

## Supporting Information of the manuscript

# A Chiral Co-Crystalline Form of Poly(2,6-dimethyl-1,4-phenylene)oxide (PPO)

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**Table S1.** Diffraction angles ( $2\theta_{obsd}$ ) and Bragg distances ( $d_{obsd}$ ) of the reflections observed in the X-ray powder diffraction patterns of Figures 3B, C, D and E. The patterns correspond to co-crystalline phases of PPO with racemic (Columns A and B) or non-racemic (Columns C and D)  $\alpha$ -pinene molecules. The  $hkl$  indices, attributed according the tetragonal unit cell ( $a=1.19$  nm,  $c=1.71$ nm) proposed in ref.9c have been also reported.

	A		B		C		D		
	PPO/racemic guest <sup>1</sup>		PPO/racemic guest <sup>2</sup>		PPO/(1S)-(-)- $\alpha$ -pinene <sup>3</sup>		PPO/(1R)-(+)- $\alpha$ -pinene <sup>4</sup>		
	$hkl$	$2\theta_{obsd}$ (deg)	$d_{obsd}$ (nm)	$2\theta_{obsd}$ (deg)	$d_{obsd}$ (nm)	$2\theta_{obsd}$ (deg)	$d_{obsd}$ (nm)	$2\theta_{obsd}$ (deg)	$d_{obsd}$ (nm)
*				7.3	1.219			7.4	1.203
<b>1</b>	101	9.0	0.983	9.1	0.969	9.2	0.966	9.2	0.962
<b>2</b>	110	10.4	0.851	10.6	0.839	10.7	0.828	10.7	0.827
<b>3</b>	111	11.8	0.750					11.8	0.749
<b>4</b>	102	12.8	0.692	12.9	0.685	13.1	0.678	13.1	0.676
<b>5</b>	200	14.8	0.599	15.0	0.592	15.0	0.590	15.1	0.587
<b>6</b>	201	15.8	0.562	15.8	0.560	15.9	0.558	15.9	0.558
<b>7</b>	210	16.7	0.531						
<b>8</b>	211	17.4	0.510	17.5	0.506	17.5	0.506	17.6	0.503
<b>9</b>	212	19.6	0.453	19.7	0.450	19.6	0.454	19.8	0.449
<b>10</b>	220	21.2	0.420	21.4	0.415	21.6	0.412	21.3	0.417
<b>11</b>	221	21.7	0.410	21.8	0.408			21.9	0.406
<b>12</b>	301	23.0	0.387	23.0	0.387	23.2	0.383	23.5	0.378
<b>13</b>				27.3	0.326	27.2	0.328	27.3	0.327

<sup>1</sup> Figure 3-E, clathrate form with non racemic guest (data from Ref. 9C).

<sup>2</sup> Figure 3-D, clathrate form with non racemic guest (our data).

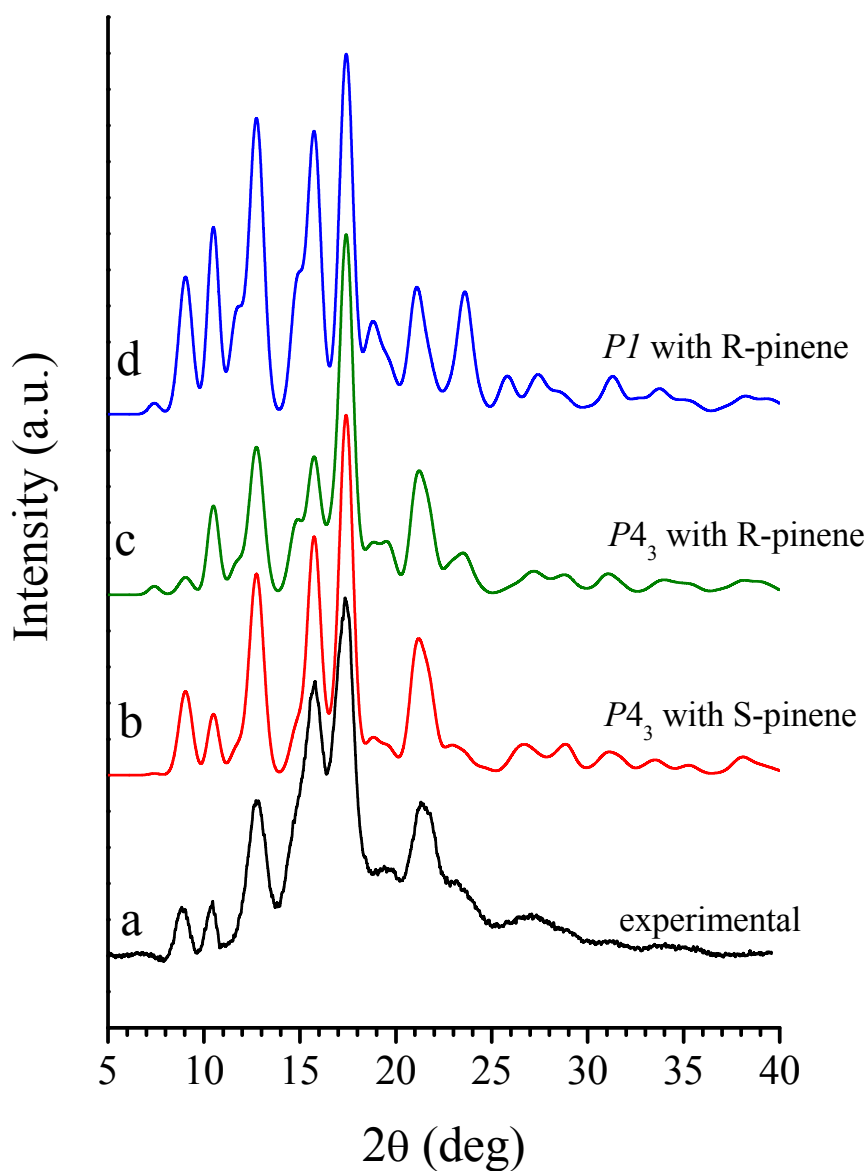
<sup>3</sup> Figure 3-B, clathrate form with (1S)-(-)- $\alpha$ -pinene (our data).

<sup>4</sup> Figure 3-C, clathrate form with (1R)-(+)- $\alpha$ -pinene (our data).

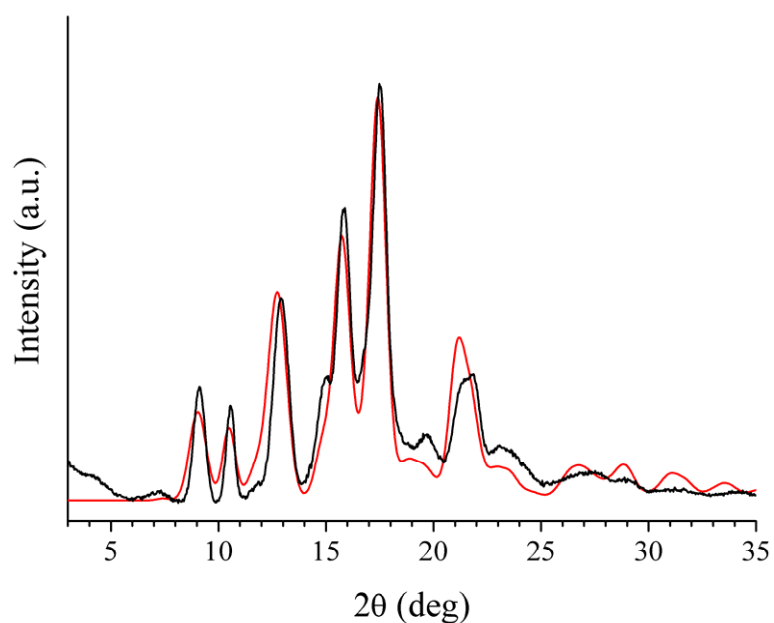
\* Reflection attributable to some minor amount of PPO nanoporous form (see Ref. 4f)

**Table S2.** Fractional coordinates of the atoms of the asymmetric unit of the co-crystalline form of PPO with (1*S*)-(-)- $\alpha$ -pinene according the model reported in Figure 4 (cell constants  $a = b = 1.19$  nm,  $c = 1.71$  nm; space group  $P4_3$ ). The fractional coordinates of the atoms of the guest are reported in italics. Hydrogen atoms were included in the structure factors calculation, but they are omitted in this table for simplicity.

	$x/a$	$y/b$	$z/c$
C1	0,159	0,028	0,098
C2	0,199	0,052	0,173
C3	0,179	-0,018	0,236
C4	0,114	-0,114	0,226
C5	0,071	-0,139	0,152
C6	0,094	-0,069	0,089
O1	0,098	-0,190	0,286
C7	0,231	0,010	0,315
C8	0,002	-0,243	0,138
C1b	-0,477	0,658	0,579
C2b	-0,455	0,701	0,505
C3b	-0,523	0,679	0,441
C4b	-0,617	0,609	0,451
C5b	-0,638	0,562	0,525
C6b	-0,570	0,587	0,587
O1	-0,692	0,591	0,391
C7b	-0,498	0,731	0,363
C8b	-0,739	0,487	0,537
<i>C</i>	<i>0,001</i>	<i>0,342</i>	<i>0,357</i>
<i>C</i>	<i>-0,073</i>	<i>0,266</i>	<i>0,382</i>
<i>C</i>	<i>-0,184</i>	<i>0,305</i>	<i>0,418</i>
<i>C</i>	<i>-0,187</i>	<i>0,432</i>	<i>0,417</i>
<i>C</i>	<i>-0,076</i>	<i>0,479</i>	<i>0,451</i>
<i>C</i>	<i>-0,030</i>	<i>0,467</i>	<i>0,367</i>
<i>C</i>	<i>0,112</i>	<i>0,314</i>	<i>0,319</i>
<i>C</i>	<i>-0,150</i>	<i>0,484</i>	<i>0,338</i>
<i>C</i>	<i>-0,186</i>	<i>0,431</i>	<i>0,259</i>



**FIGURE S1.** Comparison between the experimental X-ray powder diffraction pattern (black line) of the co-crystalline form of PPO with (1*S*)-(-)- $\alpha$ -pinene, after subtraction of the amorphous and background halos, with the calculated ones according to (b) the structural model proposed in Figure 5 of the text (space group  $P4_3$ , S guests), (c) a structural model in the space group  $P4_3$  containing only R guests, (d) a structural model in the space group  $P1$  (with antichiral helices) and containing only R guests.



**Figure S2.** Comparison between the experimental X-ray powder diffraction pattern (black solid line) of the co-crystalline form of PPO with racemic  $\alpha$ -pinene after subtraction of the amorphous and background halos (see Figure 3) with the calculated one (red solid line) according to the structural model proposed in the text in the likely hypothesis that it is constituted by a mixture of chiral crystals including only R and L polymer helices and (1*R*)-(+)- $\alpha$ -pinene and (1*S*)-(–)- $\alpha$ -pinene enantiomers, respectively.