Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic supporting information for:

Polymers of intrinsic microporosity containing aryl-phthalimide moieties: Synthesis, modeling, and membrane gas transport properties

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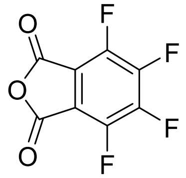
Experimental part

Monomers and polymers synthesis

3,4,5,6-tetrafluorophthalic anhydride [1]

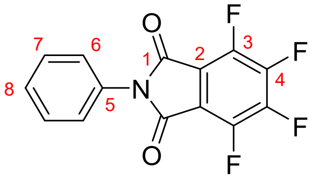


According to a literature procedure,[1] in a 100 mL three-neck flask equipped with a reflux condenser, a dropping funnel and nitrogen inlet, 3,4,5,6-tetrafluorophthalic acid (30 g, 126 mmol) was added followed by dropwise addition of tionyl cloride (40 mL, 550 mmol) over 5 min at 60 °C. Then, the reaction mixture was stirred at 80 ºC under nitrogen flow overnight. After removing the excess thionyl chloride by distillation, the resulting off-white solid was washed with *n*-hexane (2x20 mL) and dried under vacuum. Finally, the product was sublimated (75 °C, 10 mbar) to give a colorless crystalline solid (27.9 g, 117 mmol, 93%). Mp 94-95 ºC; IR (KBr, ν, cm^{-1}): 1869 (C=O, sym.), 1778 (C=O, asym.); 1520, 1401 (C=C); 1215 (C-O).

General procedure tetraflurophthalimide monomers synthesis

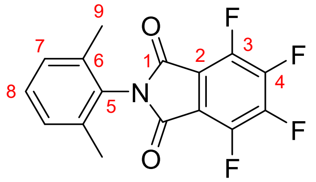
According to a modified literature procedure,[2] the appropriate amine (14.6 mmol) was dissolved in glacial acetic acid (20 mL) with stirring at room temperature. Subsequently, **1** (3.30 g, 15.0 mmol) was added and the system was refluxed for 16 h. The mixture was poured into an aqueous hydrochloric acid solution (9%, 400 mL) and stirred vigorously for 1 h. The suspended solid was collected by filtration under vacuum, washed with plenty of water and dried in the vacuum oven at 110 °C for 24 h.

3,4,5,6-tetrafluoro-*N*-phenylphthalimide [IM1]



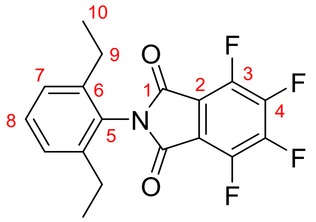
Using the general procedure tetraflurophthalimide monomers synthesis, monomer **IM1** was obtained from aniline as a very pale-yellow solid (4.01 g, 93%). Mp 204-206 ºC. IR (KBr, ν, cm^{-1}): 3068 (C-H arom.); 1784, 1720 (C=O); 1597, 1512 (C=C); 947 (C-F). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.56 (t, *J* = 7.5 Hz, 2H, H-7); 7.48 (t, *J* = 7.3 Hz, 1H, H-8); 7.44 (d, *J* = 7.2 Hz, 2H, H-6). ^{13}C NMR (DMSO-d_6, δ, ppm): 161.82 (C1); 144.14 (d, *J* = 265 Hz, C-3); 142.66 (d, *J* = 266 Hz, C-4); 130.92 (C-5); 129.09 (C-7); 128.74 (C-8); 127.37 (C-6); 114.05 (C-2). Elem. Anal. Calcd. for $C_{14}H_5F_4NO_2$ (295.19): C, 56.96%; H, 1.71%; N, 4.75%. Found: C, 56.23%; H, 1.43%; N, 4.63%.

N-(2,6-dimethylphenyl)-3,4,5,6-tetrafluorophthalimide [IM2]



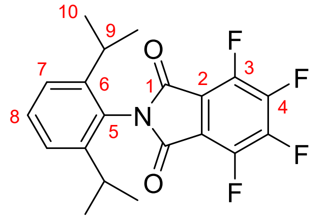
Using the general procedure tetraflurophthalimide monomers synthesis, monomer **IM2** was obtained from 2,6-dimethylaniline as a white powder (4.29 g, 91%). Mp 171-173 ºC. IR (KBr, ν, cm^{-1}): 3072 (C-H arom.); 2973, 2863 (C-H aliph.); 1789, 1711 (C=O); 1597, 1520 (C=C); 944 (C-F). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.34 (t, *J* = 7.3 Hz, 1H, H-8); 7.25 (t, *J* = 7.3 Hz, 2H, H-7); 2.11 (s, 6H, H-9). ^{13}C NMR (DMSO-d_6, δ, ppm): 161.33 (C-1); 144.37 (d, *J* = 264 Hz, C-3); 142.80 (d, *J* = 266 Hz, C-4); 136.73 (C-6); 129.72 (C-8); 128.73 (C-5); 128.42 (C-7); 113.79 (C-2); 17.42 (C-9). Elem. Anal. Calcd. for $C_{16}H_9F_4NO_2$ (323.25): C, 59.45%; H, 2.81%; N, 4.33%. Found: C, 59.23%; H, 2.67%; N, 4.15%.

N-(2,6-diethylphenyl)-3,4,5,6-tetrafluorophthalimide [IM3]



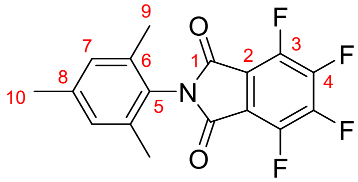
Using the general procedure tetraflurophthalimide monomers synthesis, monomer **IM3** was obtained from 2,6-diethylaniline as a colorless solid (4.58 g, 89%). Mp 181-183 ºC. IR (KBr, ν, cm^{-1}): 3067 (C-H arom.); 2973, 2935, 2872 (C-H aliph.); 1788, 1711 (C=O); 1597, 1522 (C=C); 944 (C-F). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.46 (t, *J* = 7.7 Hz, 1H, H-8); 7.30 (t, *J* = 7.7 Hz, 2H, H-7); 2.41 (d, *J* = 7.5 Hz, 4H, H-9); 1.05 (t, *J* = 7.5 Hz, 6H, H-10). ^{13}C NMR (DMSO-d_6, δ, ppm): 161.33 (C-1); 144.37 (d, *J* = 264 Hz, C-3); 142.80 (d, *J* = 266 Hz, C-4); 136.73 (C-6); 129.72 (C-8); 128.73 (C-5); 128.42 (C-7); 113.79 (C-3); 24.10 (C-9) 14.30 (C-10). Elem. Anal. Calcd. for $C_{18}H_{13}F_4NO_2$ (351.30): C, 61.54%; H, 3.73%; N, 3.99%. Found: C, 61.37%; H, 3.61%; N, 3.87%.

N-(2,6-diisopropylphenyl)-3,4,5,6-tetrafluorophthalimide [IM4]



Using the general procedure tetraflurophthalimide monomers synthesis, monomer **IM4** was obtained from 2,6-diisopropylaniline as a white powder (5.08 g, 92%). Mp 184-185 ºC. IR (KBr, ν, cm^{-1}): 3078 (C-H arom); 2970, 2874 (C-H aliph.); 1786, 1722 (C=O); 1591, 1513 (C=C); 948 (C-F). ^{1}H NMR (DMSO-d_6, δ, ppm): 7,52 (t, *J* = 7,8 Hz, 1H, H-8); 7,37 (d, *J* = 7,8 Hz, 2H, H-7); 2,74 (hept., *J* = 6.8 Hz, 2H, H-9); 1,09 (d, *J* = 6,8 Hz, 12H, H-10). ^{13}C NMR (DMSO-d_6, δ, ppm): 162.40 (C-1); 147.05 (C6); 144.59 (d, *J* = 265 Hz, C-3); 143.03 (d, *J* = 268 Hz, C-4); 130.57 (C-8); 125.63 (C-5); 124.10 (C-7); 113,52 (C-3); 28.43 (C-9); 23.76 (C-10). Elem. Anal. Calcd. for $C_{20}H_{17}F_4NO_2$ (379.35): C, 63.32%; H, 4.52%; N, 3.69%. Found: C, 63.21%; H, 4.33%; N, 3.52%.

3,4,5,6-tetrafluoro-*N*-(2,4,6-trimethylphenyl)phthalimide [IM5]



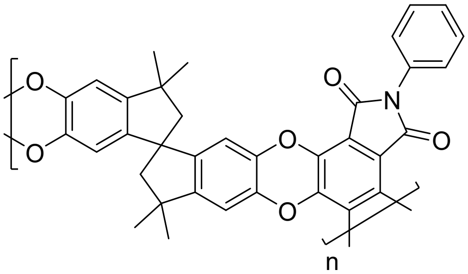
Using the general procedure tetraflurophthalimide monomers synthesis, monomer **IM5** was obtained from 2,4,6-trimethylaniline as a white powder (4.57 g, 93%). Mp 166 ºC. IR (KBr, ν, cm^{-1}): 3086 (C-H arom); 2923, 2861 (C-H aliph.); 1785, 1725 (C=O); 1507 (C=C); 945 (C-F). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.05 (s, 2H, H-7); 2.30 (s, 3H, H-10); 2.06 (s, 6H, H-9). ^{13}C NMR (DMSO-d_6, δ, ppm):

161.47 (C-1); 144.37 (d, *J* = 265 Hz, C-3); 142.88 (d, *J* = 266 Hz, C-4); 139.25 (C-8); 136.34 (C-6) 129.00 (C-7); 126.09 (C-5); 113.79 (C-2); 20.58 (C-10); 17.34 (C-9). Elem. Anal. Calcd. For $C_{17}H_{11}F_4NO_2$ (337.27): Elemental Analysis: C, 60.54%; H, 3.29%; N, 4.15%. Found: C, 60.25%; H, 3.13%; N, 4.08%.

General synthetic procedure for dibenzodioxin-based polymers

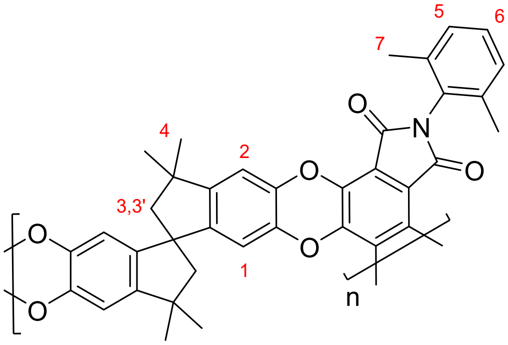
The commercially available monomer TTSBI was previously washed in chloroform, recrystallized in isopropanol and dried in the vacuum oven at 80 °C for 24 h. A mixture of **TTSBI** (1.0213 g, 3.000 mmol), the appropriate tetraflurophthalimide monomer (3,000 mmol) and anhydrous potassium carbonate (3.3200 g, 24.00 mmol) in dry DMF was stirred under nitrogen for 72 h at 65 ºC. The reaction crude was cooled to room temperature and poured into water (500 mL) with stirring. The precipitate was collected by filtration, washed with water, acetone and methanol, and then dried in the vacuum oven at 110 °C.

PIM-SBI-IM1



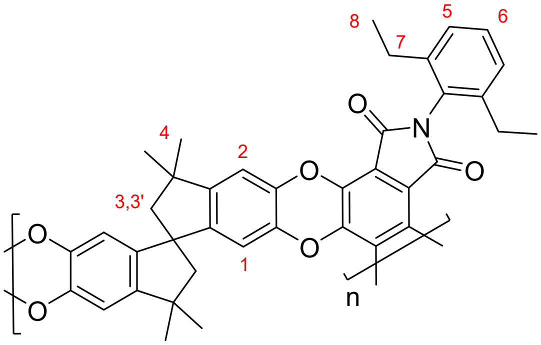
Using the general synthetic procedure for dibenzodioxin-based polymerization, **PIM-SBI-IM1** was synthesized from **IM1** (0.8856 g, 3.000 mmol) in dry DMF (25 mL). After that, the product was refluxed in THF, chloroform and finally in methanol for 6 h. The polymer was collected by filtration and dried under vacuum at 110 °C overnight. The final product was obtained as a yellow powder (1.56 g, 93%, based on the repeat unit). ATR-IR (film, ν, cm^{-1}): 2957, 2934, 2867 (C-H aliph.); 1770, 1720 (C=O); 1595, 1454 (C=C); 1362 (C-N); 1294, 1091 (C-O-C); 873, 810, 756, 689 (C–H out of plane). TGA (nitrogen): the 5% weight loss due to thermal decomposition was at 415 °C.

PIM-SBI-IM2



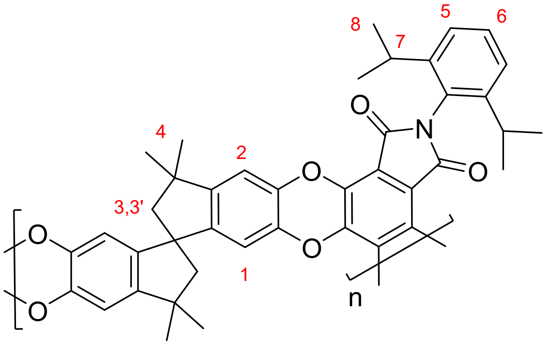
Using the general synthetic procedure for dibenzodioxin-based polymerization, **PIM-SBI-IM2** was synthesized from **IM2** (0.9698 g, 3.000 mmol) in dry DMF (27 mL). After that, the product was dissolved in THF and reprecipitated twice by dropwise addition of methanol with stirring. The solid was redissolved in tetrahydrofuran and precipitated in excess methanol, filtered under vacuum and refluxed in methanol for 6 h. Finally, the polymer was collected and dried under vacuum at 110 °C overnight. The final product was obtained as a yellow solid (1.33 g, 76%, based on the repeat unit). ATR-IR (film, ν, cm^{-1}): 2954, 2927, 2863 (C-H aliph.); 1770, 1720 (C=O); 1595, 1456 (C=C); 1362 (C-N); 1292, 1090 (C-O-C); 873, 814, 756, 694 (C–H out of plane). ^{1}H NMR (CDCl$_3$, δ, ppm): 7.30-6.98 (broad peak, 3H, H-5 and H-6); 6.98-6.66 (broad peak, 2H, H-2); 6.47 (broad peak, 2H, H-1); 2.31 (broad peak, 2H, H-3); 2.26-2.00 (broad peak, 2H, H-3'and H-7); 1.33 (broad peak, 12H, H-4). BET surface area = 471 m^2 g^{-1}; TGA (nitrogen): the 5% weight loss due to thermal decomposition was at 549 °C. η_{inh} = 1.36 dL g^{-1}.

PIM-SBI-IM3



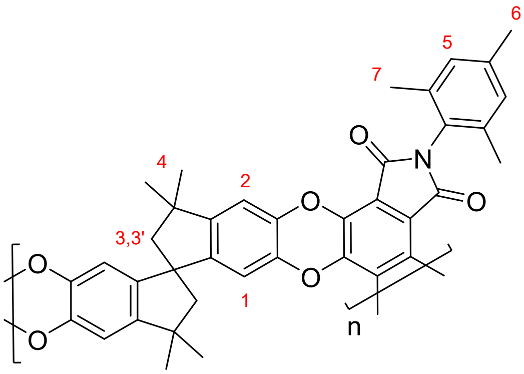
Using the general synthetic procedure for dibenzodioxin-based polymerization, **PIM-SBI-IM3** was synthesized from **IM3** (1.0539 g, 3.000 mmol) in dry DMF (32 mL). The polymer was purified following the procedure used for **PIM-SBI-IM2**. The final product was obtained as a yellow solid (1.51 g, 82%, based on the repeat unit). ATR-IR (film, ν, cm^{-1}): 2956, 2929, 2866 (C-H aliph.); 1770, 1720 (C=O); 1594, 1454 (C=C); 1362 (C-N); 1294, 1090 (C-O-C); 874, 815, 757, 696 (C–H out of plane). ^{1}H NMR (CDCl$_3$, δ, ppm): 7.34 (broad peak, 1H, H-6); 7.18 (broad peak, 2H, H-5); 6.96-6.68 (broad peak, 2H, H-2); 6.49 (broad peak, 2H, H-1); 2.62-2.24 (broad peak, 6H, H-3 and H-7); 2.17 (broad peak, 2H, H-3'); 1.30 (broad peak, 12H, H-4); 1.12 (broad peak, 6H, H-8). BET surface area = 434 m^2 g^{-1}. TGA (nitrogen): the 5% weight loss due to thermal decomposition was at 549 °C. η_{inh} = 1.27 dL g^{-1}

PIM-SBI-IM4



Using the general synthetic procedure for dibenzodioxin-based polymerization, **PIM-SBI-IM4** was synthesized from **IM4** (1.1381 g, 3.000 mmol) in dry DMF (34 mL). The polymer was purified following the procedure used for **PIM-SBI-IM2**. The final product was obtained as a yellow solid (1.53 g, 80%, based on the repeat unit). ATR-IR (film, ν, cm^{-1}): 2958, 2928, 2870 (C-H aliph.); 1770, 1720 (C=O); 1595, 1456 (C=C); 1362 (C-N); 1298, 1087 (C-O-C); 874, 816, 757, 737, 693 (C–H out of plane). ^{1}H NMR (CDCl$_3$, δ, ppm): 7.41 (broad peak, 1H, H-6); 7.23 (broad peak, 2H, H-5); 6.99-6.68 (broad peak, 2H, H-2); 6.51 (broad peak, 2H, H-1); 2.68 (broad peak, 2H, H-7); 2.32 (broad peak, 2H, H-3); 2.17 (broad peak, 2H, H-3'); 1.30 (broad peak, 12H, H-4); 1.15 (broad peak, 12H, H-8). BET surface area = 661 m^2 g^{-1}. TGA (nitrogen): the 5% weight loss due to thermal decomposition was at 537 °C. η_{inh} = 1.41 dL g^{-1}

PIM-SBI-IM5



Using the general synthetic procedure for dibenzodioxin-based polymerization, **PIM-SBI-IM5** was synthesized from **IM5** (1.0118 g, 3.000 mmol) in dry DMF (30 mL). The polymer was purified following the procedure used for **SBI-IM2**. The final product was obtained as a yellow solid (1.49 g, 83%, based on the repeat unit). ATR-IR (film, ν, cm^{-1}): 2954, 2927, 2863 (C-H aliph.); 1770, 1720 (C=O); 1595, 1456 (C=C); 1362 (C-N); 1294, 1091 (C-O-C); 874, 806, 759, 746 (C–H out of plane). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.05-6.68 (broad peak, 4H, H-2 and H-5); 6.49 (broad peak, 2H, H-1); 2.45-2.32 (broad peak, 5H, H-3 and H-6); 2.22-1.85 (broad peak, 8H, H-3' and H-7); 1.30 (broad peak, 12H, H-4). BET surface area = 495 m^2 g^{-1}. TGA (nitrogen): the 5% weight loss due to thermal decomposition was at 541 °C. η_{inh} = 1.21 dL g^{-1}

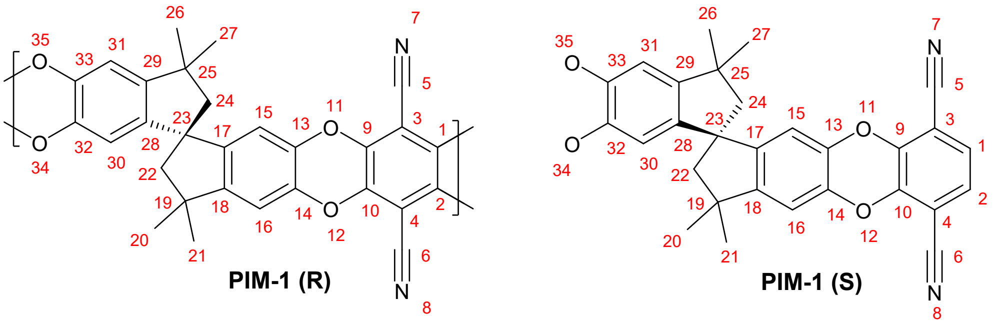


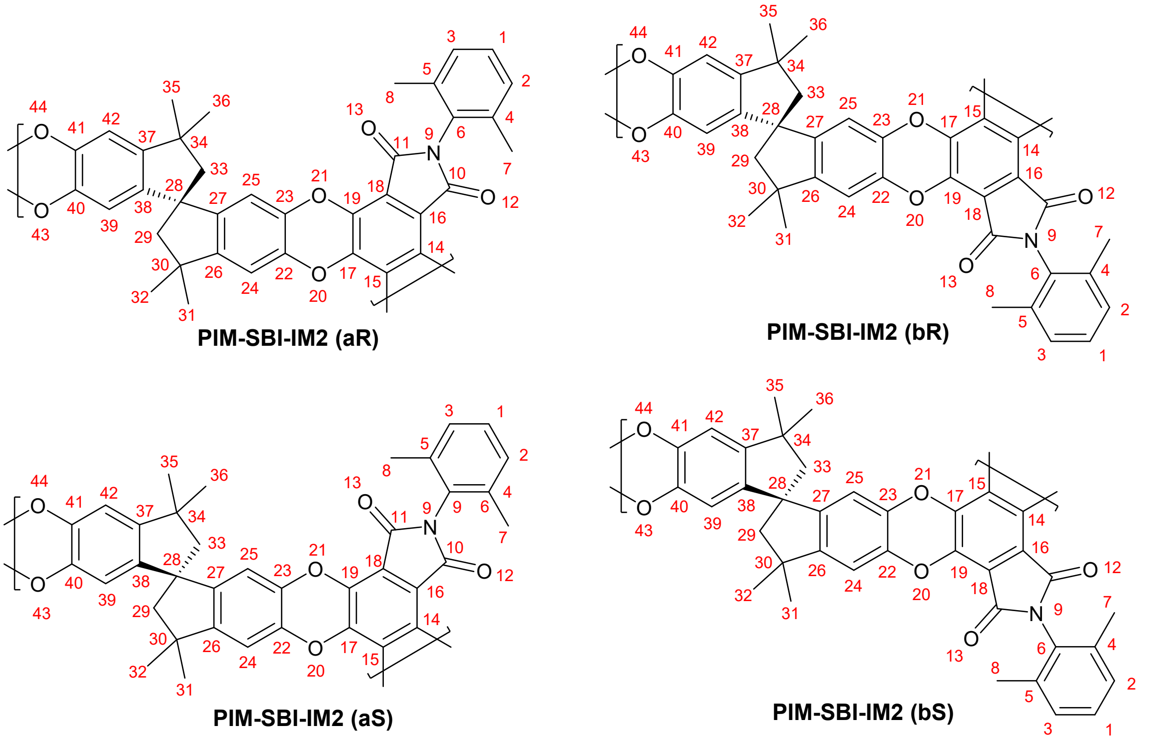
Fig. ESI1. Representation of the repeating units used for building the **PIM-1** models. The red label corresponds to **Table ESI1**, which gives atom types and partial charges.

Table ESI1. Force field atom type and partial charges assigned to the atoms and pseudo-atoms of

PIM-1 models. Atom labels refer to those shown in **Fig. ESI1**.

Label	**Atom type (GAFF)**	**Atom type (used)***	**Charge**		**Label**	**Atom type (GAFF)**	**Atom type (used)***	**Charge**
1	ca	CS0	+0.172		**19**	c3	CH0	+0.098
2	ca	CS0	+0.172		**20**	c3	CH3	0.000
3	ca	CA0	-0.123		**21**	c3	CH3	0.000
4	ca	CA0	-0.123		**22**	c3	CH2	-0.016
5	c1	CL0	+0.314		**23**	c3	CH0	+0.098
6	c1	CL0	+0.314		**24**	c3	CH2	-0.016
7	n1	NL0	-0.410		**25**	c3	CH0	+0.098
8	n1	NL0	-0.410		**26**	c3	CH3	0.000
9	ca	CSO	+0.172		**27**	c3	CH3	0.000
10	ca	CSO	+0.172		**28**	ca	CA0	+0.038
11	os	OA0	-0.219		**29**	ca	CA0	+0.038
12	os	OA0	-0.219		**30**	ca	CA1	-0.125
13	ca	CS0	+0.178		**31**	ca	CA1	-0.125
14	ca	CS0	+0.178		**32**	ca	CS0	0.178
15	ca	CA1	-0.125		**33**	ca	CS0	0.178
16	ca	CA1	-0.125		**34**	os	OA0	-0.219
17	ca	CA0	+0.038		**35**	os	OA0	-0.219
18	ca	CA0	+0.038					

* These were the atom type labels set when creating the LAMMPS readout files (containing the molecule topology information and force field parameters), conveniently changed to use the *Polymatic* program.



PIM-SBI-IM2 (aR)

PIM-SBI-IM2 (bR)

PIM-SBI-IM2 (aS)

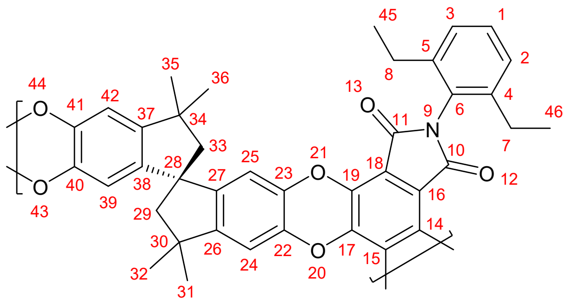
PIM-SBI-IM2 (bS)

Fig. ESI2. Representation of the repeating units used for building the **PIM-SBI-IM2** models. The red labels correspond to **Table ESI2**, which gives atom types and partial charges.

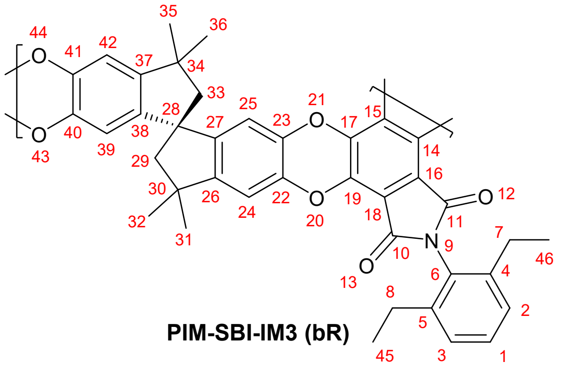
Table ESI2. Force field atom type and partial charges assigned to the atoms and pseudo-atoms of **PIM-SBI-IM2** models. Atom labels refer to those shown in **Fig. ESI2**.

Label	**Atom type (GAFF)**	**Atom type (used)***	**Charge**		**Label**	**Atom type (GAFF)**	**Atom type (used)***	**Charge**
1	ca	CA1	+0.139		**23**	ca	CS0	+0.214
2	ca	CA1	-0.197		**24**	ca	CA1	-0.131
3	ca	CA1	-0.197		**25**	ca	CA1	-0.099
4	ca	CA0	+0.276		**26**	ca	CA0	-0.127
5	ca	CA0	+0.276		**27**	ca	CA0	-0.125
6	ca	CA0	-0.128		**28**	c3	CH0	+0.713
7	c3	CH3	-0.028		**29**	c3	CH2	-0.355
8	c3	CH3	-0.028		**30**	c3	CH0	+0.668
9	n	N	-0.470		**31**	c3	CH3	-0.158
10	c	C	+0.955		**32**	c3	CH3	-0.141
11	c	C	+0.955		**33**	c3	CH2	-0.355
12	o	O	-0.609		**34**	c3	CH0	+0.668
13	o	O	-0.609		**35**	c3	CH3	-0.158
14	ca	CS0	+0.346		**36**	c3	CH3	-0.141
15	ca	CS0	+0.121		**37**	ca	CA0	-0.127
16	ca	CA0	-0.390		**38**	ca	CA0	-0.125
17	ca	CA0	+0.121		**39**	ca	CA1	-0.099
18	ca	CS0	-0.390		**40**	ca	CS0	+0.214
19	ca	CS0	+0.346		**41**	ca	CS0	+0.285
20	os	OA0	-0.316		**42**	ca	CA1	-0.131
21	os	OA0	-0.316		**43**	os	OA0	-0.316
22	ca	CS0	+0.285		**44**	os	OA0	-0.316

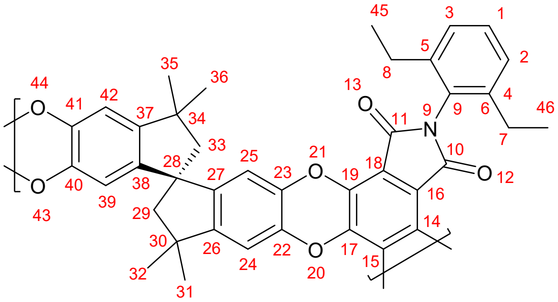
* These were the atom type labels set when creating the LAMMPS readout files (containing the molecule topology information and force field parameters), conveniently changed to use the *Polymatic* program.



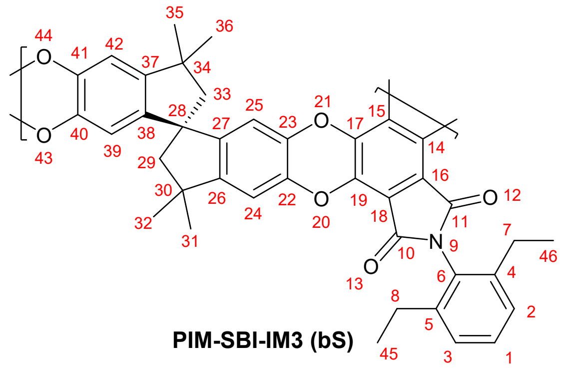
PIM-SBI-IM3 (aR)



PIM-SBI-IM3 (bR)



PIM-SBI-IM3 (aS)



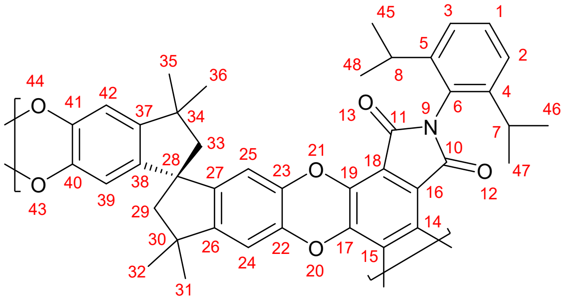
PIM-SBI-IM3 (bS)

Fig. ESI3. Representation of the repeating units used for building the **PIM-SBI-IM3** models. The red labels correspond to **Table ESI3**, which gives atom types and partial charges.

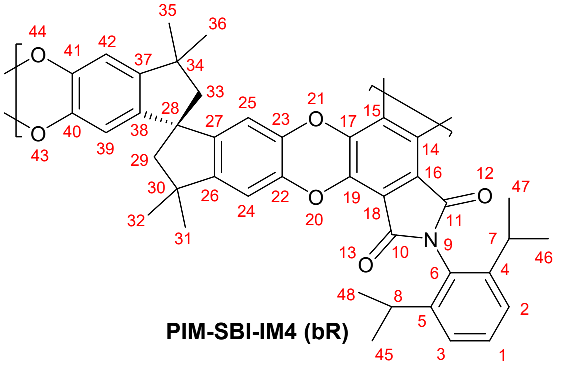
Table ESI3. Force field atom type and partial charges assigned to the atoms and pseudo-atoms of **PIM-SBI-IM3** models. Atom labels refer to those shown in **Fig. ESI3**.

Label	Atom type (GAFF)	Atom type (used)*	Charge		Label	Atom type (GAFF)	Atom type (used)*	Charge
1	ca	CA1	0.074		**24**	ca	CA1	-0.132
2	ca	CA1	-0.113		**25**	ca	CA1	-0.116
3	ca	CA1	-0.113		**26**	ca	CA0	-0.139
4	ca	CA0	0.098		**27**	ca	CA0	-0.090
5	ca	CA0	0.098		**28**	c3	CH0	0.669
6	ca	CA0	0.046		**29**	c3	CH2	-0.356
7	c3	CH2	0.117		**30**	c3	CH0	0.648
8	c3	CH2	0.117		**31**	c3	CH3	-0.140
9	n	N	-0.687		**32**	c3	CH3	-0.140
10	c	C	1.012		**33**	c3	CH2	-0.356
11	c	C	1.012		**34**	c3	CH0	0.648
12	o	O	-0.614		**35**	c3	CH3	-0.140
13	o	O	-0.614		**36**	c3	CH3	-0.140
14	ca	CS0	0.325		**37**	ca	CA0	-0.139
15	ca	CS0	0.128		**38**	ca	CA0	-0.090
16	ca	CA0	-0.376		**39**	ca	CA1	-0.116
17	ca	CA0	0.128		**40**	ca	CS0	0.249
18	ca	CS0	-0.376		**41**	ca	CS0	0.264
19	ca	CS0	0.325		**42**	ca	CA1	-0.132
20	os	OA0	-0.318		**43**	os	OA0	-0.318
21	os	OA0	-0.318		**44**	os	OA0	-0.318
22	ca	CS0	0.264		**45**	c3	CH3	-0.040
23	ca	CS0	0.249		**46**	c3	CH3	-0.040

* These were the atom type labels set when creating the LAMMPS readout files (containing the molecule topology information and force field parameters), conveniently changed to use the *Polymatic* program.



PIM-SBI-IM4 (aR)



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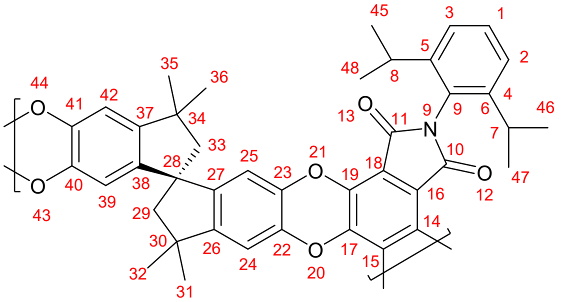
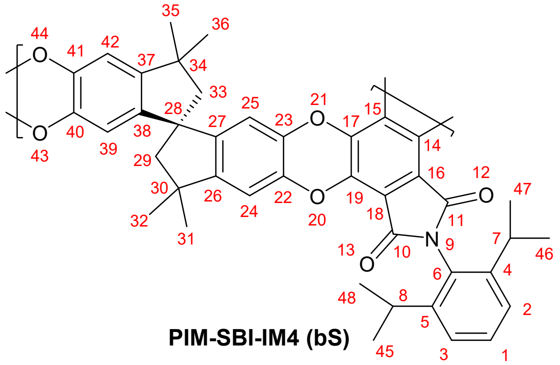


PIM-SBI-IM4 (aS)



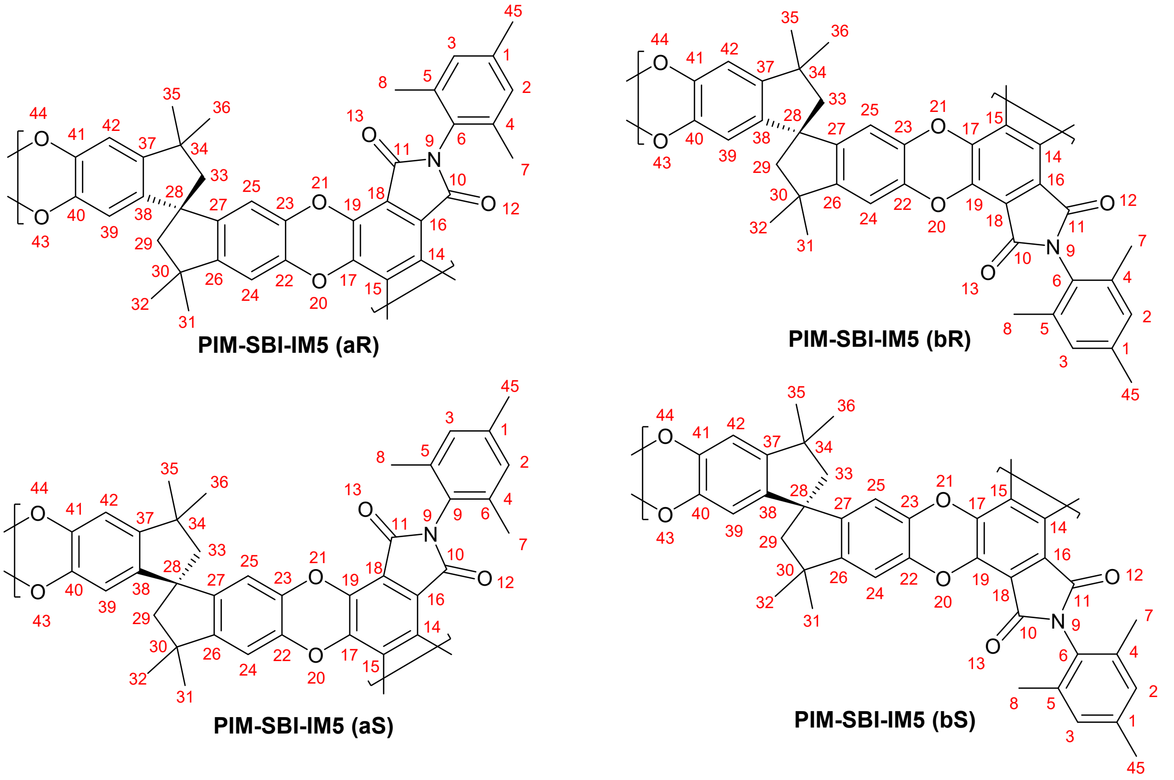
PIM-SBI-IM4 (bS)

Fig. ESI4. Representation of the repeating units used for building the **PIM-SBI-IM4** models. The red labels correspond to **Table ESI4**, which gives atom types and partial charges.

Table ESI4. Force field atom type and partial charges assigned to the atoms and pseudo-atoms of **PIM-SBI-IM4** models. Atom labels refer to those shown in **Fig. ESI4**.

Label	**Atom type (GAFF)**	**Atom type (used)***	**Charge**		**Label**	**Atom type (GAFF)**	**Atom type (used)***	**Charge**
1	ca	CA1	0.083		**25**	ca	CA1	-0.122
2	ca	CA1	-0.117		**26**	ca	CA0	-0.150
3	ca	CA1	-0.117		**27**	ca	CA0	-0.089
4	ca	CA0	0.073		**28**	c3	CH0	0.747
5	ca	CA0	0.073		**29**	c3	CH2	-0.397
6	ca	CA0	-0.050		**30**	c3	CH0	0.704
7	c3	CH1	0.301		**31**	c3	CH3	-0.151
8	c3	CH1	0.301		**32**	c3	CH3	-0.151
9	n	N	-0.416		**33**	c3	CH2	-0.397
10	c	C	0.893		**34**	c3	CH0	0.704
11	c	C	0.893		**35**	c3	CH3	-0.151
12	o	O	-0.604		**36**	c3	CH3	-0.151
13	o	O	-0.604		**37**	ca	CA0	-0.150
14	ca	CS0	0.307		**38**	ca	CA0	-0.089
15	ca	CS0	0.126		**39**	ca	CA1	-0.122
16	ca	CA0	-0.346		**40**	ca	CS0	0.239
17	ca	CA0	0.126		**41**	ca	CS0	0.267
18	ca	CS0	-0.346		**42**	ca	CA1	-0.125
19	ca	CS0	0.307		**43**	os	OA0	-0.308
20	os	OA0	-0.308		**44**	os	OA0	-0.308
21	os	OA0	-0.308		**45**	c3	CH3	-0.112
22	ca	CS0	0.267		**46**	c3	CH3	-0.112
23	ca	CS0	0.239		**47**	c3	CH3	-0.112
24	ca	CA1	-0.125		**48**	c3	CH3	-0.112

* These were the atom type labels set when creating the LAMMPS readout files (containing the molecule topology information and force field parameters), conveniently changed to use the *Polymatic* program.



PIM-SBI-IM5 (aR)

PIM-SBI-IM5 (bR)

PIM-SBI-IM5 (aS)

PIM-SBI-IM5 (bS)

Fig. ESI5. Representation of the repeating units used for building the **PIM-SBI-IM5** models. The red labels correspond to **Table ESI5**, which gives atom types and partial charges.

Table ESI5. Force field atom type and partial charges assigned to the atoms and pseudo-atoms of **PIM-SBI-IM5** models. Atom labels refer to those shown in **Fig. ESI5**.

Label	**Atom type (GAFF)**	**Atom type (used)***	**Charge**		**Label**	**Atom type (GAFF)**	**Atom type (used)***	**Charge**
1	ca	CA0	0.309		**24**	ca	CA1	-0.131
2	ca	CA1	-0.297		**25**	ca	CA1	-0.115
3	ca	CA1	-0.297		**26**	ca	CA0	-0.148
4	ca	CA0	0.308		**27**	ca	CA0	-0.094
5	ca	CA0	0.308		**28**	c3	CH0	0.715
6	ca	CA0	-0.175		**29**	c3	CH2	-0.381
7	c3	CH3	-0.021		**30**	c3	CH0	0.684
8	c3	CH3	-0.021		**31**	c3	CH3	-0.148
9	n	N	-0.462		**32**	c3	CH3	-0.148
10	c	C	0.939		**33**	c3	CH2	-0.381
11	c	C	0.939		**34**	c3	CH0	0.684
12	o	O	-0.601		**35**	c3	CH3	-0.148
13	o	O	-0.601		**36**	c3	CH3	-0.148
14	ca	CS0	0.344		**37**	ca	CA0	-0.148
15	ca	CS0	0.116		**38**	ca	CA0	-0.094
16	ca	CA0	-0.377		**39**	ca	CA1	-0.115
17	ca	CA0	0.116		**40**	ca	CS0	0.245
18	ca	CS0	-0.377		**41**	ca	CS0	0.261
19	ca	CS0	0.344		**42**	ca	CA1	-0.131
20	os	OA0	-0.315		**43**	os	OA0	-0.315
21	os	OA0	-0.315		**44**	os	OA0	-0.315
22	ca	CS0	0.261		**45**	c3	CH3	0.001
23	ca	CS0	0.245					

* These were the atom type labels set when creating the LAMMPS readout files (containing the molecule topology information and force field parameters), conveniently changed to use the *Polymatic* program.

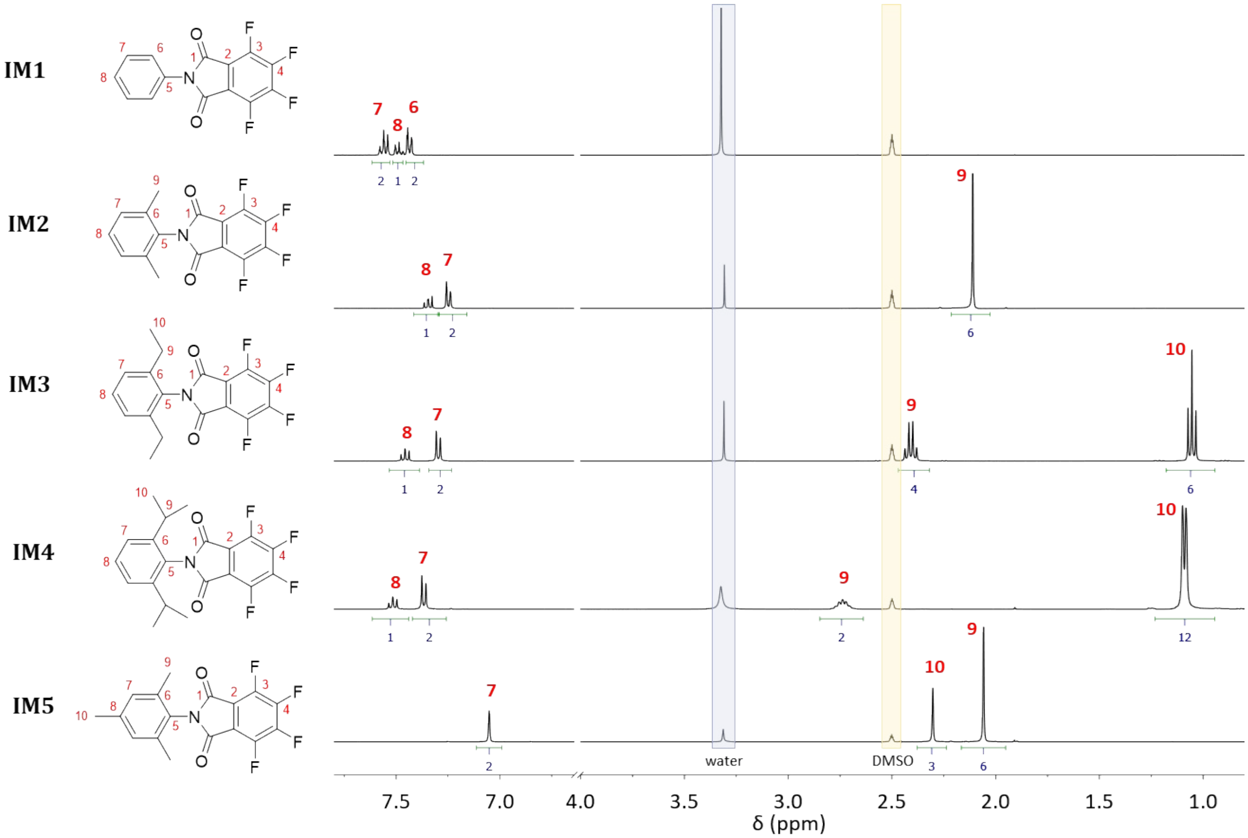


Fig. ESI6. Full assignment of ^{1}H NMR spectra in DMSO-d_6 of the tetrafluorophtalimide monomers **IM(1-5)**.

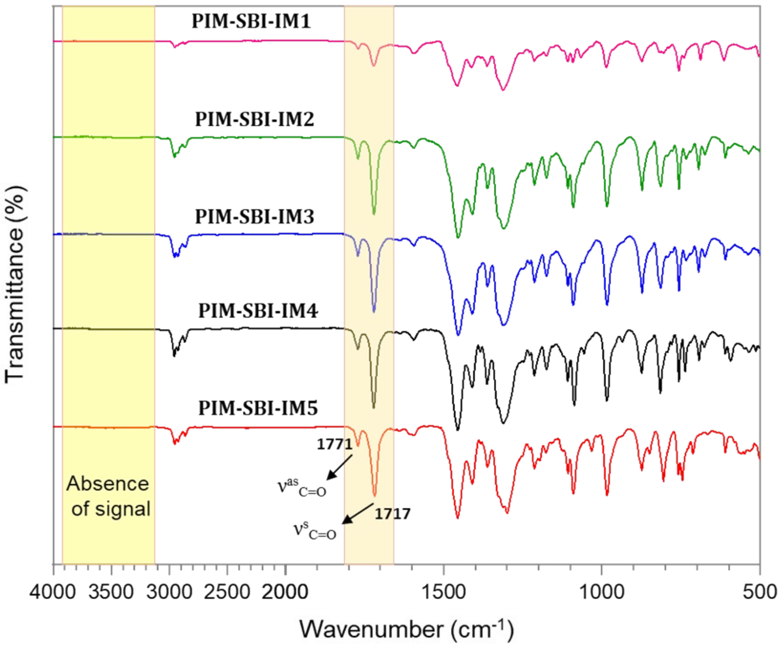


Fig. ESI7. ATR-IR spectra of the polymers **PIM-SBI-IM(2-5)**.

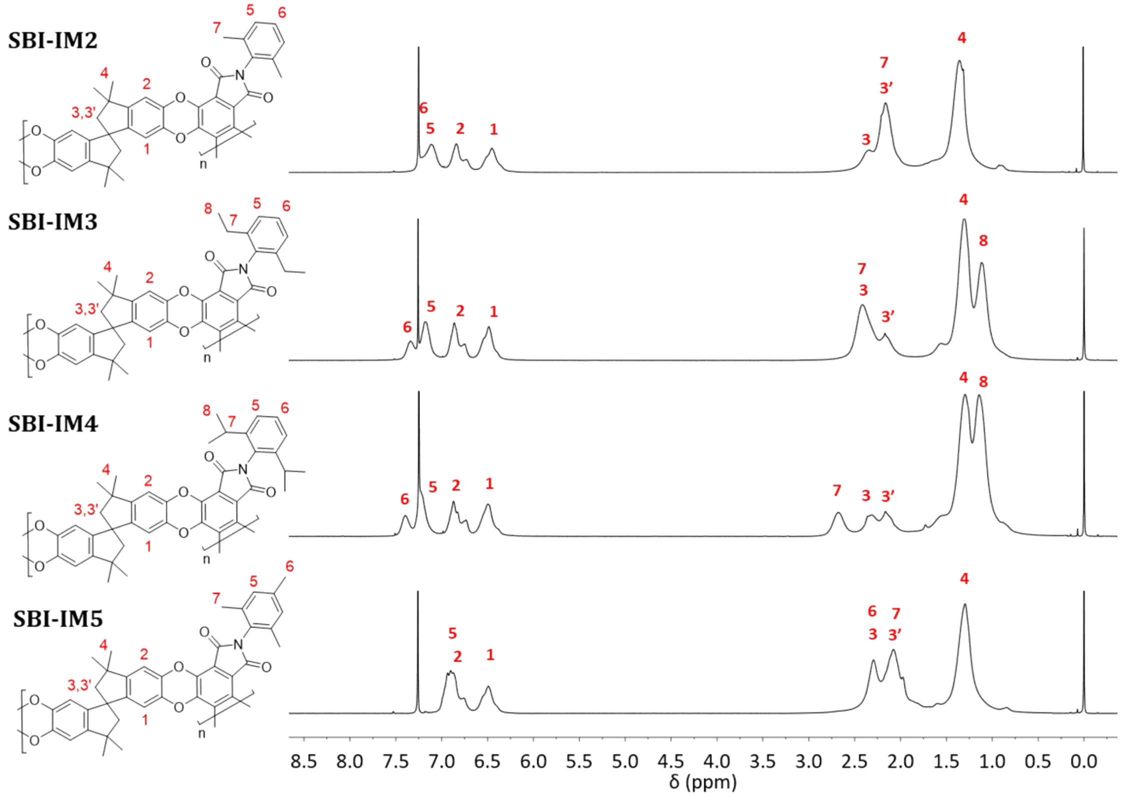


Fig. ESI8. Full assignment of ^{1}H NMR spectra in CDCl$_3$ of the polymers **PIM-SBI-IM(2-5)**.

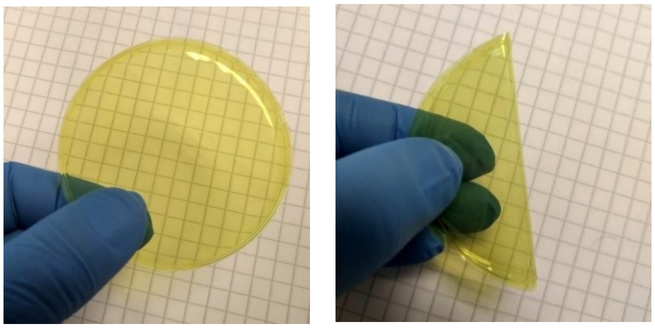


Fig. ESI9. Transparent robust self-standing films of **PIM-SBI-IM2**. The same results were obtained for **PIM-SBI-IM3, PIM-SBI-IM4 and PIM-SBI-IM5** membranes.

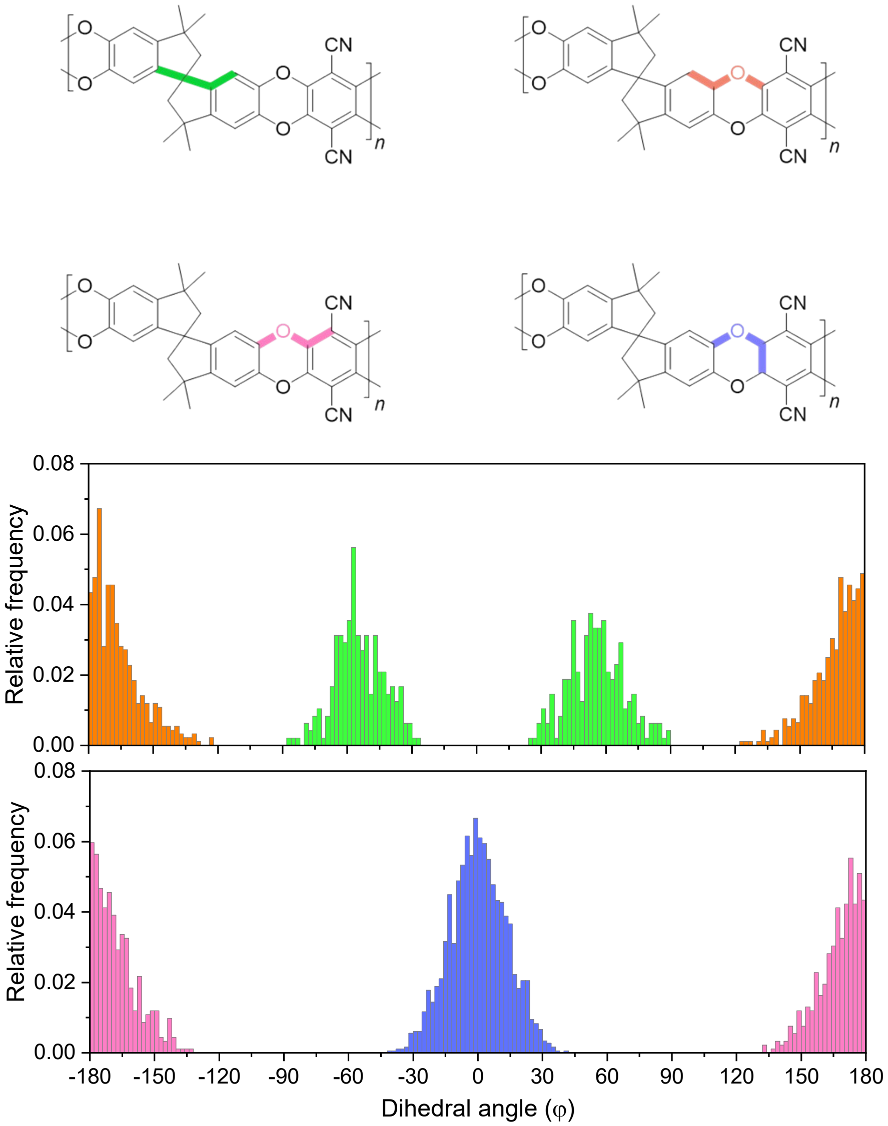


Fig. ESI10. Histograms of the dihedral angles that were calculated from the final **PIM-1** models. The dihedral angle belonging to the spirocenter is highlighted with green color, and the other three (orange, pink and blue) are those involved with the planarity of the dibenzodioxin rings.

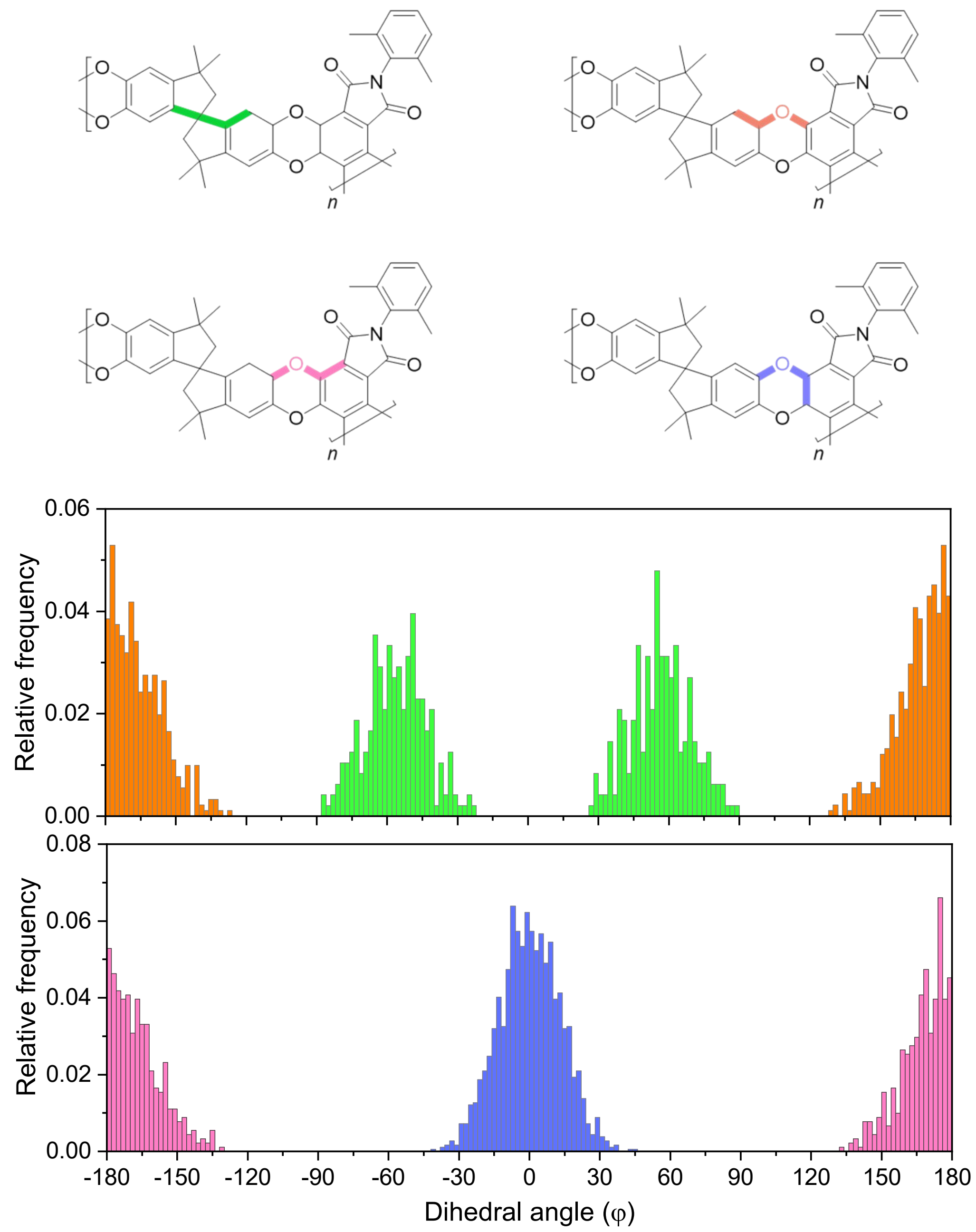


Fig. ESI11. Histograms of the dihedral angles that were calculated from the final **PIM-SBI-IM2** models. The dihedral angle belonging to the spirocenter is highlighted with green color, and the other three (orange, pink and blue) are those involved with the planarity of the dibenzodioxin rings.

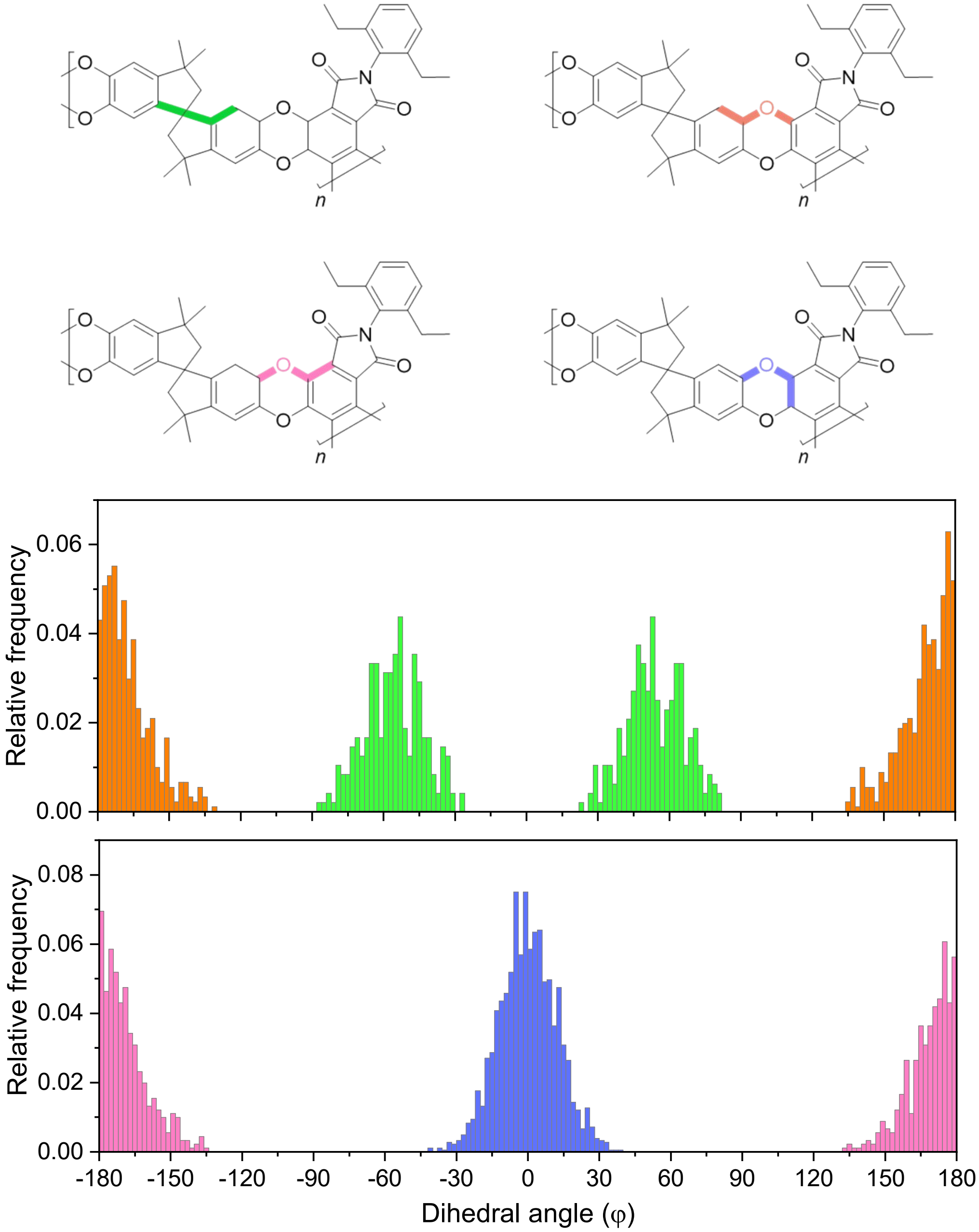


Fig. ESI12. Histograms of the dihedral angles that were calculated from the final **PIM-SBI-IM3** models. The dihedral angle belonging to the spirocenter is highlighted with green color, and the other three (orange, pink and blue) are those involved with the planarity of the dibenzodioxin rings.

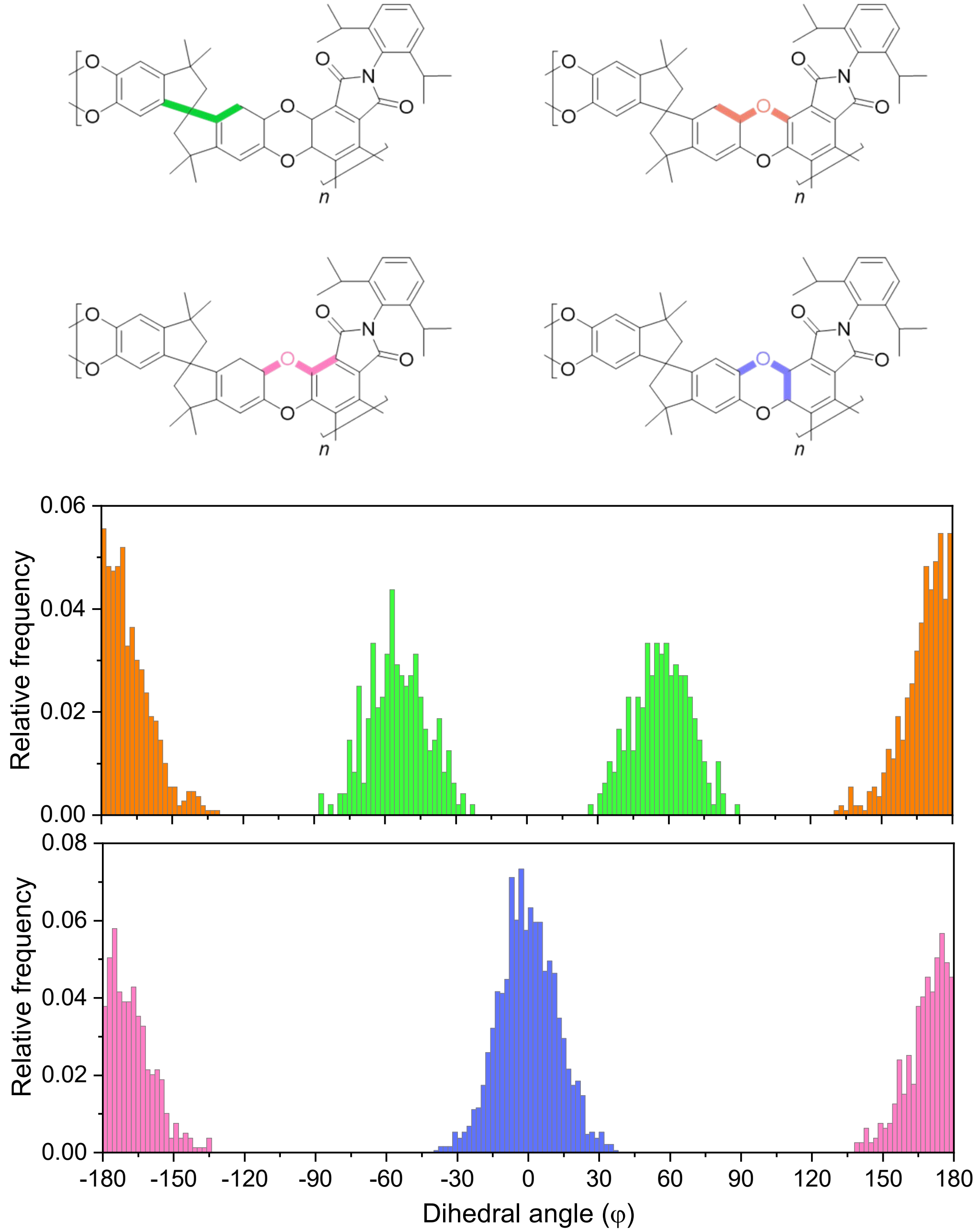


Fig. ESI13. Histograms of the dihedral angles that were calculated from the final **PIM-SBI-IM4** models. The dihedral angle belonging to the spirocenter is highlighted with green color, and the other three (orange, pink and blue) are those involved with the planarity of the dibenzodioxin rings.

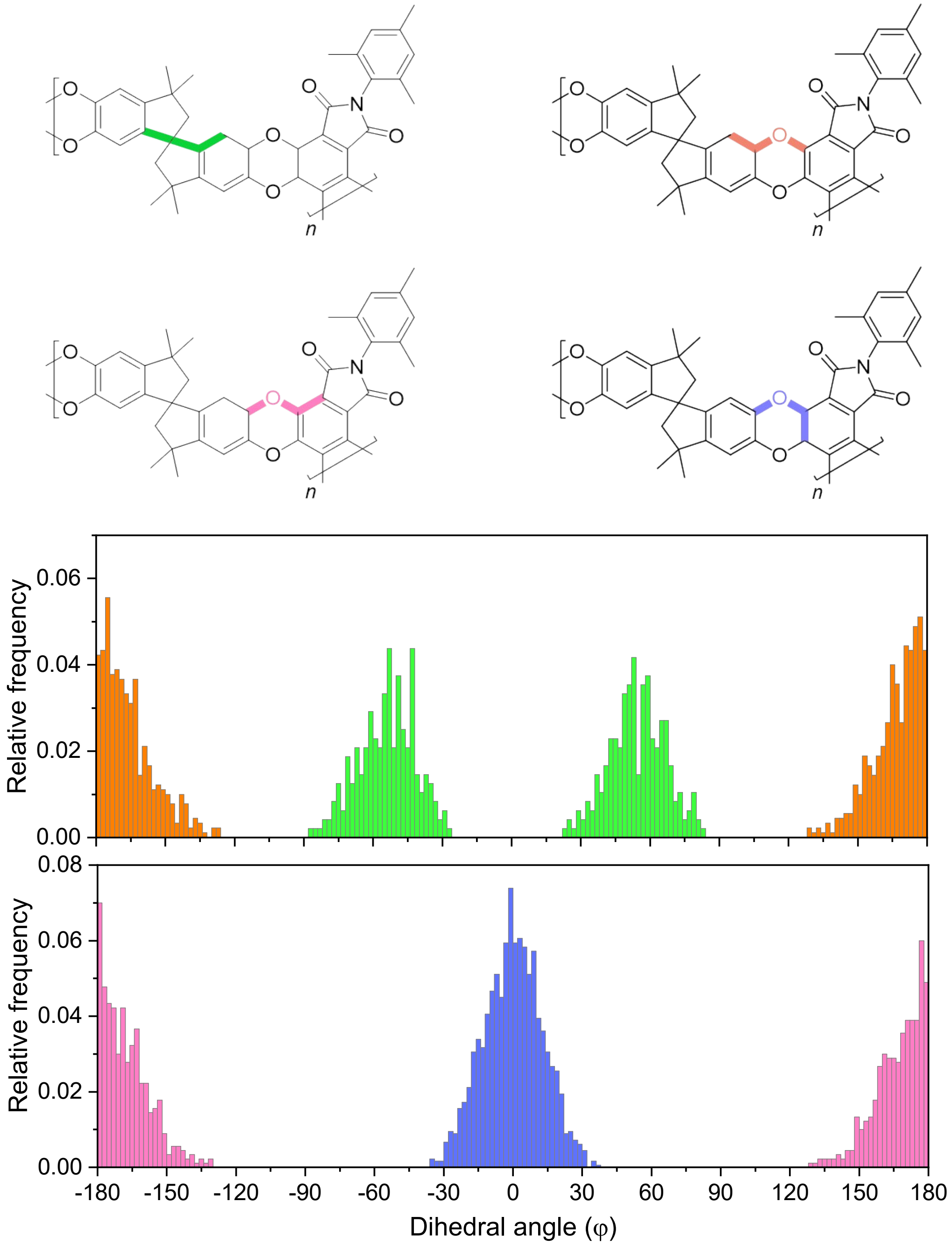


Fig. ESI14. Histograms of the dihedral angles that were calculated from the final **PIM-SBI-IM5** models. The dihedral angle belonging to the spirocenter is highlighted with green color, and the other three (orange, pink and blue) are those involved with the planarity of the dibenzodioxin rings.

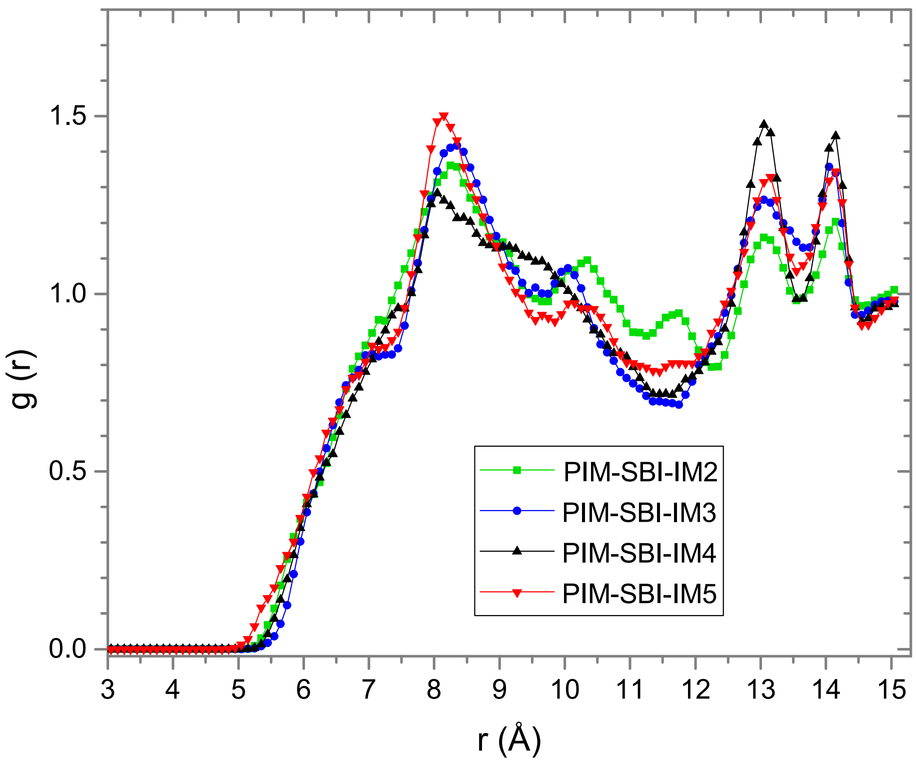


Fig. ESI15. Spirocenter-spirocenter radial distribution functions for **PIM-SBI-IM(2-5)** polymeric models. All polymers show two prominent peaks around 15 A˚ due to adjacent spirocenters on the same chain. At shorter distances, the peaks are attributed to interchain spirocenter spacing.

Table ESI6. Diffusivity and solubility coefficients of methanol treated **PIM-SBI-IM(2-5)** membranes and data from aged films (between 92 and 122 days) in parentheses.

Polymer	Diffusion coefficient (D_i) [10^{-8} cm^2 s^{-1}]				Solubility coefficient (S_i) [10^{-2} cm^3(STP) cm^{-3} cmHg^{-1}]			
	N_2	O_2	CH_4	CO_2	N_2	O_2	CH_4	CO_2
PIM-SBI-IM2	30.3	106	10.2	49.7	2.68	2.82	12.0	27.4
(122 days)	(3.29)	(16.7)	(0.950)	(6.62)	(2.46)	(2.52)	(11.7)	(26.3)
PIM-SBI-IM3	27.4	90.6	11.2	42.7	2.94	3.08	12.5	32.6
(121 days)	(17.9)	(64.2)	(7.42)	(30.1)	(2.99)	(3.10)	(11.8)	(31.3)
PIM-SBI-IM4	107	321	51.0	156.3	2.88	2.97	10.5	30.1
(63 days)	(88.4)	(288)	(39.0)	(139.2)	(2.93)	(3.01)	(10.6)	(30.2)
PIM-SBI-IM5	41.6	138	15.4	65.0	3.20	3.24	13.0	33.3
(92 days)	(27.4)	(94.3)	(9.50)	(44.0)	(2.91)	(2.96)	(12.8)	(30.2)

Table ESI7. Diffusivity-selectivity and Solubility-selectivity of methanol treated **PIM-SBI-IM(2-5)** membranes and data from aged films (between 92 and 122 days) in parentheses.

Polymer	Diffusivity-selectivity (D_i/D_j)			Solubility-selectivity (S_i/S_j)		
	O_2/N_2	CO_2/CH_4	CO_2/N_2	O_2/N_2	CO_2/CH_4	CO_2/N_2
PIM-SBI-IM2	3.51	4.89	1.64	1.05	2.28	10.22
(122 days)	5.06	6.97	2.01	1.02	2.25	10.69
PIM-SBI-IM3	3.30	3.82	1.56	1.05	2.61	11.09
(121 days)	3.59	4.05	1.68	1.04	2.65	10.47
PIM-SBI-IM4	2.99	3.06	1.46	1.03	2.87	10.45
(63 days)	3.26	3.57	1.57	1.03	2.85	10.31
PIM-SBI-IM5	3.31	4.23	1.56	1.01	2.56	10.41
(92 days)	3.45	4.62	1.61	1.02	2.36	10.38

References

1 J. F. Tannaci, M. Noji, J. McBee and T. D. Tilley, *J Org Chem*, 2007, **72**, 5567–5573.
2 S. Makhseed, F. Ibrahim and J. Samuel, *Polymer*, 2012, **53**, 2964–2972.