

Opening of an Accessible Microporosity in an Otherwise Nonporous Metal–Organic Framework by Polymeric Guests

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Materials and Methods

Synthesis of Co₂(NDC)₂(Bipy) (**1_{NP}**)

N,N-dimethylformamide (DMF, 600ml) was introduced in a 1 L glass bottle with a PBT screw cap (resistant to 180 °C), then degassed under reduced pressure. Co(NO₃)₂•6H₂O (1.000 g, 3.43 mmol), 2,6-naphthalenedicarboxylate (NDC, 0.743 g, 3.43 mmol), 4, 4'-bipyridine (Bipy, 0.269 g, 1.72 mmol) and deionized water (0.050 g, 2.78 mmol) were introduced in the reaction vessel, and stirred until dissolution of all the reagents. The bottle was then tightly sealed and placed at 120 °C for 24 h, then let to cool down. Crystals were collected by filtration over a PTFE membrane (0.1 μm), and rinsed with anhydrous DMF, hexane and methanol. The microcrystalline dark green powder was then collected and dried under reduced pressure (0.1 kPa) at room temperature for 16h, yielding **1_{NP}**. The color of the powder changed to red-purple as the methanol was removed from the pores. **1_{NP}** was then stored at 4 °C over desiccating silica to prevent further evolution.

Synthesis of **1-PSt** composites

1_{NP} (ca. 300 mg) was introduced in a flask with a 3-ways tap, and put under a N₂ atmosphere. AIBN (35 mg per 1 g of **1_{NP}**) was dissolved in neat styrene (St, ca. 3 ml), and the solution was introduced in the vial through the 3-ways tap, as a flux of N₂ was maintained. The color of the powder changed instantly from red-purple to dark green as the St was introduced. St was then removed under controlled pressure (0.3 kPa) at room temperature, until the powder became dry and the mass of the vial stopped decreasing. This resulted in the monomer-loaded **1-St**. Upon completion of the monomer introduction, St corresponded to 27 wt% of the mass of the composite (*i.e.* a mass increase of 37 wt% of the empty MOF). The vial was then put under a N₂ atmosphere, and placed at 80 °C to react. The St conversion could be controlled by adjusting the reaction time (see Table S1). After this time, the system was washed abundantly with dehydrated methanol, then dried at 80 °C under reduced pressure (0.1 kPa) to remove residual monomer and washing solvent.

Synthesis of **1-PMMA** composites

1-PMMA composites were prepared in a similar fashion as **1-PSt**, by immersing **1_{NP}** in freshly distilled methyl methacrylate. Evacuation of the monomer was performed at 1.8 kPa, and polymerization reaction was performed at 80 °C.

Synthesis of **1-PAN** composites

1-PAN composites were prepared in a similar fashion as **1-PSt**, by immersing **1_{NP}** in freshly distilled acrylonitrile. Evacuation of the monomer was performed at 8 kPa, and polymerization reaction was performed at 100 °C.

PSt extraction

1-PSt composites (ca. 100 mg) were sonicated during 2h in an aqueous solution of ethylenediaminetetraacetic acid disodium (Na₂EDTA, 0.05 mmol/L, ca. 30ml). This resulted in a color change for the suspension from dark green to orange, as the MOF was completely decomposed. The suspension is then filtered over a PTFE membrane (0.1 µm), then washed abundantly with water, HCl (1 mol/L in water), water and MeOH, then let to dry to yield PSt. A further purification from the residual salts was performed by dissolving the PSt in a minimal amount of DMF, then precipitating it with water and collecting it by filtration over a PTFE membrane.

Instrumentation

Powder X-ray diffractometry

PXRD diagrams were collected on a Rigaku SmartLab Diffractometer, using a Cu anode and a K_α monochromator ($\lambda = 0.154$ nm). Variable temperature PXRD measurements were performed under a N₂ flux, using the built-in DSC module.

Gas adsorption measurement

N₂ and CO₂ adsorption measurements were performed on a BELSORP II mini (BEL-Japan, Inc.). Propane adsorption measurements were performed using a BELSORP-Max (BEL-Japan, Inc.). Samples were activated at 80 °C for 16 h before the measurement.

Differential Scanning Calorimetry

DSC plots were collected on a DSC7020 Thermal Analysis System (Hitachi). Measurements were performed in an Al closed pan, under a N₂ flux.

Thermo-gravimetric analysis

TGA plots were recorded using a Rigaku TG 8120. Samples were heated in an aluminum pan (500 °C, 10 °C/min) under a N₂ flux (60 mL/min).

Gel permeation chromatography

Gel permeation chromatography (GPC) measurements on PSt were performed in chloroform at 40 °C on three linear-type polystyrene gel columns (Shodex K-805L) that were connected to a JASCO PU-980 precision pump, a JASCO RI-930 refractive index detector, and a JASCO UV-970 UV/vis detector set at 256 nm. The columns were calibrated against standard polystyrene samples.

Liquid state ¹H nuclear magnetic resonance spectroscopy

Spectra were collected on a JEOL ECS-400 (400 MHz).

Polymer content determination

PSt and PMMA contents in the composites were determined using TGA, under air (see Figure S1 and Table S1). Samples were heated at 500 °C for 90 minutes, so that a plateau in mass loss could be observed. This resulted in the complete decomposition of the polymers (residue after combustion $r_{polymer} = 0$), as well as the conversion of **1** into Co₃O₄. Since the cobalt is initially present as Co (II), this oxidation could explain the mass increase upon heating observed in some cases. The residue r_{MOF} after full combustion of **1_{NP}** corresponded to 23 ± 0.5 % of the initial mass. Loading rate in polymer $X_{polymer}$ (in wt% of the composite) with the formula $r_{Composite} = 0 + (1 - X_{polymer})r_{MOF}$, hence, $X_{polymer} = 1 - r_{Composite}/r_{MOF}$.

In the case of PAN, the formation of graphitized residues¹ leads to $r_{PAN} \neq 0$ and this method could not be used. Instead, X_{PAN} was determined by NMR, after dissolution in a mixture of DMSO-d₆ and DCl (37 % in D₂O) (9:1 v/v), in which the MOF could be etched and PAN could be dissolved.

Calculation of occupancy rate

The loading X (in wt% of the composite) is first converted into x , expressed in wt% of the empty MOF, using the formula $x = X/(1-X)*100$. The number N of monomeric units per unit cell is then calculated with the formula $N = x/M_{monomer} * M_{unit\ cell}/100$, with $M_{monomer} = 104.15$ g/mol, and $M_{unit\ cell} = 1404.86$ g/mol (formula: Co₄(NDC)₄(Bipy)₂).

The occupancy rate is then estimated by calculating the length of polymer available per unit cell (0.259 nm per monomeric unit),² and comparing this length to the dimension of the unit-cell along the nanochannel (*ca.* 1.38 nm).³

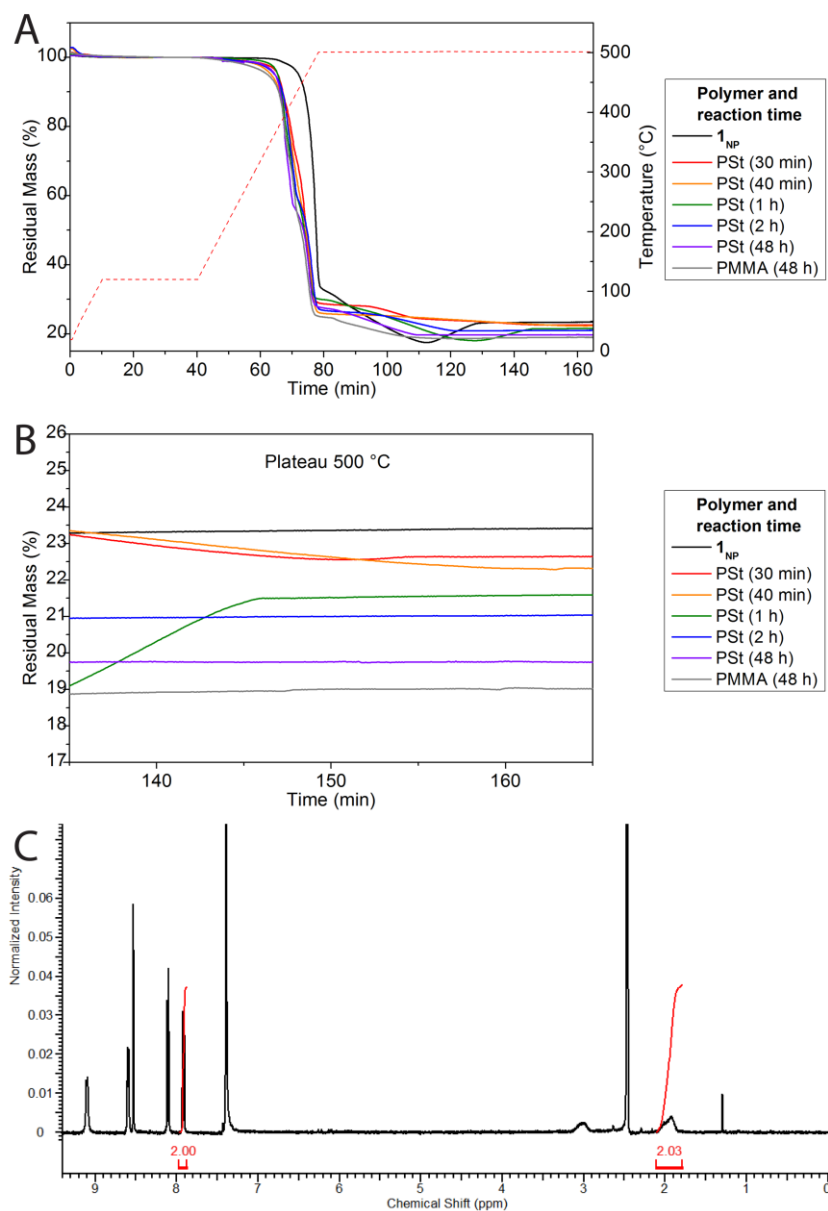


Figure S1: A-B: TGA curves for **1-PSt** and **1-PMMA** composites, obtained after various polymerization times. Analysis were performed under air. A: Full TGA range; dotted line and right axis: Temperature. B: Detail of the plateau at 500 °C. The polymer content corresponding to each reaction time can be found in Table S1. C: NMR spectrum of 1-PAN, in a mixture (9:1 v/v) of DMSO- d_6 and DCl (Solution 37% in D_2O). The integrated peaks corresponds to protons of NDC (doublet, 7.92 ppm), and to protons of PAN (CH_2CHCN , broad, 1.92 ppm). The integration ratio leads to the formula $Co(NDC)(Bipy)_{0.5} \cdot AN_{1.0}$, corresponding to a loading rate $X = 13 \text{ wt\%}$.

1-Polymer	Polymerization time	$r_{\text{composite}}$	Loading X (% of the composite)	Occupancy (% of the maximal capacity)
1-PSt	0 min	23.4	0	0
1-PSt	30 min	22.6	3	9
1-PSt	40 min	22.3	5	13
1-PSt	1 h	21.8	7	19
1-PSt	2 h	21	10	29
1-PSt	48 h	19.7	16	47.5
1-PMMA	48 h	19.0	18	59

Table S1: Dependency of the loading rate of **1-Polymer (1-PSt and 1-PMMA)** as a function of the polymerization time, as determined by TGA (Figure S1).

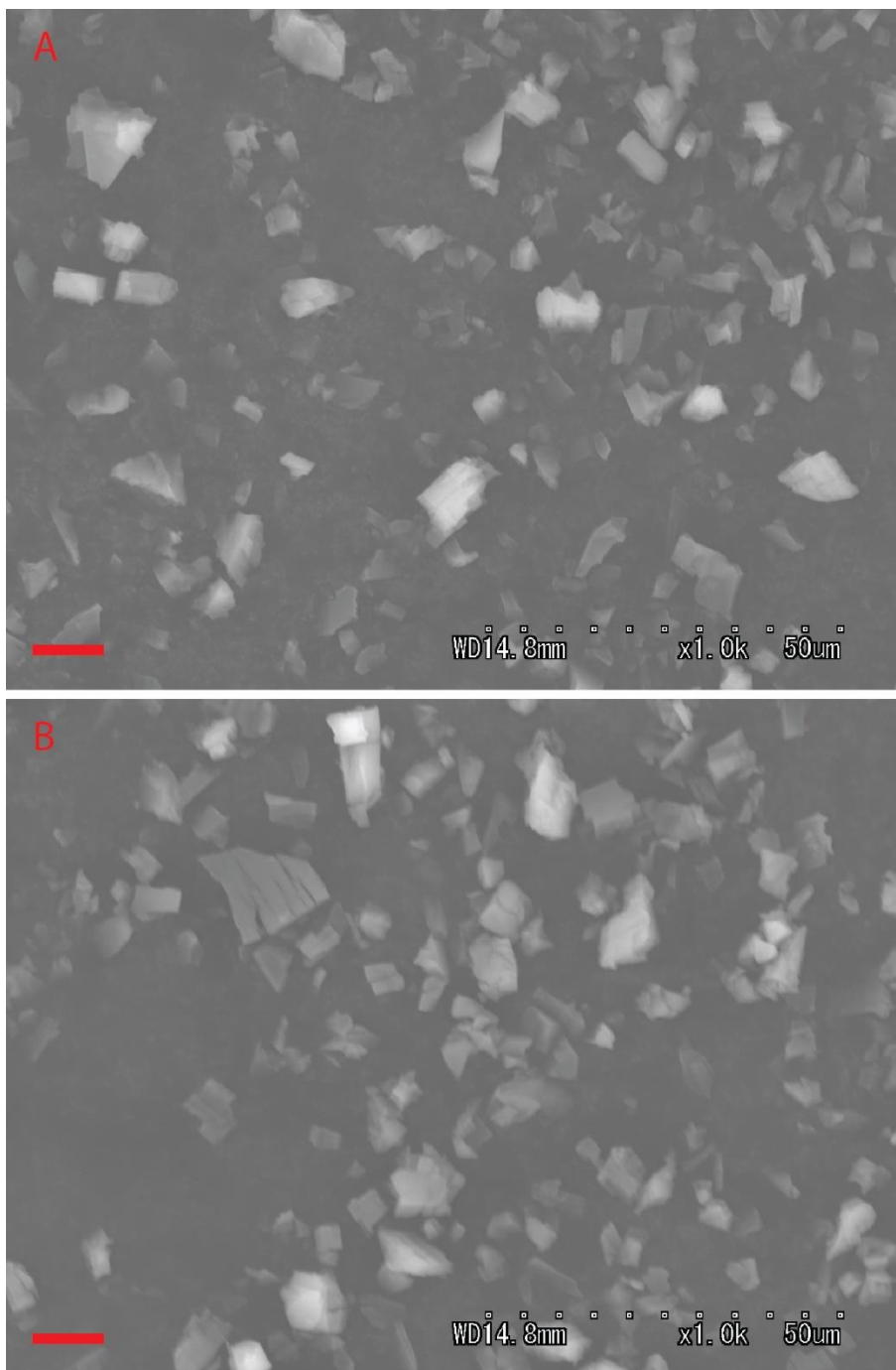


Figure S2: A, B: SEM micrographs of **1-PSt(7%)** (A) and **1-PSt(16%)** (B). The red scale bars represent 10 μm . No PSt is observed outside of the MOF particles. The composites are constituted of microcrystalline prisms (ca. 5-10 μm particles). Particles of this size have only a limited outer surface (ca. 1 m^2/g), so adsorption phenomena occur mainly in the pores inside the material.

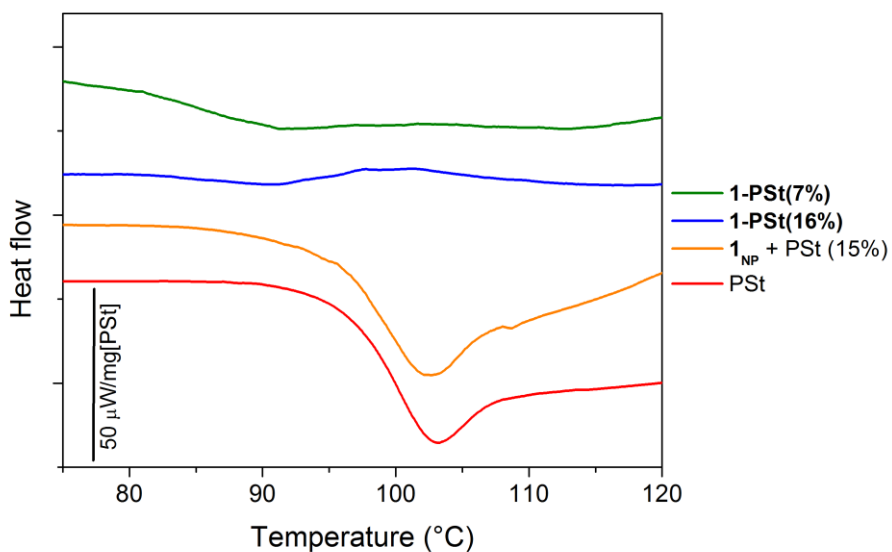


Figure S3: Differential scanning calorimetry (DSC) analysis of **1-PSt** composites, PSt (extracted from **1-PSt(16%)**), and **1** + PSt (15 wt.%, reintroduction from a solution in chloroform).

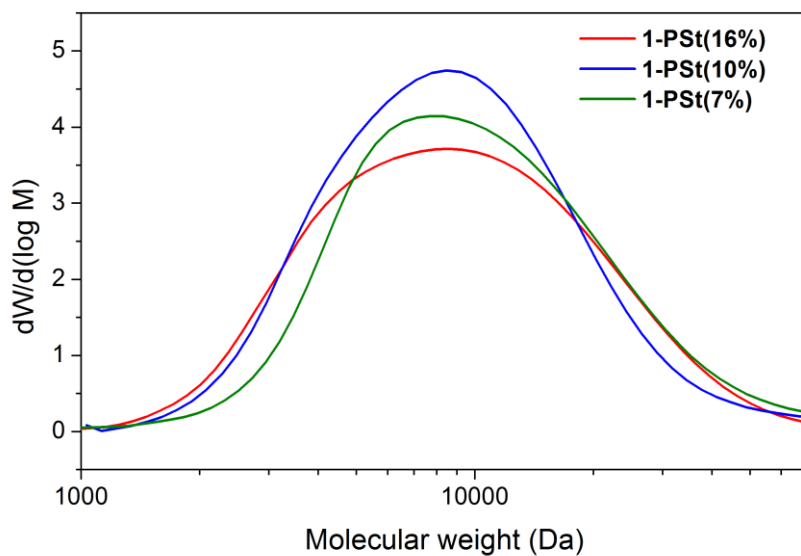


Figure S4: Molecular weight distribution (obtained by GPC) of PSt isolated from **1-PSt(N%)**. Molecular weights for the polymers are: **1-PSt(16%)**: $M_n = 7700$ Da, $I = 1.94$; **1-PSt(10%)**: $M_n = 6900$ Da, $I = 1.74$; **1-PSt(7%)**: $M_n = 8800$ Da, $I = 1.79$.

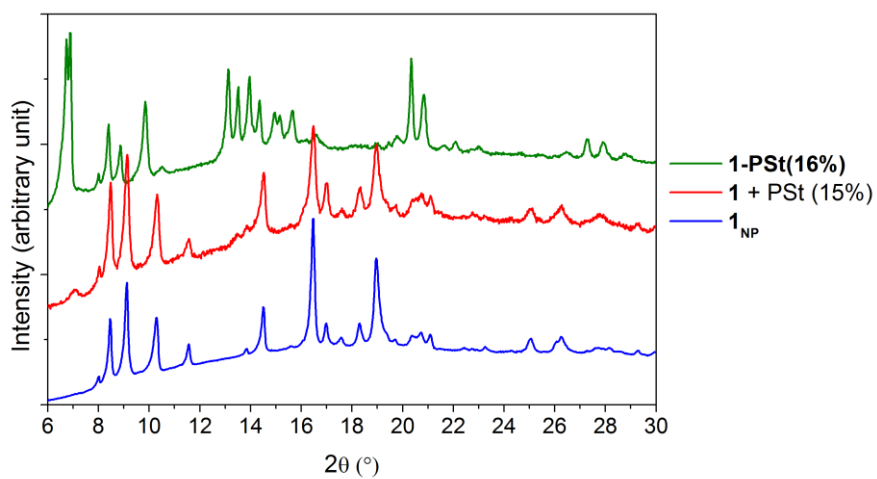


Figure S5: PXRD patterns of **1-PSt(16%)**, **1_{NP} + PSt(15%)** obtained by direct introduction from chloroform, and **1_{NP}**. The similarity between **1_{NP} + PSt(15%)** and **1_{NP}** indicates that preformed PSt cannot be included from the solution after evacuation of the volatile solvent.

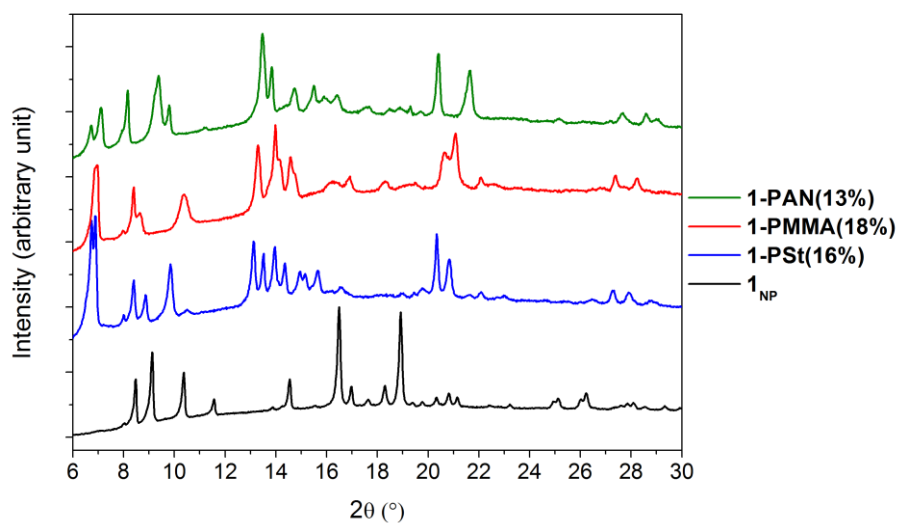


Figure S6: PXRD diagrams of composites of **1** with several polymers.

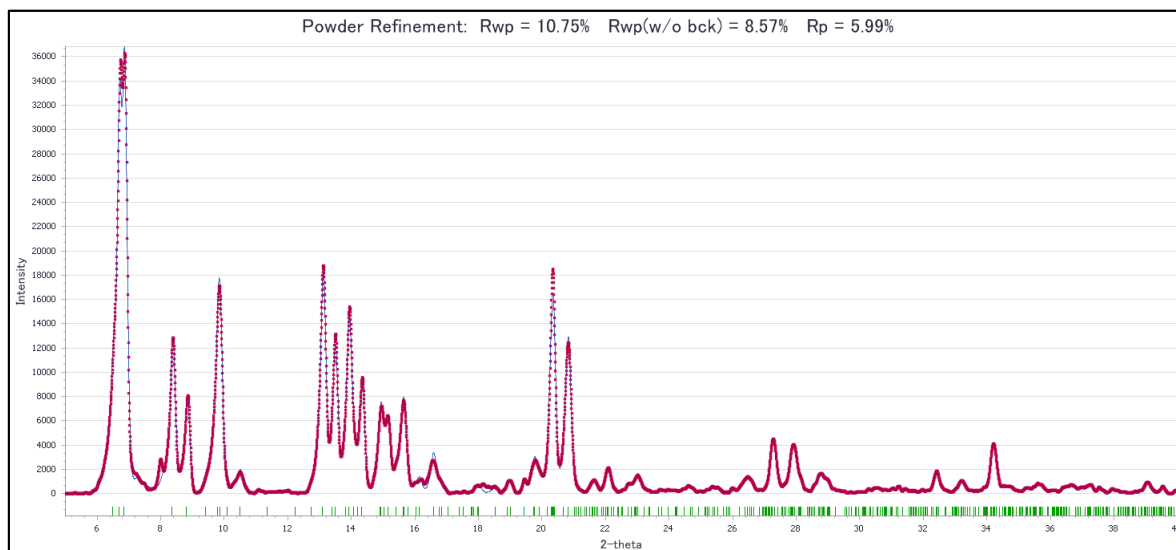


Figure S7: Results of a Pawley refinement for the PXRD pattern (Cu, $\lambda = 0.154$ nm) of **1-PSt(16%)**. Unit cell parameters are indicated on Table S2. Color code: Experimental (red), Simulated (blue), observed reflection (green).

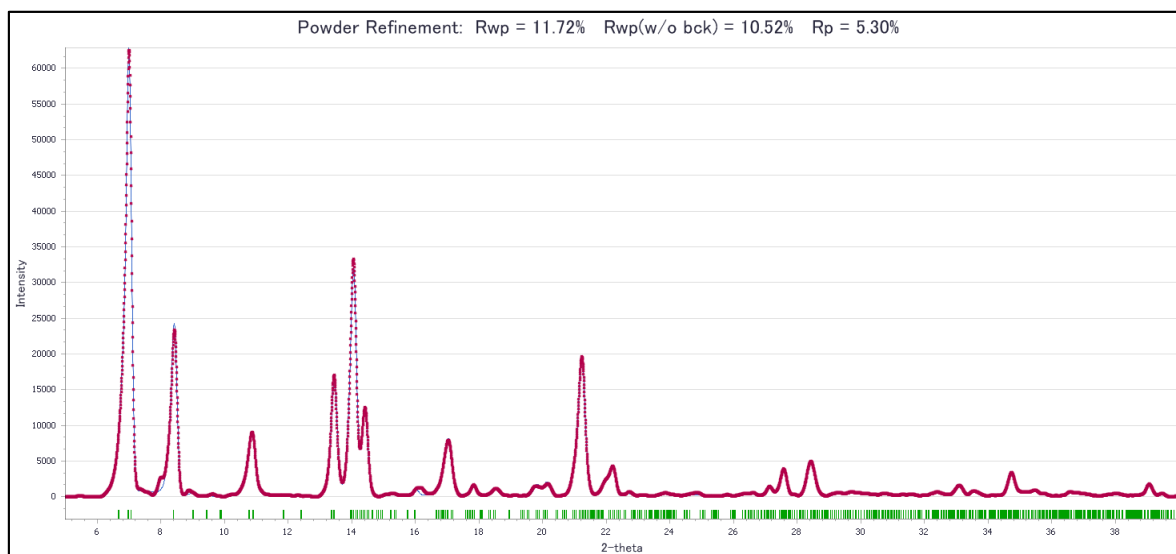


Figure S8: Results of a Pawley refinement for the PXRD pattern (Cu, $\lambda = 0.154$ nm) of **1-PSt(5%)**. Unit cell parameters are indicated on Table S2. Color code: Experimental (red), Simulated (blue), observed reflection (green).

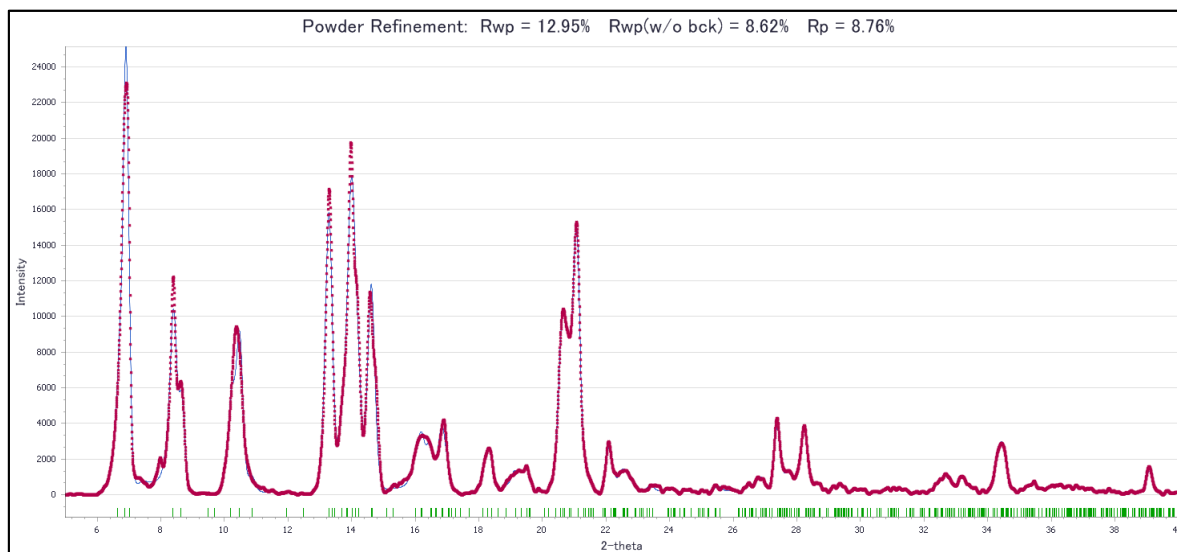


Figure S9: Results of a Pawley refinement for the PXRD pattern (Cu, $\lambda = 0.154$ nm) of **1-PMMA(18%)**. Unit cell parameters are indicated on Table S2. Color code: Experimental (red), Simulated (blue), observed reflection (green).

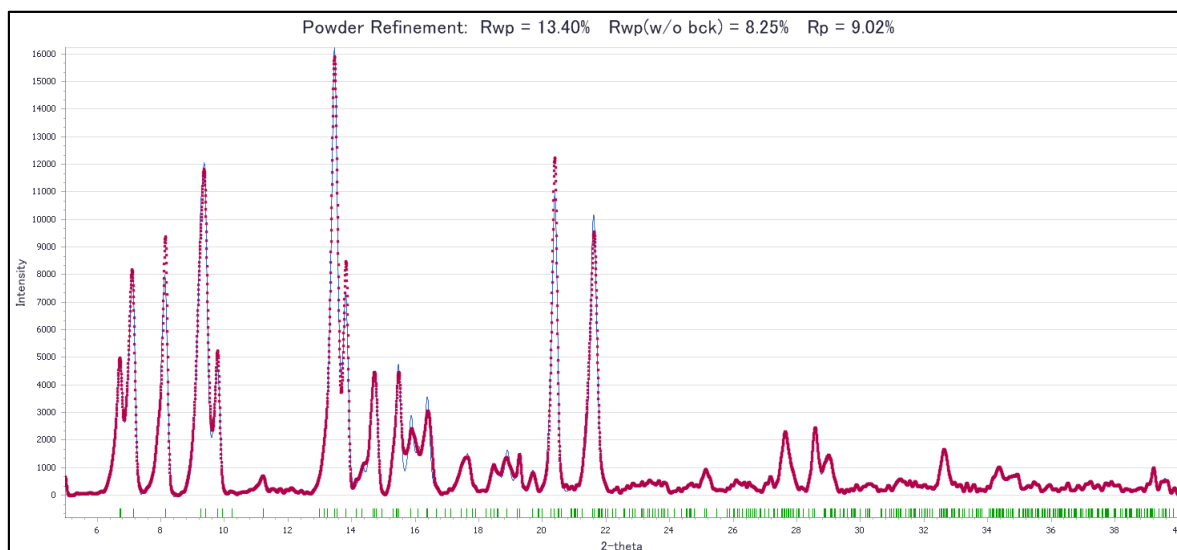


Figure S10: Results of a Pawley refinement for the PXRD pattern (Cu, $\lambda = 0.154$ nm) of **1-PAN(13%)**. Unit cell parameters are indicated on Table S2. Color code: Experimental (red), Simulated (blue), observed reflection (green).

Composite	1-PSt(5%)	1-PSt(16%)	1-PMMA(18%)	1-PAN(13%)
$a / \text{\AA}$	12.936	13.141	12.968	13.059
$b / \text{\AA}$	13.185	13.206	13.025	13.160
$c / \text{\AA}$	13.756	13.921	13.893	13.862
$\alpha / ^\circ$	74.55	82.92	77.70	84.98
$\beta / ^\circ$	84.67	76.89	74.27	71.63
$\gamma / ^\circ$	78.86	86.24	82.88	83.75
$V / \text{\AA}^3$	2217	2333	2201	2244
$R_p (\%)$	5.30	5.99	8.76	9.02

Table S2: Unit cell parameters of representative **1-Polymer** composites, determined by Pawley refinement (See Figure S6 to S9).

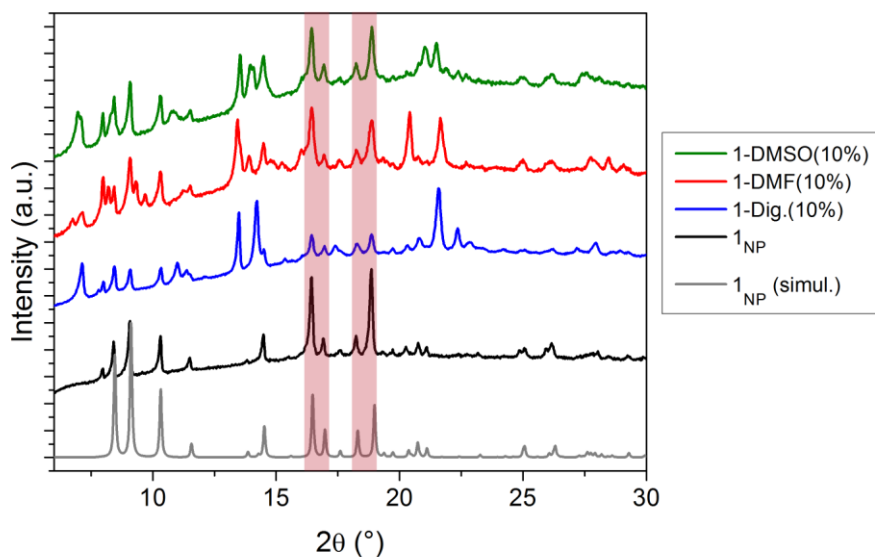


Figure S11: PXRD of **1** with various molecular guests, included at a fraction of the maximal capacity (*ca.* 25-30 % for each guest). The characteristic quadruplet of **1_{NP}** is highlighted in red. *Dig.*: Diglyme (Diethylene glycol dimethyl ether).

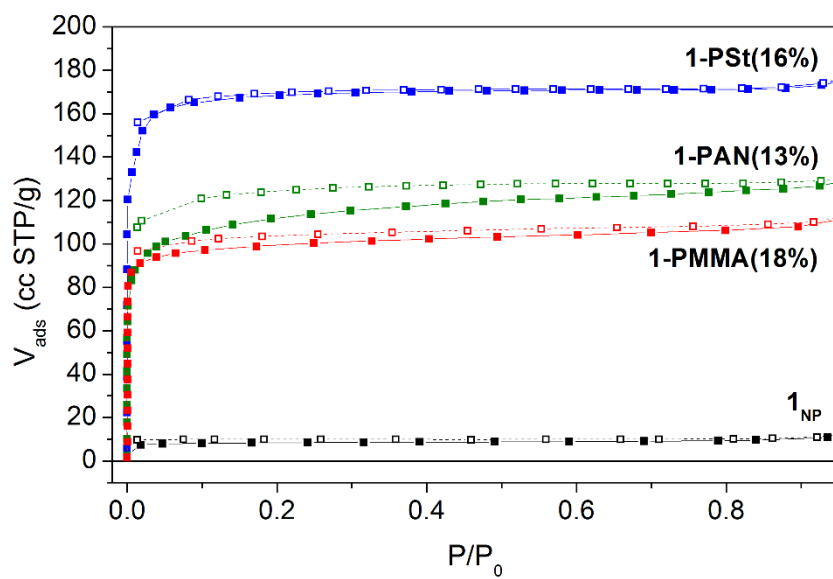


Figure S12: N_2 adsorption isotherms (77 K) of composites of **1** with several polymers.

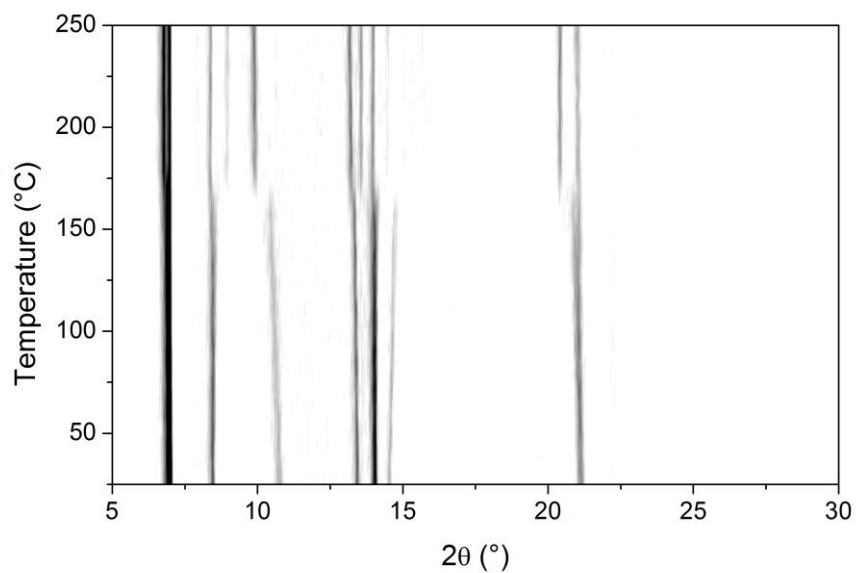


Figure S13: Variable temperature PXRD of **1-PSt(7%)**. The measurement was performed under a N_2 flux, with a heating rate of $2\text{ }^\circ\text{C}/\text{min}$.

References

- (1) Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stab.* **2007**, 92, 1421.
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