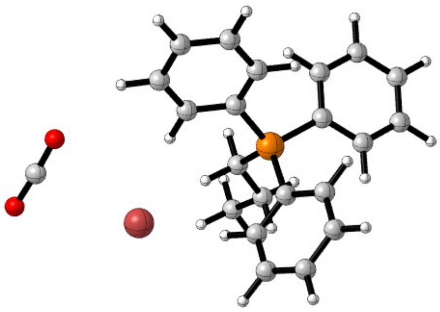
2 and CO_2



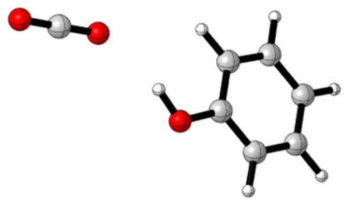
3 and CO_2



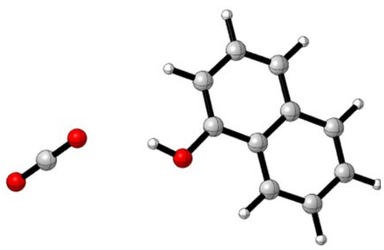
4 and CO_2



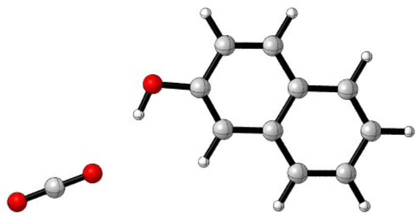
5 and CO_2



Phenol and CO_2



1-Naphthol and CO_2



2-Naphthol and CO_2

Fig. S10 The optimized structures for phosphonium salts, phenol, naphthols and CO_2

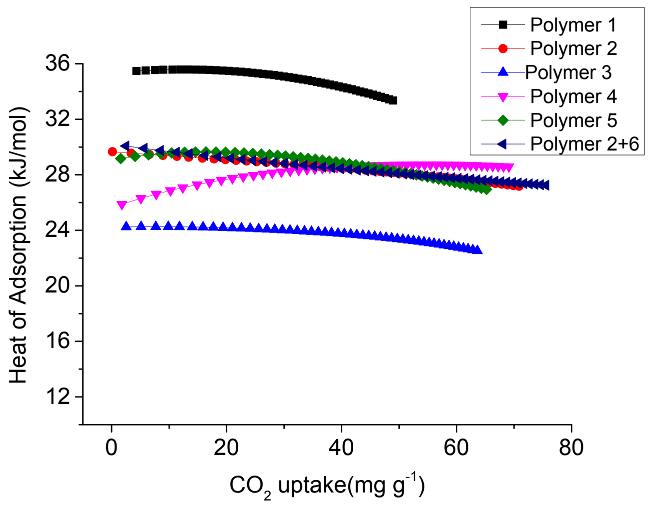


Fig. S11 The heat of adsorption

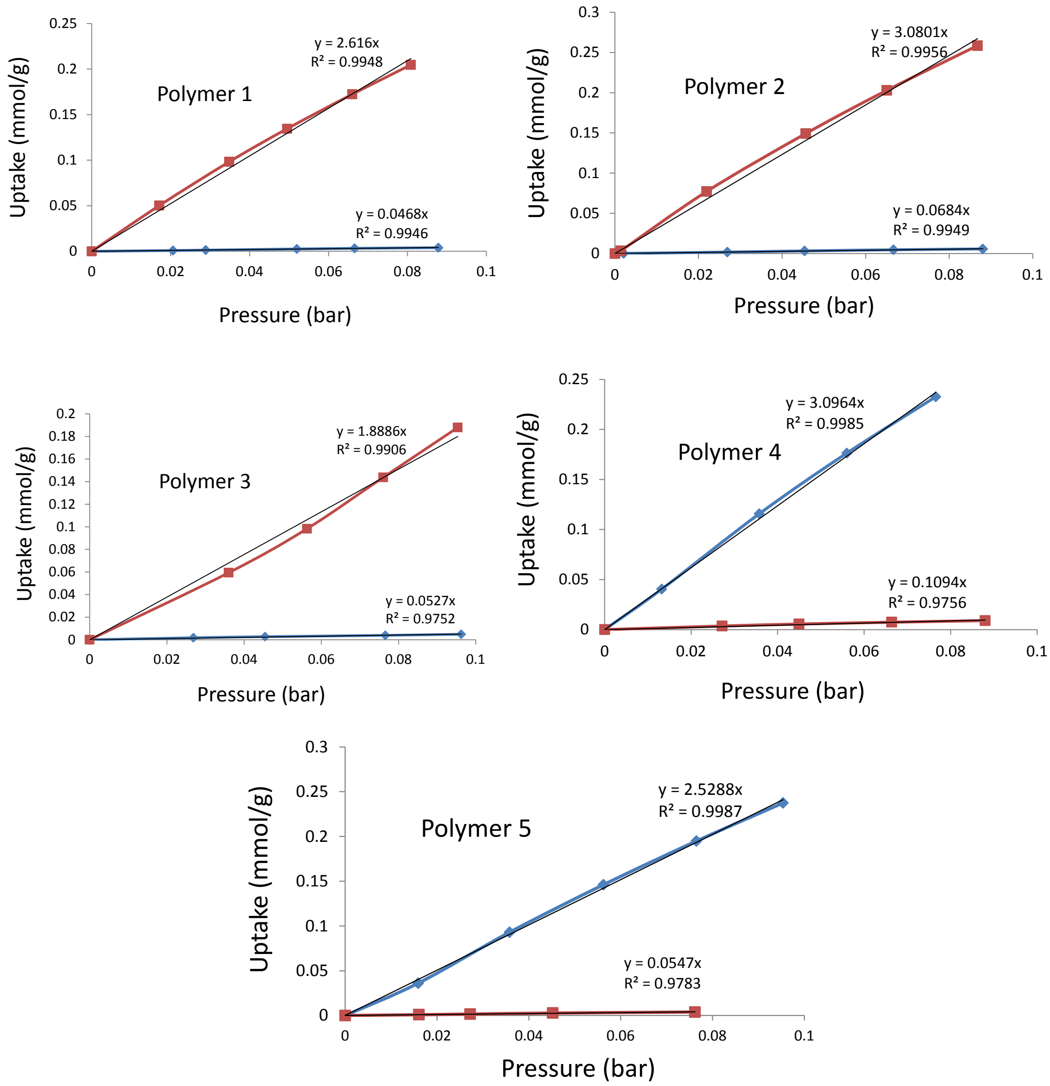


Fig. S12 Selectivity over N_2

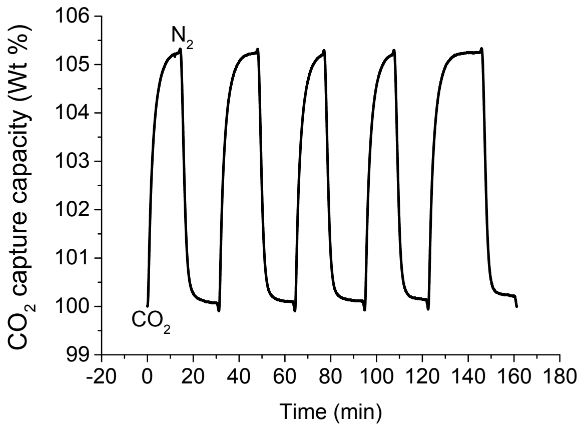


Fig. S13 Recycling for CO_2 capture using Polymer 2

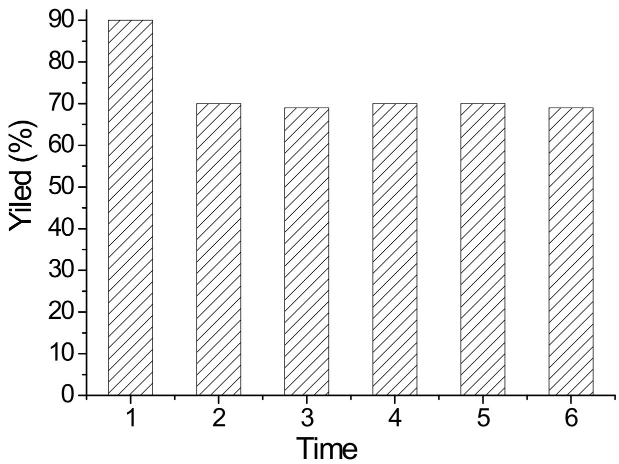


Fig. S14 Recycling of catalysts

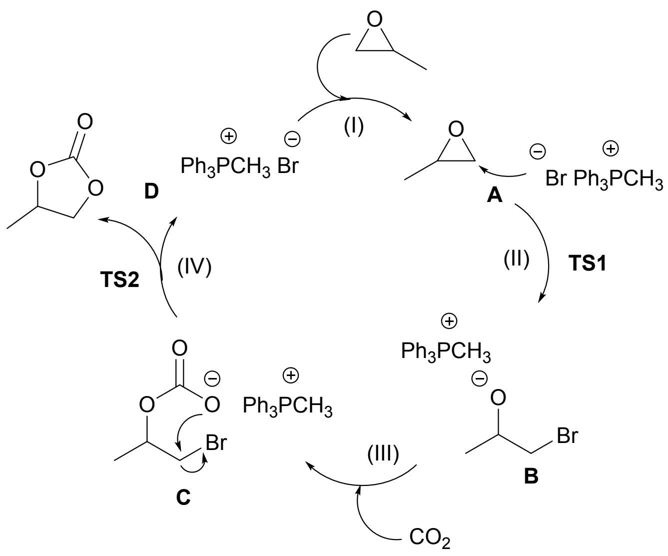


Fig. S15 Mechanistic hypothesis of the catalytic reaction

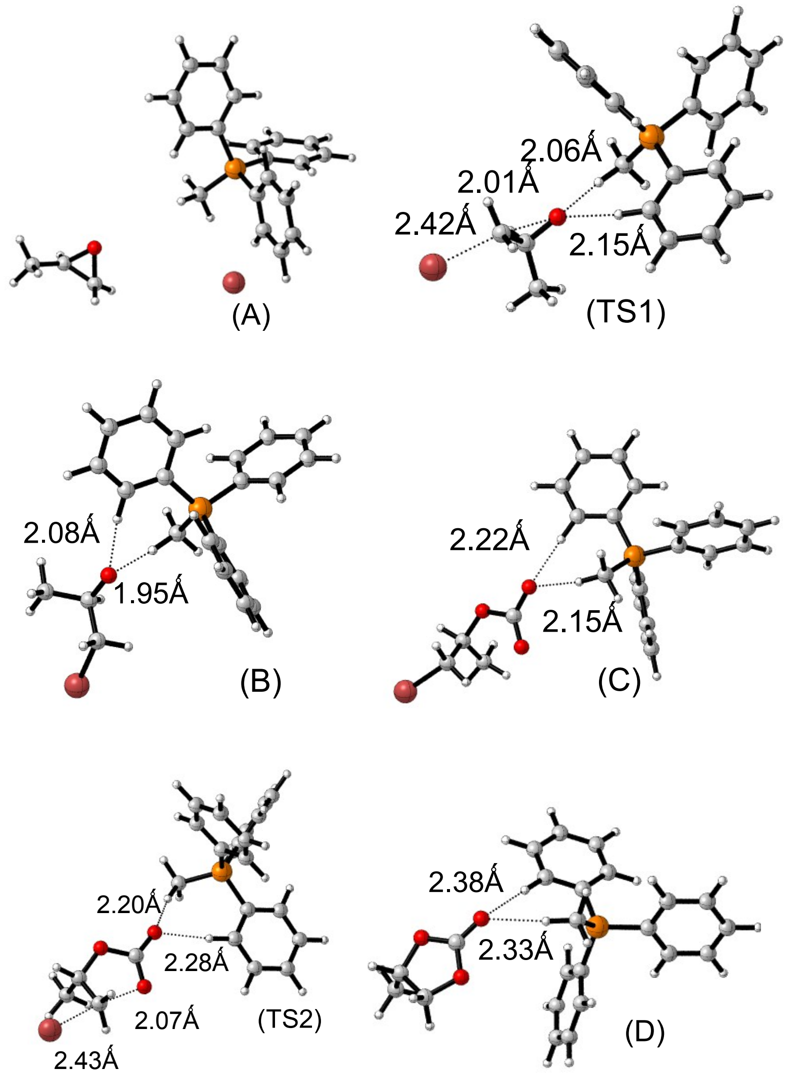


Fig. S16 Optimized geometries for the intermediates and transition states. H: white, C: gray, N: blue, O: red, Cl: green. Bond lengths and distances are in Å.

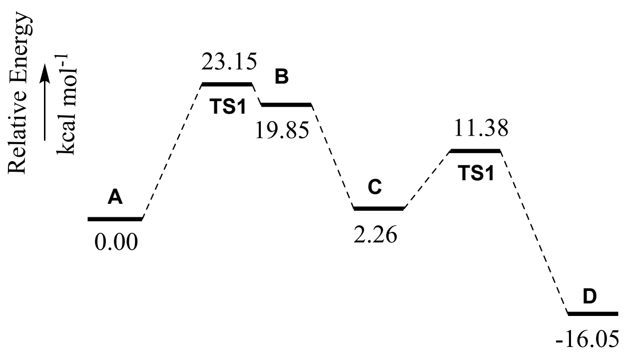


Fig. S17 Relative energies for fixation of CO_2 with PO catalyzed by methyl triphenyl phosphonium bromide in DMF, relative energies at the B3PW91/6-311++G (d, p) level.

5. *Supporting Tables*

Material	BET (m^2 g^{-1})	CO_2 uptake (wt %) at 273 K	CO_2 uptake (wt %) at 298 K	Selectivity (CO_2/N_2) at 298 K	References
Polymer 1	1168	9.6	4.8	56	This work
Polymer 2	1015	12.3	7.1	45	This work
Polymer	823	11.3	6.5	46	This work
Azo-COP-2	739	11.2	6.73	130	1
Om-ph-MR	256	11.0	7.78	100	2
DBT	493	9.7	6.06	80	3
BILP-1	1172	18.8	21.4	36	4
PECONF-2	637	12.5	8.73	44	5
PECONF-3	851	15.4	12.03	41	5
PECONF-4	-	0.6	7.93	51	5
MPI-2	814	13.8	8.9	-	6
TBI-1	609	14.0	-	-	7
BPOP-2	632	15.0	-	-	8
CTF	2011	15.7	-	-	9
HCP-E	1470	12.9	7.8	9.2	10
HCP 1	1646	-	7.5	-	11
HCP–BDM	847	12.6	7.1	-	12
Benzene	1391	13.5	-	-	13
FCBCz	1067	15.8	9.9	28.9 (273K)	14
TSP-2	913	18.0	11.4	38(273K)	15

References

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Table S2 Elemental analysis results

Polymers	C% [a]	H% [a]	P% [a]	Zn%
1	76.20 (78.78)	5.76 (8.01)	1.4 (6.16)	
2	78.55 (72.39)	5.06 (7.36)	1.1 (5.66)	
3	76.19 (66.66)	4.96 (6.78)	1.5 (5.21)	
4	78.11 (76.60)	5.15 (7.94)	1.1 (6.16)	
5	78.78 (73.03)	5.19 (7.71)	1.4 (5.38)	
2+6	76.15 (78.26)	4.89 (7.94)	1.1 (6.02)	
2+6+Zn	71.68	5.16	1.0	0.9

[a]The theoretical values list in the parentheses

6. *Cartesian coordinates for all the optimized geometries*

(A)

C	-0.60999000	0.52280600	-0.11817300
H	-0.88501700	1.07199700	-1.01891500
H	-1.04437700	-0.48061000	-0.14945100
C	-6.39323500	0.58409400	-0.06011400
C	-6.83856200	1.89759400	-0.53600700
H	-6.44180500	-0.27852600	-0.71843400
H	-6.42565500	0.36670100	1.00411900
H	-7.18769800	1.95482300	-1.56528700
Br	-2.32496700	-3.06398900	0.01278300
O	-5.42845300	1.58802300	-0.44181800
C	1.92001000	2.06432000	-0.02707700
C	1.37288300	3.05728300	0.79941600
C	3.02711500	2.35563700	-0.83305300
C	1.93223500	4.33118300	0.81154600
H	0.52099300	2.84809600	1.43513900
C	3.58079000	3.63436200	-0.81268600
H	3.45617700	1.59622200	-1.47436800
C	3.03476700	4.62044300	0.00647700
H	1.50613200	5.09656200	1.44897100
H	4.43668100	3.85658300	-1.43863700
H	3.46619000	5.61453700	0.01817900
C	1.65192400	-0.45371700	1.51682500
C	2.73965500	-0.00952200	2.27933500
C	0.91507200	-1.57600000	1.92388800
C	3.08725600	-0.68697400	3.44606500
H	3.31003900	0.85828200	1.97253800
C	1.27189700	-2.24345800	3.09216700
H	0.07133300	-1.93696600	1.34447300
C	2.35488600	-1.80124900	3.85237800
H	3.92739400	-0.34077400	4.03604000
H	0.70083400	-3.10840900	3.40804500
H	2.62616100	-2.32412500	4.76216300

C	1.80790000	-0.53969100	-1.44837400
C	1.32480200	-0.24032900	-2.73105200
C	2.76090600	-1.55046500	-1.27631200
C	1.79538900	-0.95329200	-3.82926300
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C	3.22644200	-2.25802900	-2.38279800
H	3.13669300	-1.78918800	-0.28944300
C	2.74488900	-1.96122300	-3.65618000
H	1.41893000	-0.72220000	-4.81847800
H	3.96238600	-3.04122100	-2.24608000
H	3.10672400	-2.51532400	-4.51440100
H	-0.98344800	1.05428100	0.75760900
P	1.19744600	0.39823400	-0.01852200
C	-7.36154600	2.96221800	0.38856100
H	-7.07524000	3.95636100	0.03386800
H	-8.45415300	2.92120200	0.42730000
H	-6.97290400	2.82624100	1.40029400

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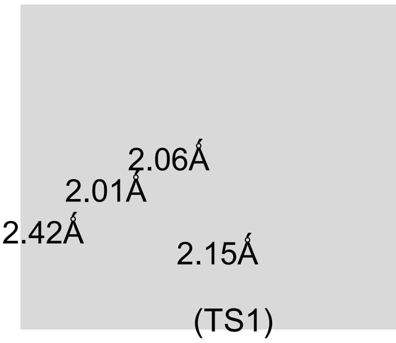

(TS1)

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C	0.27880800	-1.98537000	0.82210700
C	2.67294900	-2.08485400	1.25346600
C	0.10213100	-3.11026800	1.62488700
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C	4.39011400	1.04262700	-0.16918300
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C	1.12087700	2.69307800	-0.16539900
C	0.70591800	2.57856500	2.59498900
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H	-3.16458100	-2.37274700	-2.40485000
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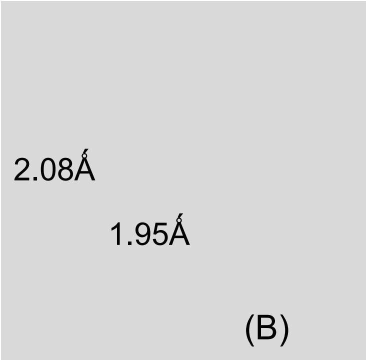

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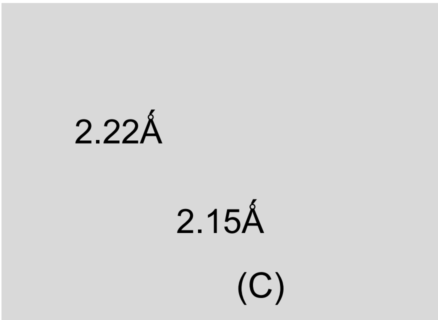

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C	4.73747900	0.42100200	0.40456800
H	5.14140400	-0.90206800	-1.30350300
H	5.33968300	0.84171500	-1.64067400
H	5.29388800	1.24052400	0.86564500
Br	7.42377100	-0.09963000	-0.62050600
O	3.46168000	1.03624600	0.12261700
C	2.44200300	0.31878300	-0.55354000
O	1.37557500	0.96704000	-0.61423900
O	2.71486400	-0.81073600	-0.99631000
C	-4.26388100	-0.46176200	-0.98551200
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C	-6.05182900	-0.24330600	-2.59747100
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C	-2.62067500	1.62746900	0.33795800
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C	-1.41108200	2.31220200	0.53393800
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C	-2.01722200	-1.24605500	0.77832300
C	-1.98460900	-0.93915000	2.14373500
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C	-1.55493500	-1.89807100	3.05916000
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H	5.62460800	-1.06529300	1.69807700
H	4.11386700	-0.37866300	2.30679200
H	-1.47566400	-0.97048400	-2.33109400
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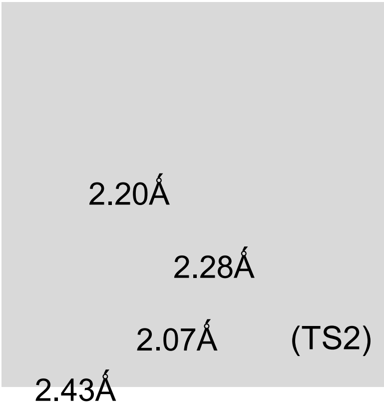

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C	4.73012500	-0.83762500	-2.05441100
C	5.35144900	0.81326500	-0.38668400
C	6.04308600	-0.85878000	-2.51525800
H	3.99337500	-1.47561000	-2.52734400
C	6.66361300	0.78367900	-0.85430500
H	5.09029900	1.46639900	0.43666700
C	7.00924300	-0.04933100	-1.91675300
H	6.30963400	-1.50629900	-3.34193200
H	7.41186800	1.41375300	-0.38864300
H	8.03002200	-0.06778700	-2.28028300
C	2.38266800	1.51954000	0.59237800
C	2.24192800	2.74695100	-0.07230900
C	2.31127000	1.46711100	1.98935000
C	2.02951600	3.90945900	0.66209700
H	2.29871600	2.80683500	-1.15258600
C	2.09964300	2.63729100	2.71599100
H	2.41597800	0.52389300	2.51060800
C	1.95834400	3.85558500	2.05477000
H	1.91850300	4.85564300	0.14621000
H	2.04420600	2.59299100	3.79704500
H	1.79108400	4.76338400	2.62260400
C	2.39017200	-1.45159000	0.66559500
C	3.47346600	-2.19070000	1.15672500
C	1.07446100	-1.82591200	0.98063800
C	3.24109500	-3.30429000	1.96105900
H	4.48995200	-1.90674100	0.91467500
C	0.85736400	-2.94186100	1.78485600

H	0.22541700	-1.25847500	0.61123900
C	1.93577800	-3.68002700	2.27383700
H	4.07992100	-3.87649200	2.33898100
H	-0.15727000	-3.23468200	2.02800100
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H	1.72715800	0.81857300	-2.43168000
P	2.67148500	0.00918400	-0.37307800
C	-5.21817300	-0.34748300	0.15056300
C	-4.77087400	0.18990000	-1.19802300
H	-5.50193500	-1.37614700	0.27655100
H	-5.10003100	0.25949400	1.03120100
H	-5.32577000	1.09832700	-1.42296600
Br	-7.58091700	0.23308800	0.07893900
O	-3.39487900	0.63356200	-1.10258500
C	-2.61385900	-0.14325300	-0.26287200
O	-1.39905600	0.07258800	-0.27522400
O	-3.26478700	-0.98092600	0.43479400
C	-4.92639400	-0.82196900	-2.32562400
H	-5.97720200	-1.09580200	-2.44074600
H	-4.57584500	-0.39042300	-3.26483700
H	-4.35052600	-1.72658300	-2.11610100

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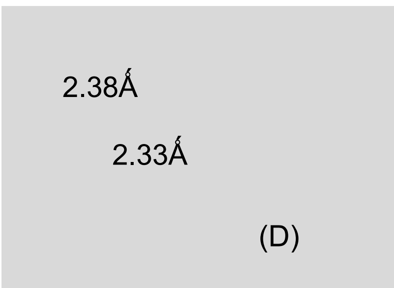

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C	-1.84840000	-0.04175300	-2.03201900
H	-2.48915000	0.48904100	-2.73629100
H	-0.92102700	0.51542100	-1.88650400
C	4.00977400	0.50103800	-0.98254300
C	4.18989300	1.88059800	-0.32333200

H	4.28278000	-0.32564600	-0.33028600
H	4.52669900	0.41481200	-1.93763000
H	4.97326400	2.45830300	-0.81047100
Br	8.17714000	-1.21973900	-0.14539100
O	2.92662700	2.54217400	-0.65643300
C	2.03563800	1.64556500	-1.09970700
O	0.88388500	1.89811000	-1.34663700
O	2.58318300	0.42722600	-1.23434600
C	-4.20552600	-1.19933900	-0.66165400
C	-4.56094000	-2.16343900	0.28974100
C	-5.02134700	-0.98530900	-1.78271800
C	-5.72651200	-2.90752200	0.11860100
H	-3.93568700	-2.33804000	1.15632300
C	-6.18234600	-1.73488600	-1.94521800
H	-4.76426600	-0.24146300	-2.52704900
C	-6.53549100	-2.69464300	-0.99593700
H	-5.99798100	-3.65339500	0.85595000
H	-6.80897900	-1.56920200	-2.81330100
H	-7.44001600	-3.27696000	-1.12718600
C	-3.15376300	1.45110600	0.16292100
C	-4.41957900	1.68389100	0.71452700
C	-2.21239100	2.48937600	0.09075900
C	-4.74235400	2.95235300	1.19200100
H	-5.15092200	0.88744800	0.77101200
C	-2.54750800	3.75252700	0.57031500
H	-1.22730100	2.32419900	-0.32973600
C	-3.80887400	3.98470800	1.12003200
H	-5.72285500	3.13086500	1.61683900
H	-1.82201700	4.55526700	0.51319000
H	-4.06346300	4.97085600	1.49066400
H	-1.62551300	-1.03464000	-2.42298700
P	-2.70634600	-0.20027700	-0.44098600
C	4.37823100	1.85577100	1.18017200
H	5.34008200	1.39269700	1.41381600
H	4.37844800	2.87009300	1.58302000
H	3.58835400	1.27888400	1.66794900
C	-1.60372200	-1.01228000	0.75068300
C	-0.88837600	-2.15459500	0.36172500
C	-1.47518400	-0.51403400	2.05266000
C	-0.05085500	-2.78834800	1.27424600
H	-0.97890900	-2.55566500	-0.64040700
C	-0.63496200	-1.15698600	2.95951900
H	-2.02130600	0.36885900	2.36018100
C	0.07610700	-2.29084800	2.57188100

H	0.50238600	-3.66902100	0.97100200
H	-0.53687700	-0.76856400	3.96608200
H	0.73092900	-2.78691100	3.27870100

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