Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

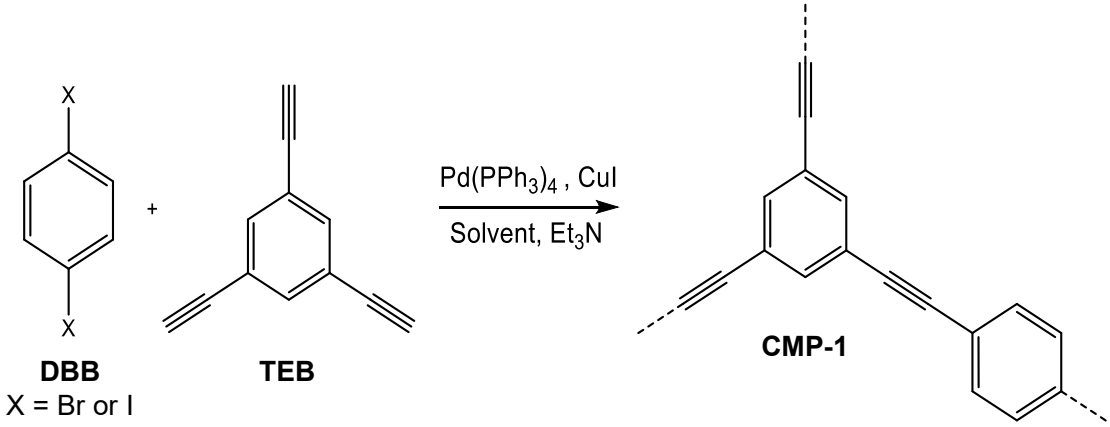
Conjugated Microporous Polymer Frameworks for Sustainable Energy Materials – elucidating the influence of solvents on the porosity properties for future design principles

Catherine Mollart and Abbie Trewin*

Supporting Information

Contents

1. CMP-1



Scheme SI.1. Reaction scheme to synthesise CMP-1 from 1,4-dibromobenzene (DBB) and 1,3,5-triethynylbenzene (TEB) in the presence of a tetrakis(triphenylphosphine)palladium (0) catalyst, copper(I) iodide and solvent.

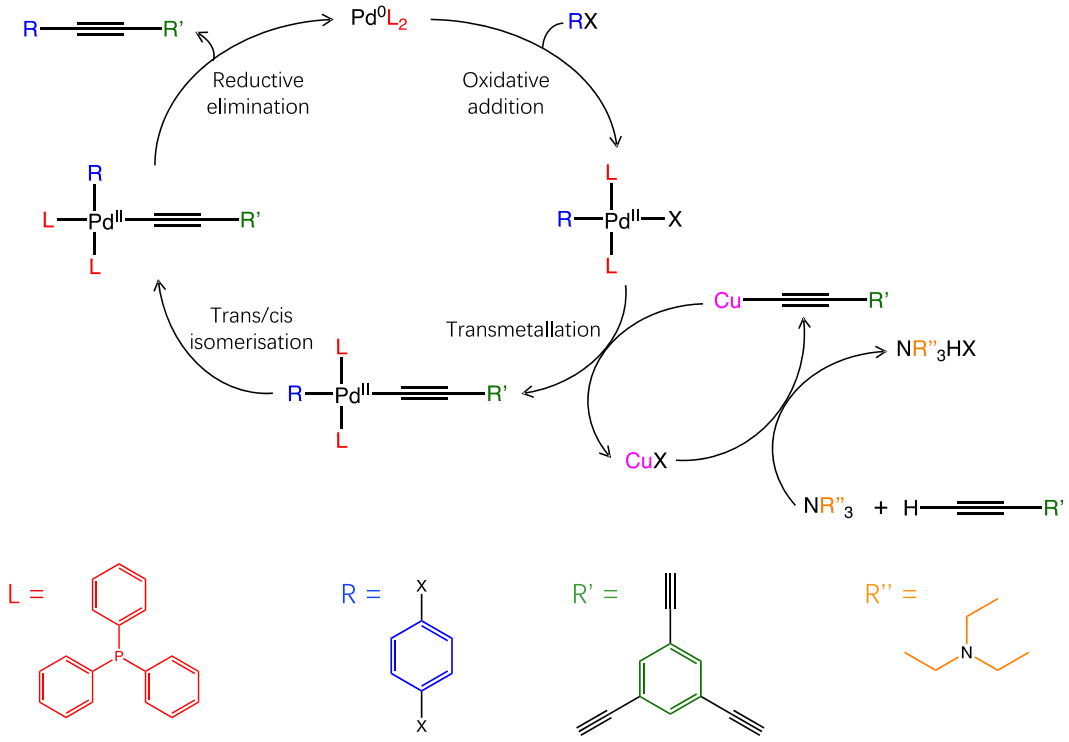


Figure SI.1. Sonogashira–Hagihara catalytic cycle to produce CMP-1. This consists of oxidative addition of DBB to the catalyst, transmetallation to substitute the bromine ligand with TEB, and reductive elimination of the cross-coupled product, regenerating the active catalyst. In the artificial synthesis, we take the approach described in reference 1 where we assume that the transmetallation side cycle has already occurred, and the TEB molecules are all terminated with copper atoms.[1]

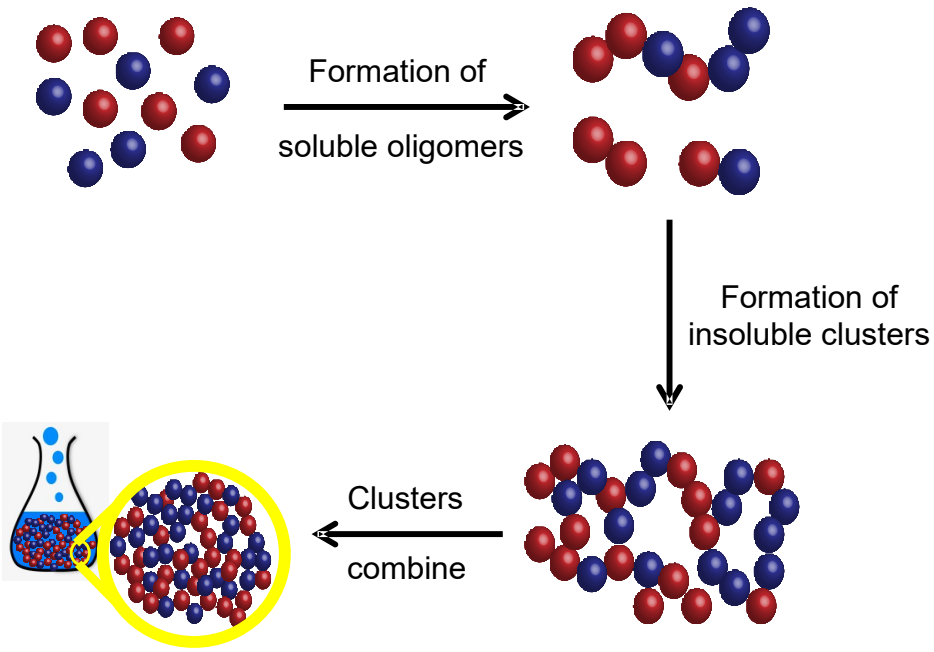


Figure SI.2. Cartoon representation of the polymer formation mechanism proposed for CMP-1 by Laybourn *et al.*[2]

2. Experimental

Table SI.1. Quantity of reagents used in the experimental synthesis of CMP-1 reported by Dawson *et al.*[3]

Reagent	Quantity	Millimoles
$Pd(PPh_3)_4$	50 mg	0.04
1,4-Dibromobenzene	236 mg	1
1,3,5-Triethynylbenzene	150 mg	1
Copper(I) iodide	15 mg	0.08
Triethylamine	1.5 mL	10.76
N,N-dimethylformamide	2.5 mL	32.29
Toluene	2.5 mL	23.47
Tetrahydrofuran	2.5 mL	30.82
1,4-Dioxane	2.5 mL	29.34

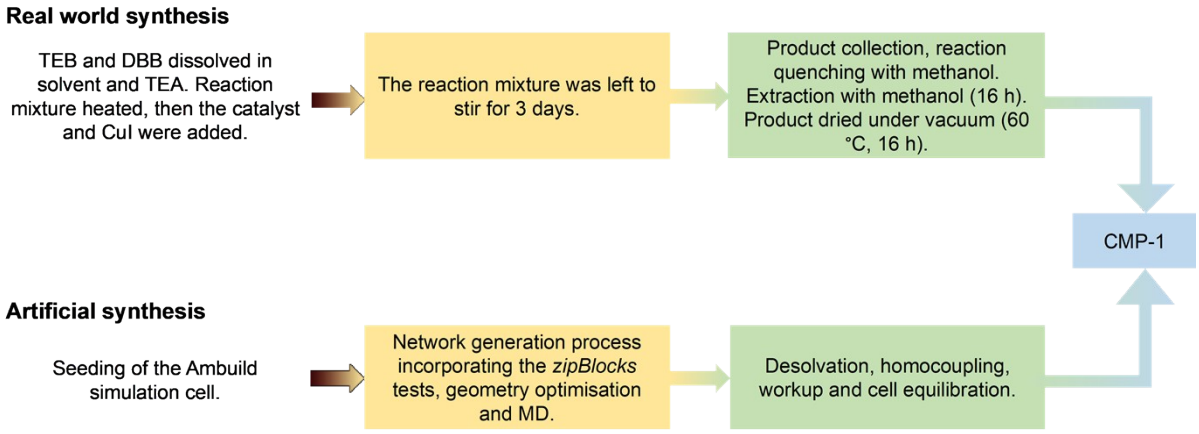
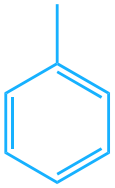
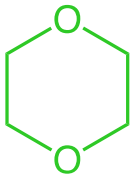
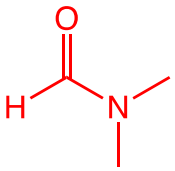


Figure SI.3. Comparison of how each step of the experimental synthesis procedure[13] is mimicked computationally.[3]

Table SI.2. Experimental porosity data for CMP-1 generated in DMF, toluene, THF and 1,4-dioxane by Dawson *et al.*,[3] solvent polarity indices,[4] Hildebrand solubility parameters and their contributing Hansen components.[5] SA – surface area.

Solvent	**Toluene**	**THF**	**1,4-Dioxane**	**DMF**
Structure				
Polarity index	2.4	4.0	4.8	6.4
Hildebrand solubility parameter / $MPa^{0.5}$	18.2	19.4	20.5	24.8
Dispersion component / $MPa^{0.5}$	18.0	16.8	19.0	17.4
Polar component / $MPa^{0.5}$	1.4	5.7	1.8	13.7
Hydrogen bonding component / $MPa^{0.5}$	2.0	8.0	7.4	11.3
Total CMP-1 SA / $m^2\ g^{-1}$	867	941	609	837
Microporous CMP-1 SA / $m^2\ g^{-1}$	286	273	390	594
Micropore volume / $cm^3\ g^{-1}$	0.33	0.36	0.23	0.32
Mesoporous CMP-1 SA / $m^2\ g^{-1}$	581	668	219	243

Hansen solubility parameters

The Hansen solubility parameters, first designed by Charles Hansen in 1966, are designed to split the total Hildebrand solubility parameter into three components to better understand why two solvents with very similar Hildebrand solubility parameters exhibit different solubility behaviours.[5] The Hansen parameters separate the total Hildebrand solubility parameter as follows (Equation 1):

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \textbf{Equation 1}$$

Where δ_t^2 is the total Hildebrand solubility parameter, δ_d^2 is the dispersion component arising from induced attractions between molecules, δ_p^2 is the polar component arising from permanent dipole – permanent dipole interactions between polar molecules, or from permanent dipole – induced dipole interactions between a polar and non-polar molecule, respectively, and δ_h^2 is the hydrogen bonding component.[5]

The three HSP values for a particular molecule can be used to define a three-dimensional point at the centre of the solubility sphere for that molecule. The radius of the sphere is referred to as the interaction radius for that molecule. If the HSP values of the solvent correspond to a coordinate that is within the solubility sphere of the polymer, the polymer should be soluble in that solvent.[5] The distance between the HSP coordinates of the solvent and polymer can be calculated as in Equation 2:

$$D_{S-P} = 4(\delta_{d(s)} - \delta_{d(p)})^2 + (\delta_{p(s)} - \delta_{p(p)})^2 + (\delta_{h(s)} - \delta_{h(p)})^2 \qquad \textbf{Equation 2}^5$$

Where $D_{S\text{-}P}$ is the distance between the HSP coordinates of the solvent and the polymer, $\delta_{x(s)}$ is the Hansen solubility component of the solvent (x referring to the dispersion, polar, or hydrogen bonding components depending on the location within the equation), and $\delta_{x(p)}$ is the Hansen solubility component of the polymer. If the $D_{S\text{-}P}$ value is smaller than the interaction radius of the polymer, the polymer should be soluble in that solvent.[5]

Table SI.3. Experimental elemental analysis data for CMP-1.[3]

Solvent	Elemental Analysis / %		
	C	H	Remaining
Toluene	78.72	3.45	17.83
THF	78.81	3.35	17.84
1,4-Dioxane	75.77	3.42	20.81
DMF	80.10	3.55	16.35

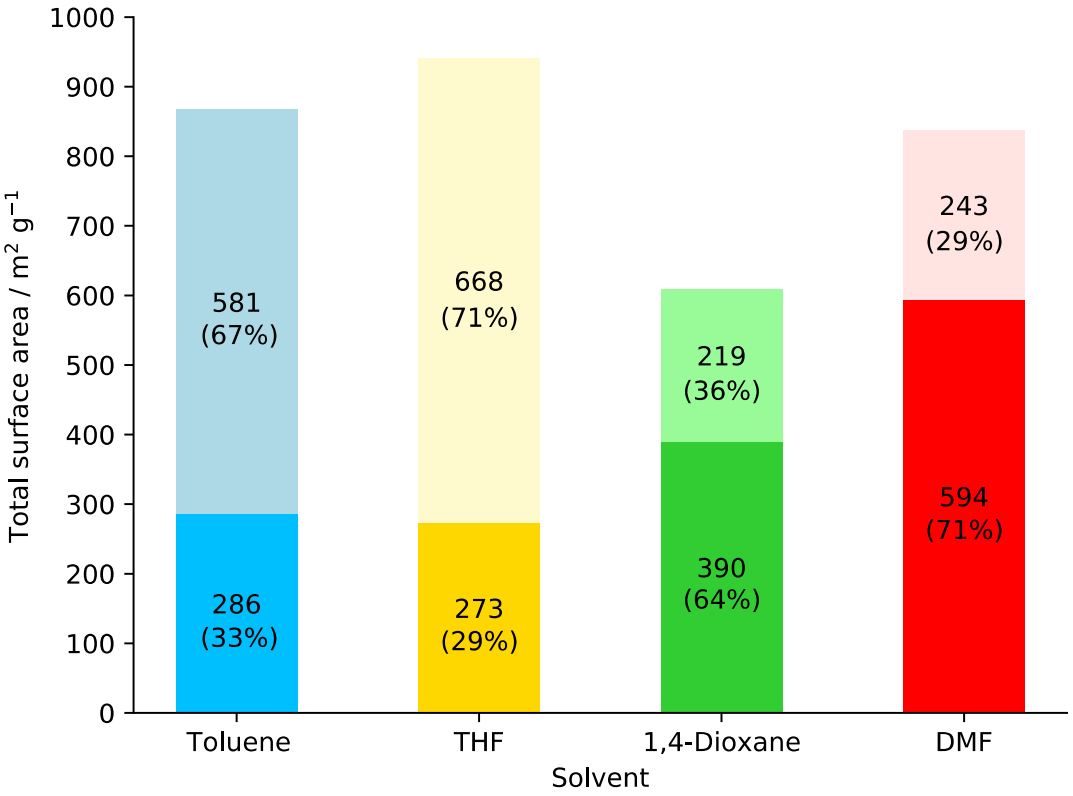


Figure SI.4. Plot of the micro- (bottom) and mesoporous (top) contributions to the total surface area of the experimental CMP-1 systems reported by Dawson *et al*.[3] Key: Microporosity – dark shades, Mesoporosity – pale shades. The respective percentages of micro- and mesoporosity in each system are given in brackets below the actual surface area values.

3. Ambuild

The structural models discussed in this work were generated using the Ambuild code, which has been discussed previously.[1, 6-10] Ambuild, a python-based code, is specifically designed to model amorphous hyper-crosslinked polymers (HCPs) such as covalent triazine frameworks (CTFs) and conjugated microporous polymers (CMPs), and due to the nature of the code, the full synthetic conditions and catalytic cycle are modelled, allowing the generation of structural models that can be compared to experiment. Ambuild is able to take advantage of GPU acceleration, meaning larger simulation cell sizes can be modelled within a reasonable timescale, a factor that is especially important when modelling amorphous materials in order to sample multiple regions of the experimental material. HOOMD-blue[11, 12] was utilised as the geometry optimisation and molecular dynamics (MD) engine throughout, and porosity analysis was conducted using Poreblazer.[13, 14] The Polymer Consistent Forcefield (PCFF)[15] was used throughout our modelling approach, as it is an appropriate forcefield to model microporous polymers such as CMP-1.

In the case of CMP-1, the building blocks were set up as in reference 1, where the end group and cap atoms of the DBB, TEB and catalyst molecules are set to be: DBB – C, Br; TEB – C, Cu and catalyst – Pd, H 'placeholder' atom, respectively. New bonds may form between the end group atoms if they meet the required bond and angle criteria, with the cap atoms, which create a vector for the new bond to lie along, being lost on forming the bond. To mimic the Sonogashira–Hagihara catalytic cycle, monomer end groups must first bond to a catalyst molecule before being able to form a bond to another monomer bound to a catalyst molecule, breaking the respective bonds to the catalyst on forming the new bond.

4. Degree of Solvation Systems

The initial models generated in the presence of various quantities of solvent (1%, 33%, 67%, 100% of the experimental quantity) were generated by firstly seeding the smallest possible simulation cell size (Table SI.4) with the quantities of building blocks given in Table SI.5, with four repeat models generated per system.

Table SI.4. Minimum cell lengths used for each of the fully mixed systems generated with varying quantities of solvent.

Solvent	Quantity of solvent with respect to experimental stoichiometry			
	1%	33%	67%	100%
Toluene	47 Å	64 Å	77 Å	87 Å
THF	48 Å	56 Å	68 Å	76 Å
Dioxane	48 Å	61 Å	75 Å	84 Å
DMF	47 Å	58 Å	70 Å	80 Å

Table SI.5. Number of building blocks seeded to the simulation cell for each of the fully mixed systems generated with varying quantities of solvent.

Building block	Quantity of solvent with respect to experimental stoichiometry			
	1%	33%	67%	100%
Catalyst	4	4	4	4
DBB	100	100	100	100
TEB	100	100	100	100
TEA	11	359	717	1076
Toluene	23	782	1565	2347
THF	31	1027	2055	3082
Dioxane	29	978	1956	2934
DMF	32	1076	2153	3229

Once seeded, a loop was undertaken comprising of zipBlocks tests, geometry optimisation, and NVT (constant number of molecules, cell volume and temperature) MD. The zipBlocks test is designed to increase the bond length and angle margins from those initially determined, before looping over all of the free end groups within the cell and allowing any that meet the relaxed criteria to form bonds, followed by a further geometry optimisation. This loop continued until no new bonds had formed during the final twenty zipBlocks tests, at which point the network generation was deemed complete. Following this, the cell was desolvated using schemes 1-6, described in detail in reference 1 and summarised below:

Scheme 1 – Remove solvent, monomers, and catalyst (quickly) with NVT MD throughout, followed by cell workup and NPT (constant number of molecules, cell pressure and temperature) MD.
Scheme 2 – Remove solvent, monomers, oligomers up to three building blocks, and catalyst with NVT MD throughout, followed by cell workup and NPT MD.

Scheme 3 – Remove solvent, monomers, oligomers up to two building blocks, and catalyst with NVT MD throughout, followed by cell workup and NPT MD.
Scheme 4 – Remove solvent, monomers, and catalyst (slowly) with NVT MD throughout, followed by cell workup and NPT MD.
Scheme 5 – Remove solvent with NVT MD throughout, followed by cell workup and NPT MD.
Scheme 6 – Remove solvent, monomers, and catalyst with NVT MD throughout, followed by alkyne-alkyne homocoupling, cell workup and NPT MD.

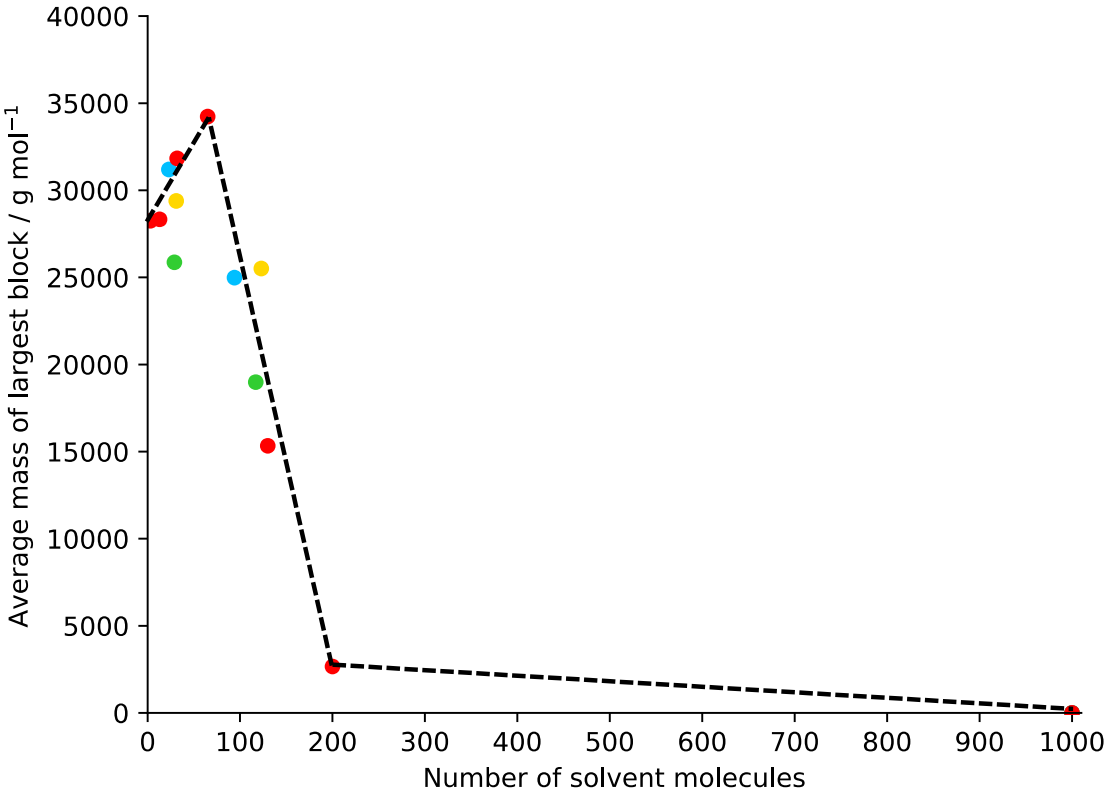


Figure SI.5. Plot of the average mass of the largest block in the cell for each model set against the number of solvent molecules. Key: toluene – blue, THF – yellow, 1,4-dioxane – green, DMF – red, overall trendline based on DMF data – black dashed.

The porosity analysis for the fully mixed systems calculated using various quantities of solvent, calculated using Poreblazer, is given in Tables SI.6–SI.9.

Table SI.6. Porosity data for the fully mixed CMP-1 models generated using various quantities of toluene, averaged across repeat models 1–4. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

% Solvent	Desolvation scheme	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
100	1	3.50	6.65	0.368	724	1.079	20.75
	2	2.74	4.90	0.196	0	1.177	15.23
	3	2.45	4.47	0.146	0	1.242	18.93
	4	3.48	6.80	0.429	886	1.091	20.95
	5	4.16	7.64	0.324	517	1.139	24.82
	6	2.94	6.08	0.194	227	1.203	21.41
67	1	6.17	10.21	0.920	2365	0.640	27.05
	2	Empty cell after desolvation.					
	3	15.06	18.29	5.708	2216	0.159	27.03
	4	7.23	10.86	0.920	2406	0.640	27.04
	5	5.38	9.82	0.584	1318	0.845	27.06
	6	2.75	6.07	0.213	184	1.123	22.47
33	1	7.13	10.57	0.918	2224	0.638	32.52
	2	10.01	13.57	2.351	5562	0.344	32.54
	3	9.28	12.86	2.040	4818	0.383	32.55
	4	6.31	9.98	0.925	2385	0.638	32.52
	5	6.36	11.22	0.334	761	1.143	45.05
	6	3.89	8.14	0.256	429	1.184	36.82
1	1	6.11	11.89	0.874	2030	0.640	100.00
	2	6.10	12.47	1.068	2562	0.562	99.60
	3	6.43	12.67	1.044	2477	0.566	99.80
	4	5.34	11.91	0.889	2011	0.631	100.00
	5	2.64	7.24	0.227	48	1.049	100.00
	6	4.07	9.51	0.433	612	0.896	100.00

Table SI.7. Porosity data for the fully mixed CMP-1 models generated using various quantities of THF, averaged across repeat models 1–4. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

% Solvent	Desolvation scheme	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
100	1	2.18	4.65	0.236	0	1.038	14.21
	2	Empty cell after desolvation.					
	3	Empty cell after desolvation.					
	4	2.40	4.30	0.233	0	1.038	14.21
	5	7.30	11.39	1.169	2716	0.640	25.68
	6	2.60	4.25	0.273	0	1.035	14.22
67	1	15.71	21.19	6.452	4398	0.142	30.82
	2	Empty cell after desolvation.					
	3	Empty cell after desolvation.					
	4	16.02	20.41	6.452	4331	0.142	30.82
	5	8.40	12.81	1.413	3552	0.487	30.69
	6	2.55	5.34	0.320	0	0.953	16.34
33	1	6.92	11.60	1.078	2878	0.580	37.24
	2	Empty cell after desolvation.					
	3	14.33	18.42	5.715	2093	0.158	37.21
	4	7.54	10.95	1.069	2721	0.580	37.24
	5	7.43	11.16	1.050	2709	0.591	37.23
	6	2.57	5.16	0.155	27	1.213	29.13
1	1	6.05	12.41	0.999	2286	0.570	93.27
	2	6.12	12.37	1.082	2540	0.539	91.33
	3	6.20	12.90	1.085	2542	0.538	92.09
	4	6.64	12.72	1.000	2308	0.570	93.28
	5	3.33	8.90	0.337	296	0.920	100.00
	6	5.65	12.54	0.600	1218	0.778	98.89

Table SI.8. Porosity data for the fully mixed CMP-1 models generated using various quantities of 1,4-dioxane, averaged across repeat models 1–4. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

% Solvent	Desolvation scheme	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
100	1	1.93	4.27	0.109	0	1.287	17.15
	2	Empty cell after desolvation.					
	3	Empty cell after desolvation.					
	4	2.42	4.72	0.137	74	1.267	17.28
	5	1.97	4.63	0.121	0	1.270	19.01
	6	2.63	4.79	0.174	82	1.199	17.56
67	1	7.40	11.15	1.026	2678	0.594	27.75
	2	Empty cell after desolvation.					
	3	Empty cell after desolvation.					
	4	7.38	10.77	1.026	2630	0.595	27.74
	5	7.34	11.46	0.977	2489	0.616	27.75
	6	2.47	4.76	0.152	0	1.218	21.86
33	1	6.60	10.62	0.876	2179	0.657	34.16
	2	14.17	20.70	5.173	1898	0.173	34.11
	3	14.05	16.04	5.180	2167	0.173	34.11
	4	6.78	10.32	0.880	2403	0.658	34.13
	5	6.46	9.55	0.626	1622	0.821	34.14
	6	3.05	5.45	0.238	137	1.079	28.98
1	1	5.99	12.33	0.958	2155	0.581	89.54
	2	6.17	12.16	1.012	2281	0.554	87.34
	3	6.06	12.06	1.011	2329	0.555	89.18
	4	6.16	12.48	0.953	2091	0.581	89.53
	5	3.47	8.91	0.373	430	0.895	100.00
	6	4.84	11.13	0.475	737	0.847	95.18

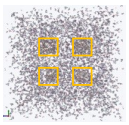
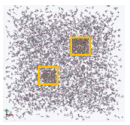
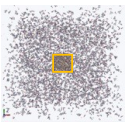
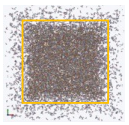
Table SI.9. Porosity data for the fully mixed CMP-1 models generated using various quantities of DMF, averaged across repeat models 1–4. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

% Solvent	Desolvation scheme	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / g cm^{-3}	% Size of Initial Cell
100	1	Empty cell after desolvation.					
	2	Empty cell after desolvation.					
	3	Empty cell after desolvation.					
	4	Empty cell after desolvation.					
	5	13.64	24.24	1.221	2285	0.519	63.74
	6	7.743	15.12	0.728	1646	0.732	50.31
67	1	15.33	20.47	6.311	2169	0.145	29.73
	2	Empty cell after desolvation.					
	3	Empty cell after desolvation.					
	4	16.11	21.48	6.309	2162	0.145	29.73
	5	12.91	20.16	1.264	2576	0.513	62.06
	6	7.38	12.45	1.249	2922	0.649	48.57
33	1	7.54	10.26	0.974	2571	0.625	35.92
	2	Empty cell after desolvation.					
	3	15.29	21.46	5.753	1882	0.158	20.87
	4	6.98	10.57	0.978	2592	0.624	20.84
	5	6.41	10.00	0.843	1967	0.711	20.84
	6	2.59	5.24	0.180	171	1.173	16.95
1	1	6.60	12.98	0.835	1907	0.688	92.57
	2	6.59	12.08	0.874	2006	0.679	88.93
	3	6.23	12.62	0.854	1976	0.684	88.34
	4	7.11	11.51	0.823	1846	0.700	91.64
	5	3.25	8.09	0.281	189	1.000	100.00
	6	5.05	11.33	0.467	826	0.873	98.28

5. Phase Separated Systems

The Phase Separated Systems were all generated using the experimental quantity of solvent and TEA (100%, Table SI.10) but differ in the configuration of monomers with respect to the solvent during the seeding process (Figure 4). A range of models were generated, ranging from the fully mixed systems, where the building blocks were randomly added into the simulation cell, to a system with four clusters of monomers and catalyst surrounded by solvent, to a system with two clusters of monomers and catalyst surrounded by solvent, to a system with one cluster of monomers and catalyst surrounded by monomers and solvent. We also generated a one large cluster model for the Solvent/Monomer Phase Interface Systems, where the number of monomers and catalyst molecules were scaled up by 15x, whilst keeping the quantity of solvent constant, which are analysed together with the Phase Separated Systems. To ensure that the building blocks could find their optimal orientation, these models were generated in a much larger starting cell size (cell length – 200 angstrom).

Table SI.10. Number of building blocks seeded to the simulation cell for each of the phase separation systems generated with the experimental quantity of solvent.

	Configuration				
Building block	Fully mixed large cell	Four clusters	Two clusters	One small cluster	One large cluster
					
Catalyst	4	4	4	4	60
DBB	100	100	100	100	1500
TEB	100	100	100	100	1500
TEA	1076	1076	1076	1076	1076
Toluene	2347	2347	2347	2347	2347
THF	3082	3082	3082	3082	3082
Dioxane	2934	2934	2934	2934	2934
DMF	3229	3229	3229	3229	3229

After the network generation was complete, again judged by the point at which no new bonds had formed during at least the last twenty zipBlocks tests, an extra NPT MD step was undertaken to equilibrate the cell volume. This was followed by a desolvation protocol consisting of: alkyne-alkyne homocoupling, solvent removal, monomer removal, catalyst removal, and cell workup, with NPT MD throughout to equilibrate the cell.

Potential Energies

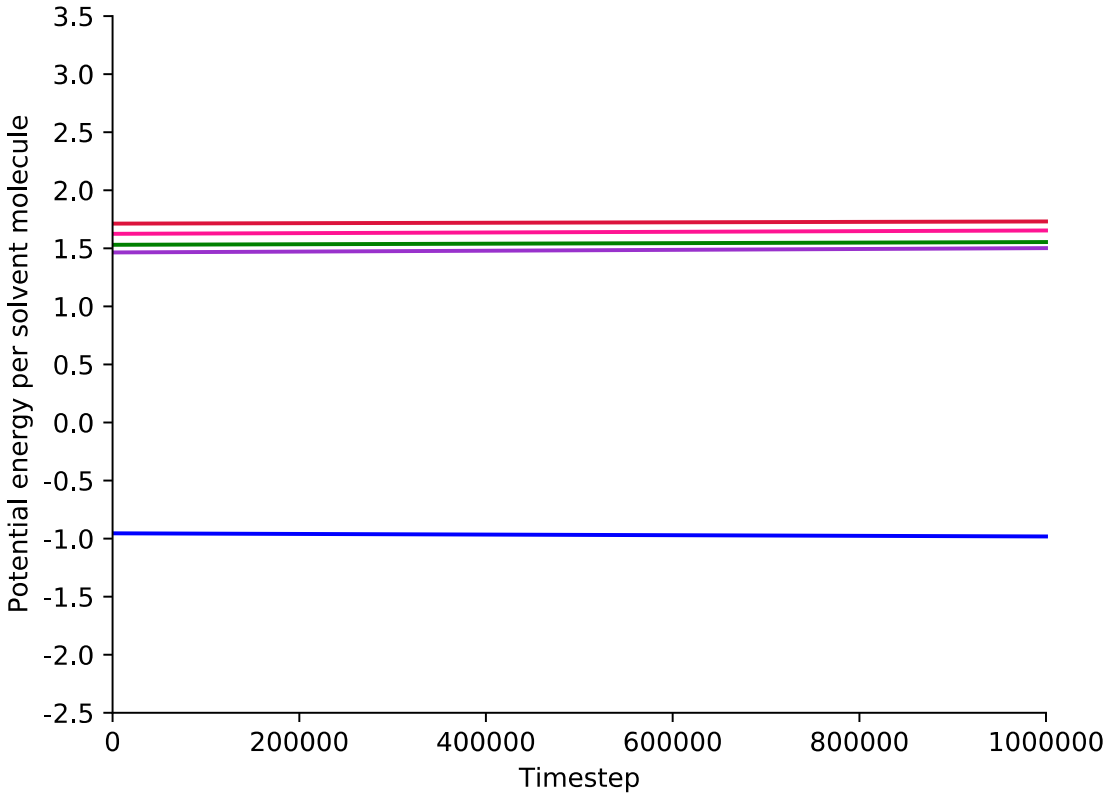


Figure SI.6. Plot of the average potential energy trend per solvent molecule against the reaction timestep for the CMP-1 phase separated systems generated in toluene solvent using molecular dynamic simulations without any possibility of bond formation. Also included are the Solvent/Monomer Phase Interface Systems one large cluster models for comparison. Key: Fully mixed large cell – purple, four clusters – green, two clusters – red, one small cluster – pink, one large cluster – blue.

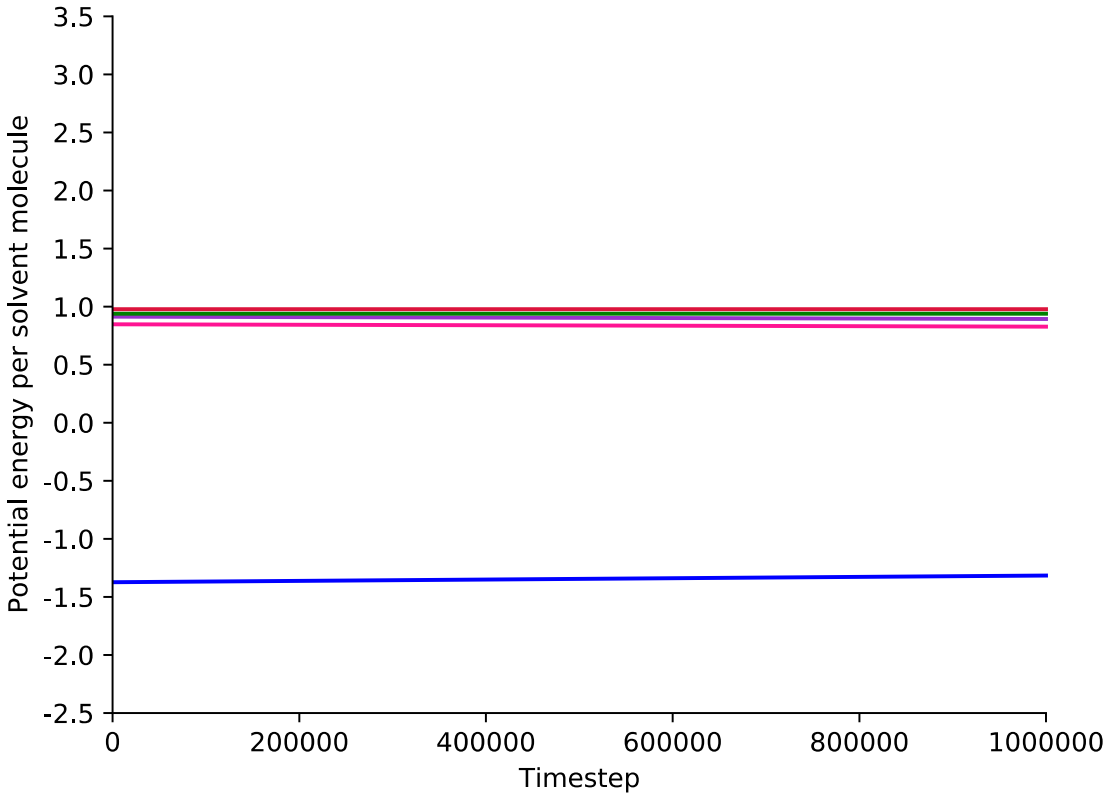


Figure SI.7. Plot of the average potential energy trend per solvent molecule against the reaction timestep for the CMP-1 phase separated systems generated in THF solvent using molecular dynamic simulations without any possibility of bond formation. Also included are the Solvent/Monomer Phase Interface Systems one large cluster models for comparison. Key: Fully mixed large cell – purple, four clusters – green, two clusters – red, one small cluster – pink, one large cluster – blue.

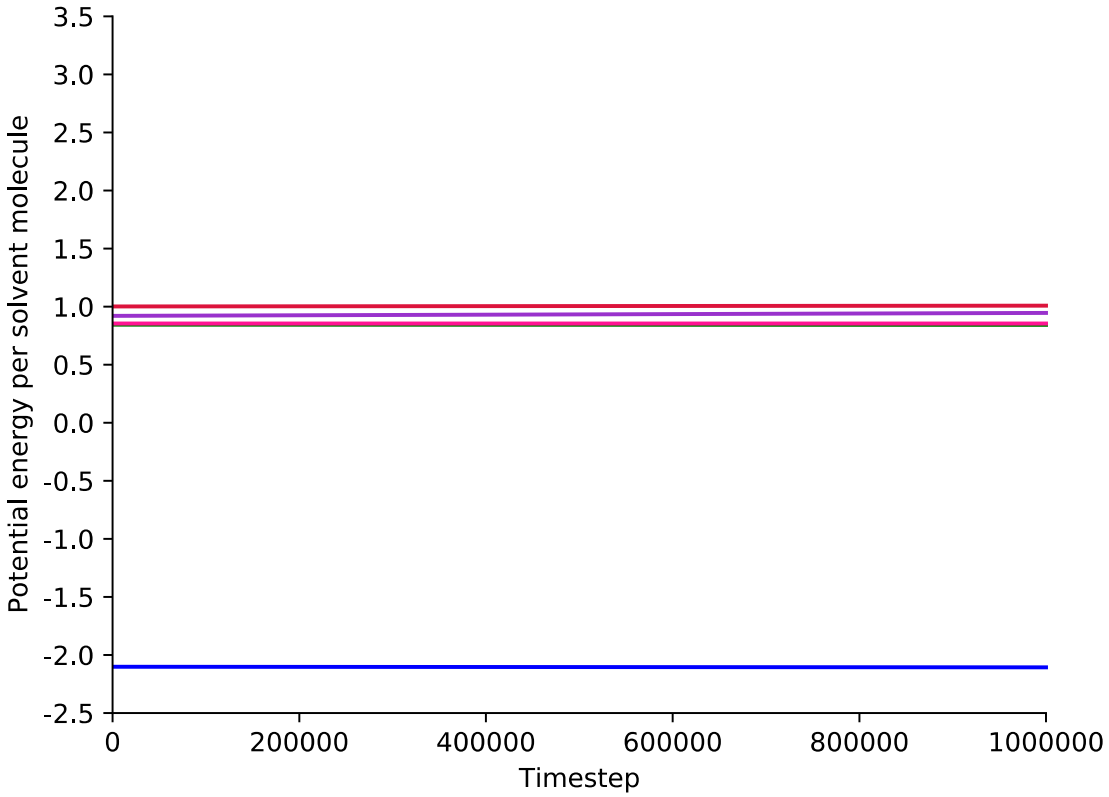


Figure SI.8. Plot of the average potential energy trend per solvent molecule against the reaction timestep for the CMP-1 phase separated systems generated in 1,4-dioxane solvent using molecular dynamic simulations without any possibility of bond formation. Also included are the Solvent/Monomer Phase Interface Systems one large cluster models for comparison. Key: Fully mixed large cell – purple, four clusters – green, two clusters – red, one small cluster – pink, one large cluster – blue.

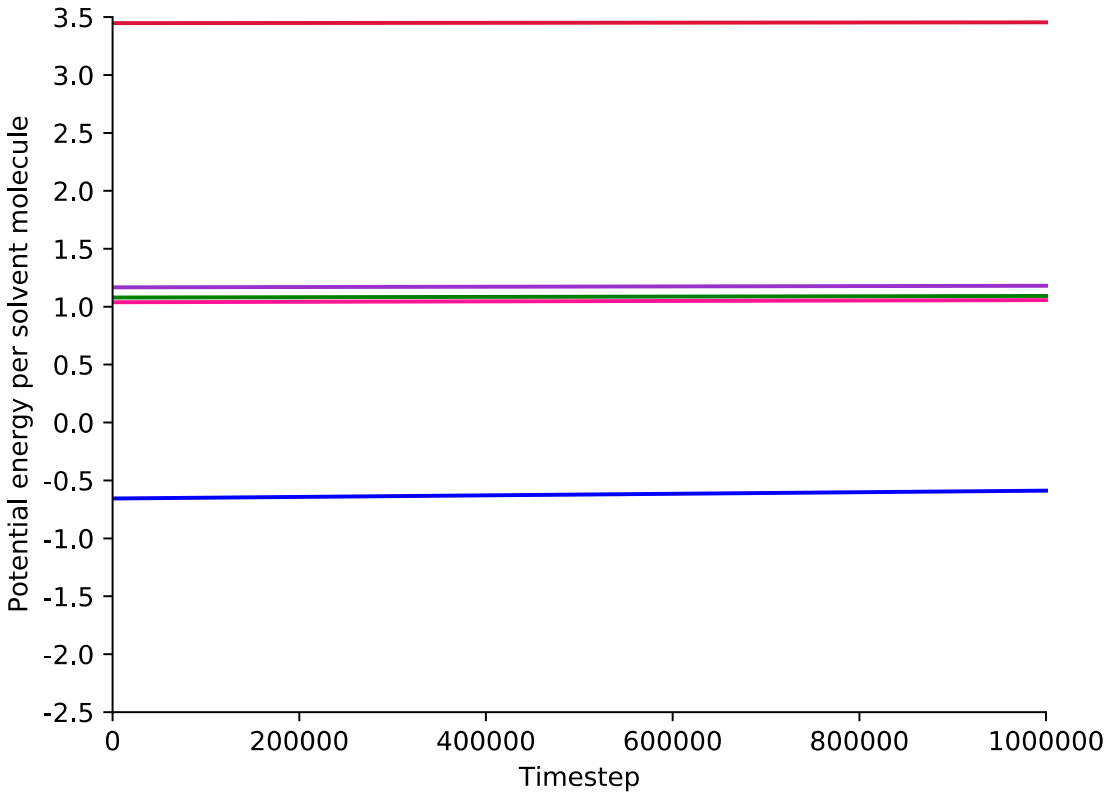


Figure SI.9. Plot of the average potential energy trend per solvent molecule against the reaction timestep for the CMP-1 phase separated systems generated in DMF solvent using molecular dynamic simulations without any possibility of bond formation. Also included are the Solvent/Monomer Phase Interface Systems one large cluster models for comparison. Key: Fully mixed large cell – purple, four clusters – green, two clusters – red, one small cluster – pink, one large cluster – blue.

Surface Areas

Table SI.11. Porosity data for the CMP-1 models generated in the fully mixed large cell configuration. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

Solvent	Model	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
Toluene	1	18.37	25.46	8.311	11275	0.111	32.55
	2	15.44	23.55	6.067	10461	0.148	29.77
	3	15.38	21.29	5.543	10038	0.160	28.62
	4	19.80	29.41	10.962	12109	0.086	35.36
	Average	17.25	24.93	7.721	10971	0.126	31.57
THF	1	17.78	29.98	8.951	11648	0.104	33.15
	2	13.84	20.73	4.788	9229	0.182	27.52
	3	17.26	26.48	9.146	12060	0.102	33.48
	4	23.05	33.49	12.822	12818	0.074	36.90
	Average	17.98	27.67	8.927	11439	0.116	32.77
Dioxane	1	21.88	29.30	11.832	12883	0.080	35.94
	2	21.78	29.94	11.837	12458	0.080	36.06
	3	20.16	26.74	8.768	11821	0.106	32.91
	4	13.51	21.30	5.040	9382	0.174	28.03
	Average	19.33	26.82	9.369	11636	0.110	33.24
DMF	1	18.29	27.90	9.280	11549	0.100	33.64
	2	19.99	29.75	9.069	11849	0.103	33.28
	3	20.18	29.32	10.553	11970	0.089	34.83
	4	20.65	32.62	11.926	12345	0.079	36.02
	Average	19.78	29.90	10.207	11928	0.093	34.44

Table SI.12. Porosity data for the CMP-1 models generated in the four clusters configuration. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

Solvent	Model	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
Toluene	1	4.67	9.65	0.769	1286	0.616	18.65
	2	3.45	7.37	0.500	306	0.728	17.48
	3	6.84	12.01	1.145	2658	0.514	19.96
	4	18.92	25.69	4.866	7349	0.179	27.86
	Average	8.47	13.68	1.820	2900	0.509	20.99
THF	1	6.74	11.43	1.233	3039	0.493	20.48
	2	4.01	9.67	0.675	999	0.652	18.41
	3	8.26	14.59	1.843	4689	0.382	21.87
	4	14.24	22.87	3.065	6354	0.265	24.50
	Average	8.31	14.64	1.704	3770	0.448	21.31
Dioxane	1	14.41	22.50	2.528	5247	0.305	23.75
	2	16.45	24.90	4.166	7667	0.205	26.73
	3	19.11	33.35	5.774	8755	0.155	30.16
	4	4.42	9.81	0.887	1792	0.582	18.85
	Average	13.60	22.64	3.339	5865	0.312	24.87
DMF	1	9.59	20.98	2.438	5517	0.315	23.35
	2	12.59	23.70	3.539	7280	0.234	25.43
	3	10.60	19.98	2.167	5024	0.343	22.50
	4	4.42	9.29	0.647	1110	0.672	18.60
	Average	9.30	18.49	2.198	4733	0.391	22.47

Table SI.13. Porosity data for the CMP-1 models generated in the two clusters configuration. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

Solvent	Model	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
Toluene	1	8.95	12.91	1.724	4551	0.405	20.96
	2	21.48	35.76	6.829	7499	0.133	30.30
	3	8.56	16.36	1.748	4327	0.401	20.81
	4	6.49	11.46	0.991	2340	0.561	18.07
	Average	11.37	19.12	2.823	4679	0.375	22.54
THF	1	11.30	19.90	2.277	4980	0.331	22.79
	2	18.15	23.16	3.384	5321	0.243	24.73
	3	6.42	11.41	0.767	1488	0.632	18.09
	4	13.58	24.26	3.540	6487	0.235	24.44
	Average	12.36	19.68	2.492	4569	0.360	22.51
Dioxane	1	9.36	16.60	2.186	5261	0.343	21.95
	2	5.36	10.41	0.908	1903	0.581	18.48
	3	17.86	25.62	4.241	6904	0.201	26.58
	4	5.04	8.80	0.533	787	0.726	17.48
	Average	9.41	15.36	1.967	3714	0.463	21.12
DMF	1	24.45	37.88	7.917	7173	0.116	31.57
	2	16.47	23.27	3.758	6415	0.223	25.23
	3	2.85	6.09	0.308	0	0.832	16.59
	4	11.84	17.55	2.365	5731	0.323	22.55
	Average	13.90	21.20	3.587	4829	0.374	23.98

Table SI.14. Porosity data for the CMP-1 models generated in the one small cluster configuration. PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

Solvent	Model	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
Toluene	1	6.95	12.07	1.194	2682	0.505	19.08
	2	13.89	20.81	2.123	4358	0.348	21.48
	3	15.32	23.35	4.118	6554	0.206	26.35
	4	10.45	18.57	2.033	4906	0.358	21.77
	Average	11.65	18.70	2.367	4625	0.354	22.17
THF	1	11.22	17.73	2.463	5546	0.314	23.05
	2	21.94	30.22	5.407	6862	0.164	28.84
	3	14.26	21.76	2.964	5983	0.271	24.57
	4	7.45	12.43	1.203	2852	0.501	19.28
	Average	13.72	20.54	3.009	5311	0.313	23.94
Dioxane	1	7.30	14.06	1.512	3902	0.438	20.66
	2	23.67	35.26	5.717	6376	0.155	29.02
	3	20.88	34.50	4.618	5797	0.186	26.30
	4	15.53	22.77	3.973	7029	0.214	25.25
	Average	16.85	26.65	3.955	5776	0.248	25.31
DMF	1	19.24	24.43	3.263	5015	0.248	24.58
	2	26.43	36.17	7.600	7030	0.120	30.93
	3	6.01	11.49	1.004	2334	0.552	19.01
	4	18.95	35.46	4.932	6751	0.178	27.84
	Average	17.66	26.89	4.200	5282	0.275	25.59

Table SI.15. Comparison of the porosity data for the CMP-1 models generated in the various phase separation configurations. Cluster SA relative to number of DBB blocks – surface area of the initial cluster regions composed of monomers and catalyst relative to the number of 1,4-dibromobenzene building blocks within the cell (we assume that the cluster surface area of the fully mixed large cells will be approaching infinity, so use a very large surface area value here), PLD – pore limiting diameter, MPD – maximum pore diameter, He volume – pore volume based on a helium probe, accessible SA – network accessible surface area.

Solvent	Phase separation	Cluster SA relative to number of DBB blocks	PLD / Å	MPD / Å	He Volume / $cm^3\ g^{-1}$	Accessible SA / $m^2\ g^{-1}$	Density / $g\ cm^{-3}$	% Size of Initial Cell
Toluene	Fully mixed large	1E+15	17.25	24.93	7.72	10971	0.13	31.57
	Four clusters	216	8.47	13.68	1.82	2900	0.51	20.99
	Two clusters	108	11.37	19.12	2.82	4679	0.38	22.54
	One small cluster	96	11.65	18.70	2.37	4625	0.35	22.17
THF	Fully mixed large	1E+15	17.98	27.67	8.93	11439	0.12	32.77
	Four clusters	216	8.31	14.64	1.70	3770	0.45	21.31
	Two clusters	108	12.36	19.68	2.49	4569	0.36	22.51
	One small cluster	96	13.72	20.54	3.01	5311	0.31	23.94
Dioxane	Fully mixed large	1E+15	19.33	26.82	9.37	11636	0.11	33.24
	Four clusters	216	13.60	22.64	3.34	5865	0.31	24.87
	Two clusters	108	9.41	15.36	1.97	3714	0.46	21.12
	One small cluster	96	16.85	26.65	3.96	5776	0.25	25.31
DMF	Fully mixed large	1E+15	19.78	29.90	10.21	11928	0.09	34.44
	Four clusters	216	9.30	18.49	2.20	4733	0.39	22.47
	Two clusters	108	13.90	21.20	3.59	4829	0.37	23.98
	One small cluster	96	17.66	26.89	4.20	5282	0.27	25.59

Table SI.16. Elemental analysis data for the CMP-1 models generated in the fully mixed large cell configuration.

Solvent	Model	wt% C	wt% H	wt% N	wt% O	wt% P	wt% Cu	wt% Br	wt% Pd
Toluene	1	89.50	2.91	0.00	0.00	1.34	3.09	0.86	2.30
	2	88.55	2.83	0.00	0.00	1.31	5.05	0.00	2.25
	3	91.02	2.98	0.00	0.00	1.37	1.40	0.88	2.35
	4	90.43	2.95	0.00	0.00	1.35	2.08	0.87	2.32
	Average	89.88	2.92	0.00	0.00	1.34	2.90	0.65	2.31
THF	1	90.74	2.96	0.00	0.00	1.36	1.74	0.87	2.33
	2	90.54	2.92	0.00	0.00	1.35	2.43	0.44	2.33
	3	90.66	2.93	0.00	0.00	1.34	2.76	0.00	2.31
	4	90.62	2.98	0.00	0.00	1.38	1.77	0.89	2.37
	Average	90.64	2.95	0.00	0.00	1.36	2.17	0.55	2.33
Dioxane	1	90.93	2.99	0.00	0.00	1.38	1.42	0.89	2.38
	2	91.22	2.95	0.00	0.00	1.37	2.11	0.00	2.35
	3	90.62	2.97	0.00	0.00	1.36	1.40	1.32	2.34
	4	90.31	2.95	0.00	0.00	1.34	1.37	1.73	2.30
	Average	90.77	2.97	0.00	0.00	1.36	1.57	0.98	2.34
DMF	1	90.24	2.92	0.00	0.00	1.34	2.76	0.43	2.31
	2	90.05	2.94	0.00	0.00	1.36	2.44	0.88	2.33
	3	90.54	2.94	0.00	0.00	1.37	2.80	0.00	2.35
	4	90.53	2.95	0.00	0.00	1.38	1.42	1.34	2.38
	Average	90.34	2.94	0.00	0.00	1.36	2.35	0.66	2.34

Table SI.17. Elemental analysis data for the CMP-1 models generated in the four clusters configuration.

Solvent	Model	wt% C	wt% H	wt% N	wt% O	wt% P	wt% Cu	wt% Br	wt% Pd
Toluene	1	88.56	2.74	0.00	0.00	1.28	2.31	2.90	2.21
	2	90.64	2.80	0.00	0.00	1.32	1.69	1.28	2.27
	3	88.49	2.68	0.00	0.00	1.26	4.19	1.22	2.16
	4	90.73	2.85	0.00	0.00	1.33	2.38	0.43	2.28
	Average	89.61	2.77	0.00	0.00	1.30	2.64	1.46	2.23
THF	1	88.93	2.77	0.00	0.00	1.21	1.87	3.13	2.08
	2	89.70	2.73	0.00	0.00	1.26	2.92	1.22	2.17
	3	89.61	2.77	0.00	0.00	1.28	1.65	2.48	2.21
	4	88.16	2.68	0.00	0.00	1.32	4.73	0.85	2.26
	Average	89.10	2.74	0.00	0.00	1.27	2.79	1.92	2.18
Dioxane	1	89.67	2.78	0.00	0.00	1.26	2.90	1.22	2.16
	2	91.40	2.82	0.00	0.00	1.32	1.35	0.85	2.26
	3	89.44	2.75	0.00	0.00	1.21	2.17	2.34	2.08
	4	90.49	2.79	0.00	0.00	1.32	2.70	0.43	2.26
	Average	90.25	2.79	0.00	0.00	1.28	2.28	1.21	2.19
DMF	1	89.08	2.74	0.00	0.00	1.28	2.63	2.07	2.20
	2	90.37	2.83	0.00	0.00	1.33	1.03	2.15	2.29
	3	90.20	2.77	0.00	0.00	1.31	3.03	0.42	2.26
	4	88.44	2.75	0.00	0.00	1.19	2.13	3.45	2.04
	Average	89.52	2.77	0.00	0.00	1.28	2.21	2.02	2.20

Table SI.18. Elemental analysis data for the CMP-1 models generated in the two clusters configuration.

Solvent	Model	wt% C	wt% H	wt% N	wt% O	wt% P	wt% Cu	wt% Br	wt% Pd
Toluene	1	87.47	2.75	0.00	0.00	1.38	4.25	1.78	2.37
	2	88.95	2.80	0.00	0.00	1.39	1.78	2.69	2.39
	3	88.01	2.75	0.00	0.00	1.42	4.01	1.37	2.44
	4	87.56	2.65	0.00	0.00	1.55	5.57	0.00	2.67
	Average	88.00	2.74	0.00	0.00	1.44	3.90	1.46	2.47
THF	1	88.08	2.70	0.00	0.00	1.31	2.69	2.96	2.25
	2	89.55	2.69	0.00	0.00	1.40	3.95	0.00	2.40
	3	89.54	2.75	0.00	0.00	1.37	1.76	2.22	2.36
	4	89.67	2.80	0.00	0.00	1.50	1.54	1.93	2.57
	Average	89.21	2.74	0.00	0.00	1.40	2.48	1.78	2.40
Dioxane	1	89.44	2.79	0.00	0.00	1.42	2.54	1.37	2.43
	2	88.56	2.67	0.00	0.00	1.40	3.60	1.36	2.41
	3	89.94	2.85	0.00	0.00	1.36	1.75	1.76	2.34
	4	88.29	2.74	0.00	0.00	1.33	2.38	2.99	2.28
	Average	89.06	2.76	0.00	0.00	1.38	2.57	1.87	2.37
DMF	1	91.51	2.63	0.00	0.00	1.06	2.53	0.45	1.82
	2	89.89	2.79	0.00	0.00	1.44	2.95	0.46	2.47
	3	88.17	2.84	0.00	0.00	1.35	1.39	3.93	2.33
	4	88.68	2.75	0.00	0.00	1.39	3.91	0.89	2.38
	Average	89.56	2.75	0.00	0.00	1.31	2.70	1.44	2.25

Table SI.19. Elemental analysis data for the CMP-1 models generated in the one small cluster configuration.

Solvent	Model	wt% C	wt% H	wt% N	wt% O	wt% P	wt% Cu	wt% Br	wt% Pd
Toluene	1	89.03	2.75	0.00	0.00	1.46	1.88	2.36	2.52
	2	89.72	2.78	0.00	0.00	1.49	1.53	1.92	2.56
	3	89.12	2.80	0.00	0.00	1.36	1.75	2.64	2.34
	4	88.70	2.76	0.00	0.00	1.39	2.50	2.25	2.39
	Average	89.14	2.77	0.00	0.00	1.43	1.91	2.29	2.45
THF	1	88.54	2.68	0.00	0.00	1.34	3.42	1.72	2.29
	2	89.87	2.70	0.00	0.00	1.31	3.02	0.84	2.25
	3	88.12	2.73	0.00	0.00	1.28	1.97	3.71	2.20
	4	89.75	2.71	0.00	0.00	1.43	3.66	0.00	2.45
	Average	89.07	2.71	0.00	0.00	1.34	3.02	1.57	2.30
Dioxane	1	90.12	2.68	0.00	0.00	1.33	2.73	0.86	2.28
	2	88.91	2.72	0.00	0.00	1.35	2.08	2.62	2.32
	3	88.84	2.83	0.00	0.00	1.52	2.73	1.47	2.61
	4	90.26	2.81	0.00	0.00	1.49	1.91	0.96	2.56
	Average	89.53	2.76	0.00	0.00	1.42	2.36	1.48	2.45
DMF	1	90.05	2.75	0.00	0.00	1.39	2.50	0.90	2.40
	2	90.67	2.67	0.00	0.00	1.08	1.85	1.86	1.86
	3	89.51	2.71	0.00	0.00	1.36	2.78	1.31	2.33
	4	89.65	2.74	0.00	0.00	1.34	1.37	2.59	2.30
	Average	89.97	2.72	0.00	0.00	1.29	2.13	1.67	2.22

Table SI.20. Comparison of the elemental analysis data for the CMP-1 models generated in the various phase separation configurations.

Solvent	Phase separation	wt% C	wt% H	wt% N	wt% O	wt% P	wt% Cu	wt% Br	wt% Pd
Toluene	Fully mixed large	89.88	2.92	0.00	0.00	1.34	2.90	0.65	2.31
	Four clusters	89.61	2.77	0.00	0.00	1.30	2.64	1.46	2.23
	Two clusters	88.00	2.74	0.00	0.00	1.44	3.90	1.46	2.47
	One small cluster	89.14	2.77	0.00	0.00	1.43	1.91	2.29	2.45
THF	Fully mixed large	90.64	2.95	0.00	0.00	1.36	2.17	0.55	2.33
	Four clusters	89.10	2.74	0.00	0.00	1.27	2.79	1.92	2.18
	Two clusters	89.21	2.74	0.00	0.00	1.40	2.48	1.78	2.40
	One small cluster	89.07	2.71	0.00	0.00	1.34	3.02	1.57	2.30
Dioxane	Fully mixed large	90.77	2.97	0.00	0.00	1.36	1.57	0.98	2.34
	Four clusters	90.25	2.79	0.00	0.00	1.28	2.28	1.21	2.19
	Two clusters	89.06	2.76	0.00	0.00	1.38	2.57	1.87	2.37
	One small cluster	89.53	2.76	0.00	0.00	1.42	2.36	1.48	2.45
DMF	Fully mixed large	90.34	2.94	0.00	0.00	1.36	2.35	0.66	2.34
	Four clusters	89.52	2.77	0.00	0.00	1.28	2.21	2.02	2.20
	Two clusters	89.56	2.75	0.00	0.00	1.31	2.70	1.44	2.25
	One small cluster	89.97	2.72	0.00	0.00	1.29	2.13	1.67	2.22

6. Solvent/Monomer Phase Interface Systems

Degree of solvent diffusion – pre-network formation

The concentration profiles generated show how the normalised number/count of solvent molecules changes going across the centre of the simulation cell from one edge to the other in each of the three dimensions using the following lattice ranges:
x: 0.45–0.55, y: 0–1 and z: 0.45–0.55 (slice A),
x: 0–1, y: 0.45–0.55 and z: 0.45–0.55 (slice B), and
x: 0.45–0.55, y: 0.45–0.55 and z: 0–1 (slice C).
Figure SI.10 shows a cartoon representation of the method taken. In each case, a slice was taken through the centre of the cell in the plane of the two dimensions with the lattice ranges of 0.45–0.55, and then fragments were taken by travelling across the third axis (with the lattice range of 0–1), binning the structures into fragments of lattice range size 0.1, and counting the number of solvent molecules within each fragment.
E.g., for slice A, the slice was taken through the *xz* plane, keeping the molecules that were within x = 0.45–0.55 and z = 0.45–0.55, and fragments were sampled at y ranges of 0–0.1, 0.1–0.2, 0.2–0.3, 0.3–0.4, 0.4–0.5, 0.5–0.6, 0.6–0.7, 0.7–0.8, 0.8–0.9, and 0.9–1. Then, the number of solvent molecules within each fragment were calculated, and normalised to a percentage using the following formula:

$$Normalised\ count = 100\ x \frac{Number\ of\ solvent\ molecules\ in\ the\ fragment}{Total\ number\ of\ solvent\ molecules}$$

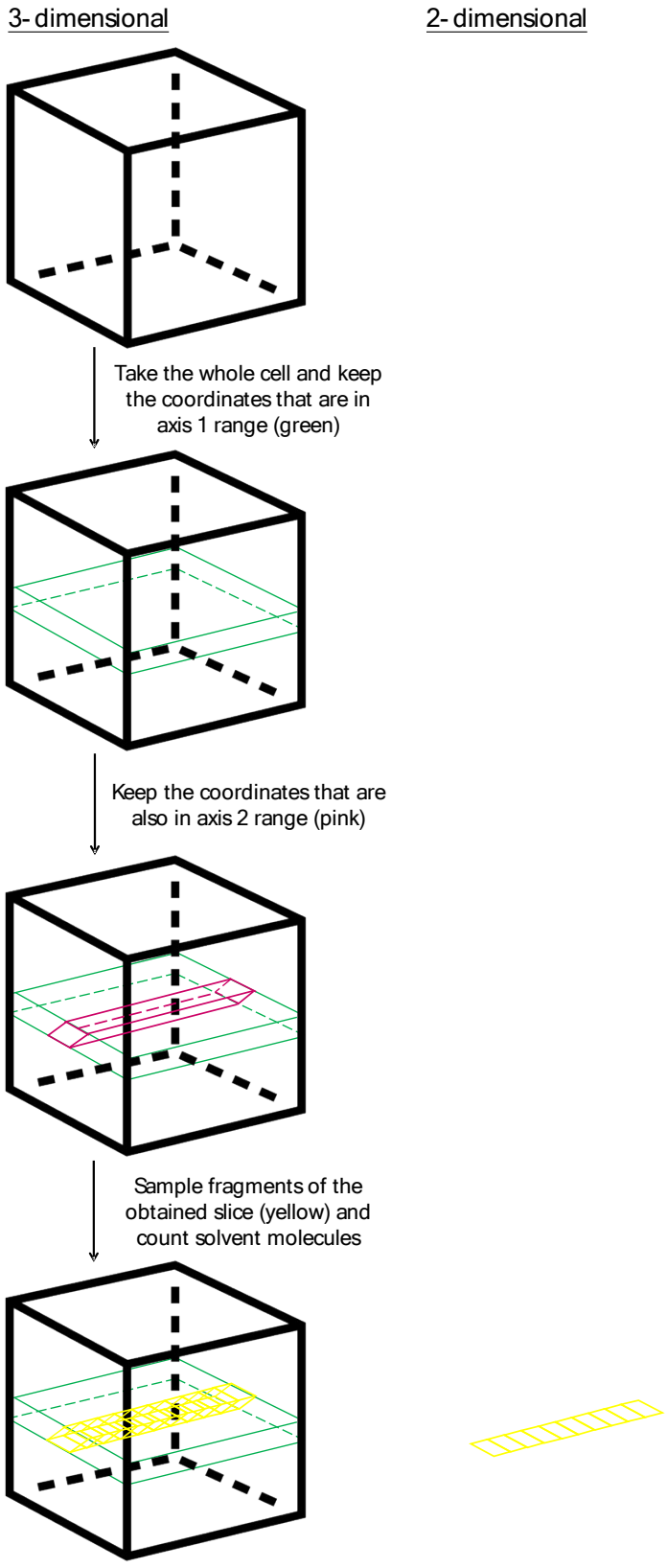


Figure SI.10. Cartoon representation of the methodology undertaken to calculate the concentration profiles for the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in each solvent. For clarity, a 2-dimensional representation of the slice is also shown.

The concentration profiles for the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in each solvent are given in Figures SI.11–SI.14.

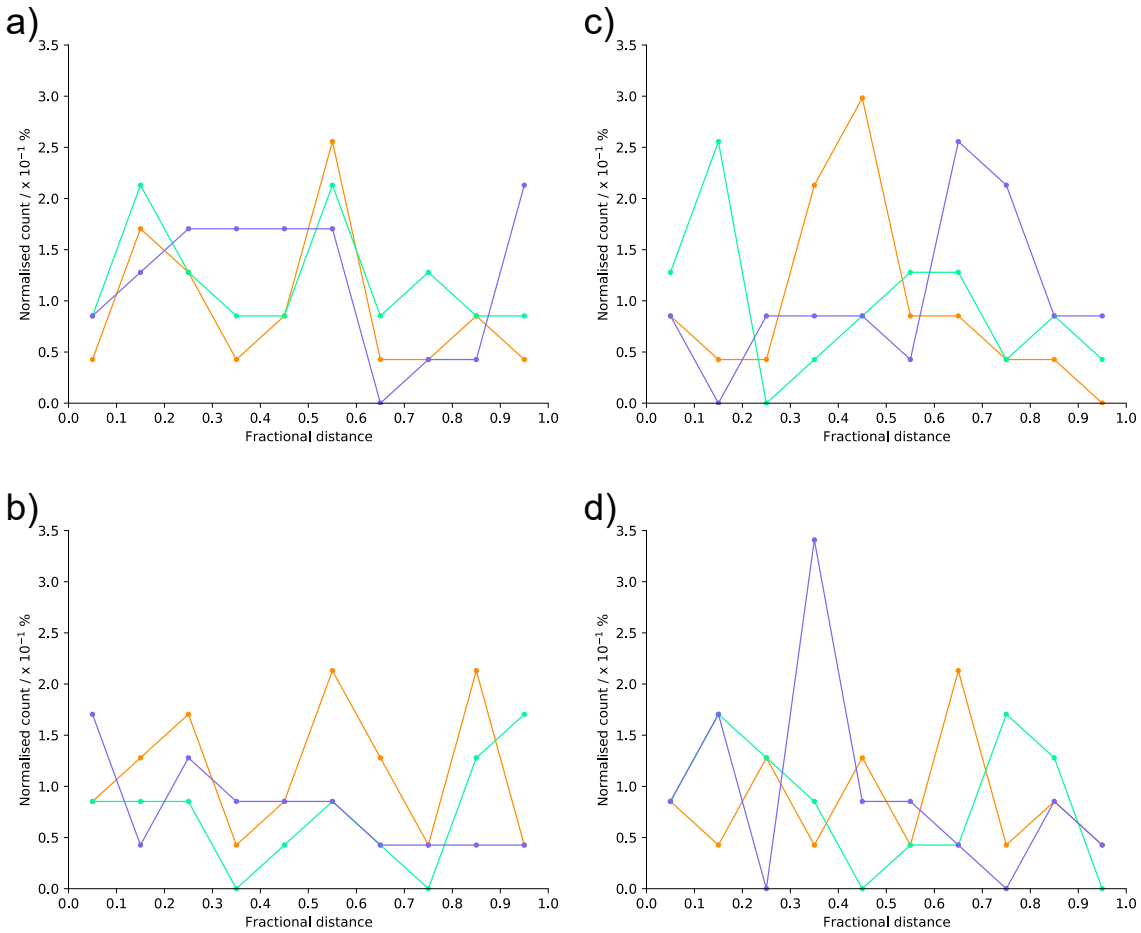


Figure SI.11. Plot of the concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in toluene solvent. a) Model 1, b) Model 2, c) Model 3, d) Model 4. Key: slice A – orange, slice B – green, slice C – purple.

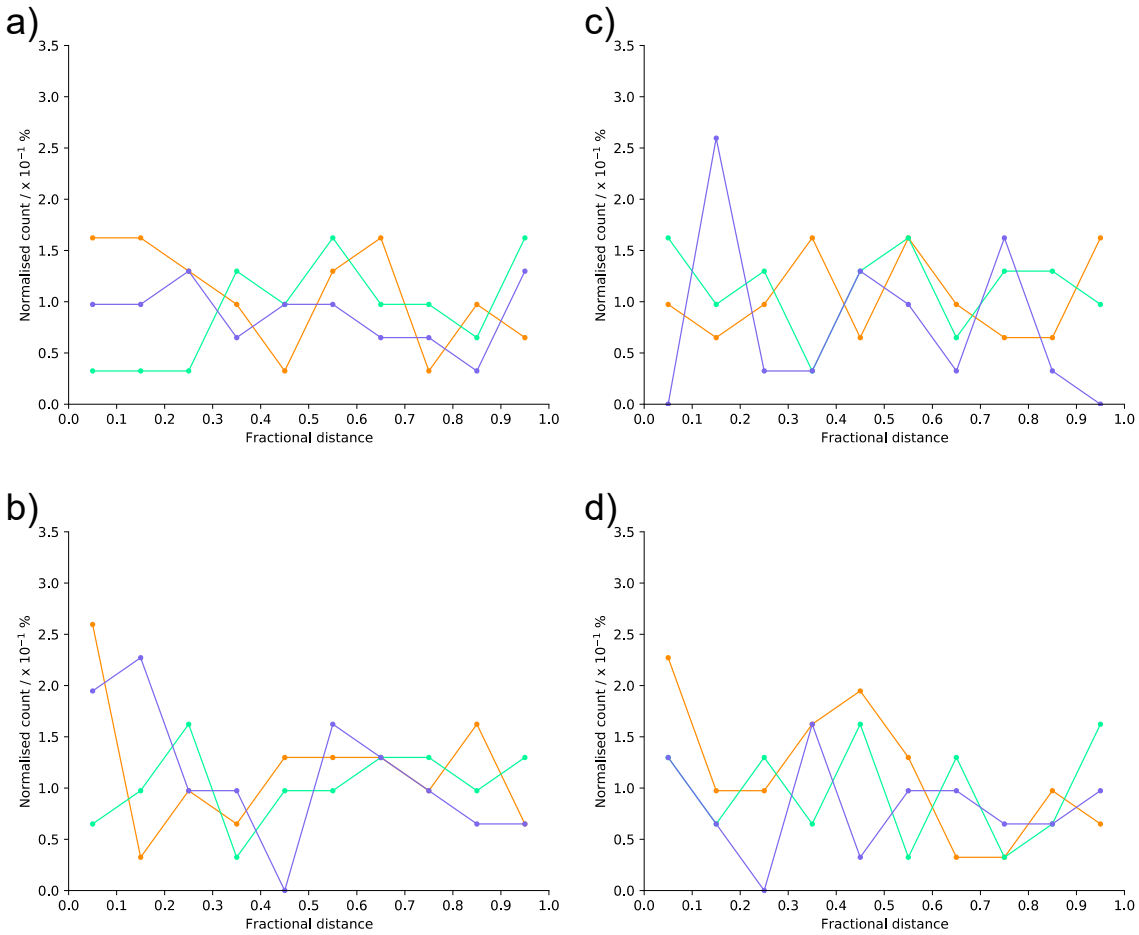


Figure SI.12. Plot of the concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in THF solvent. a) Model 1, b) Model 2, c) Model 3, d) Model 4. Key: slice A – orange, slice B – green, slice C – purple.

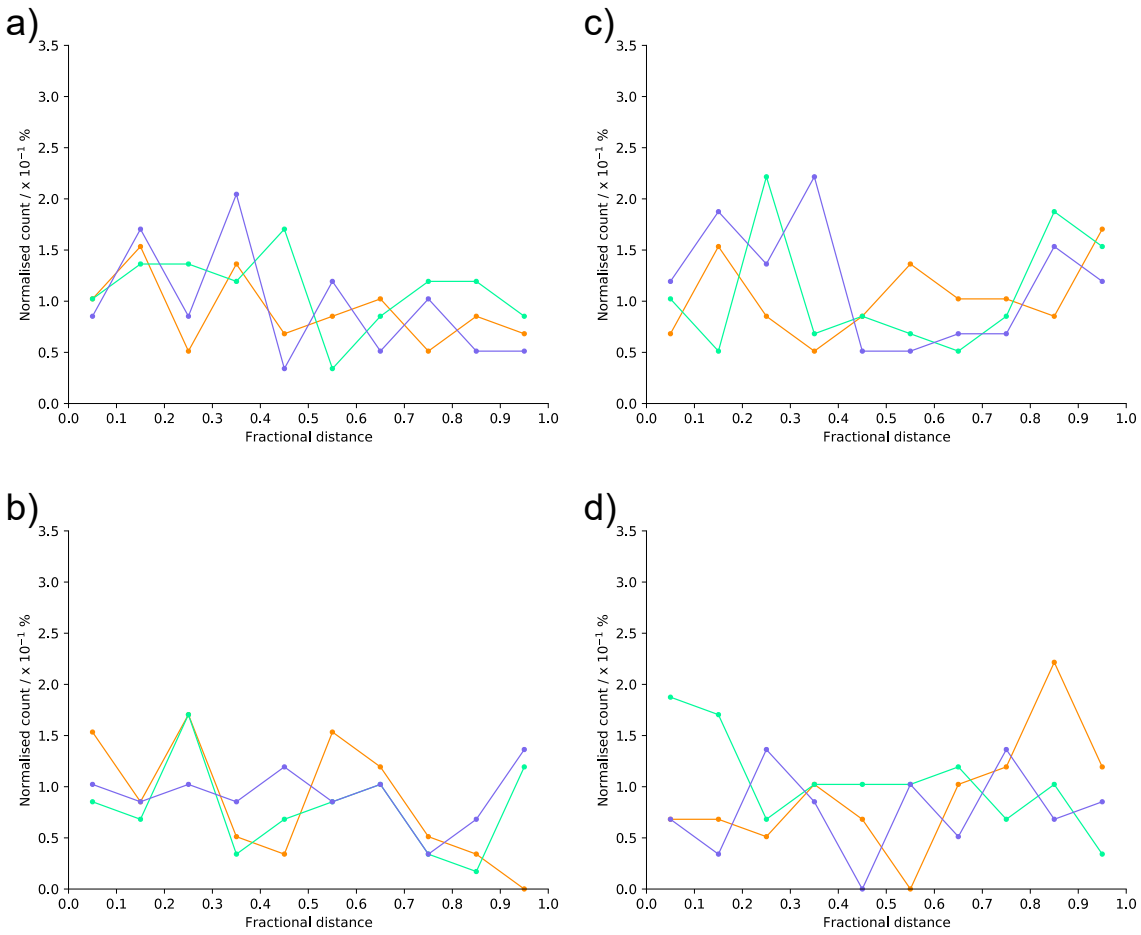


Figure SI.13. Plot of the concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in 1,4-dioxane solvent. a) Model 1, b) Model 2, c) Model 3, d) Model 4. Key: slice A – orange, slice B – green, slice C – purple.

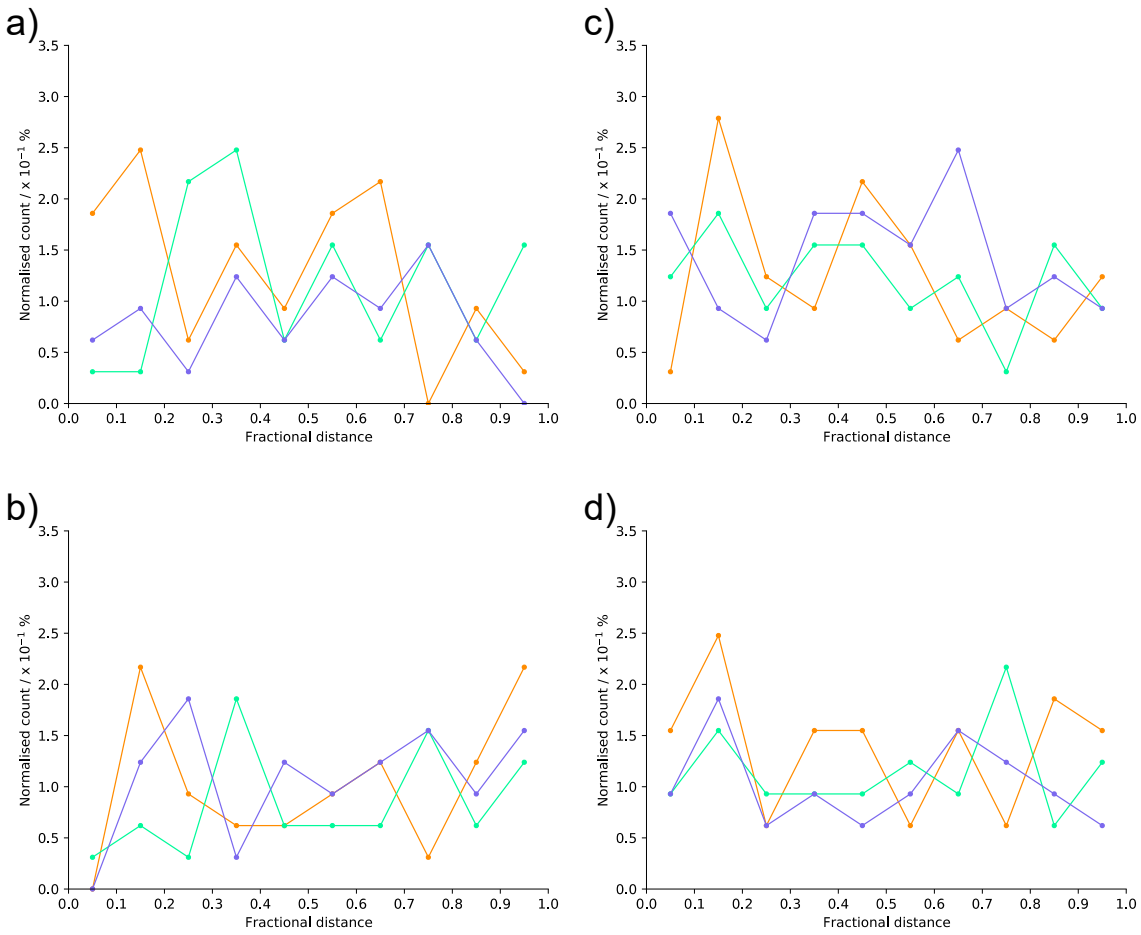


Figure SI.14. Plot of the concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in DMF solvent. a) Model 1, b) Model 2, c) Model 3, d) Model 4. Key: slice A – orange, slice B – green, slice C – purple.

We also generated some 'four-dimensional concentration profiles', where each point on the plot represents the xyz coordinates of the centre of one of the studied fragments, *e.g.,* for the first fragment taken in slice A, the coordinates plotted would be (0.5, 0.05, 0.5). The points are then colour coded by taking the average of the normalised counts across models 1–4 for that fragment. The four-dimensional concentration profiles are given in Figures SI.15–SI.18.

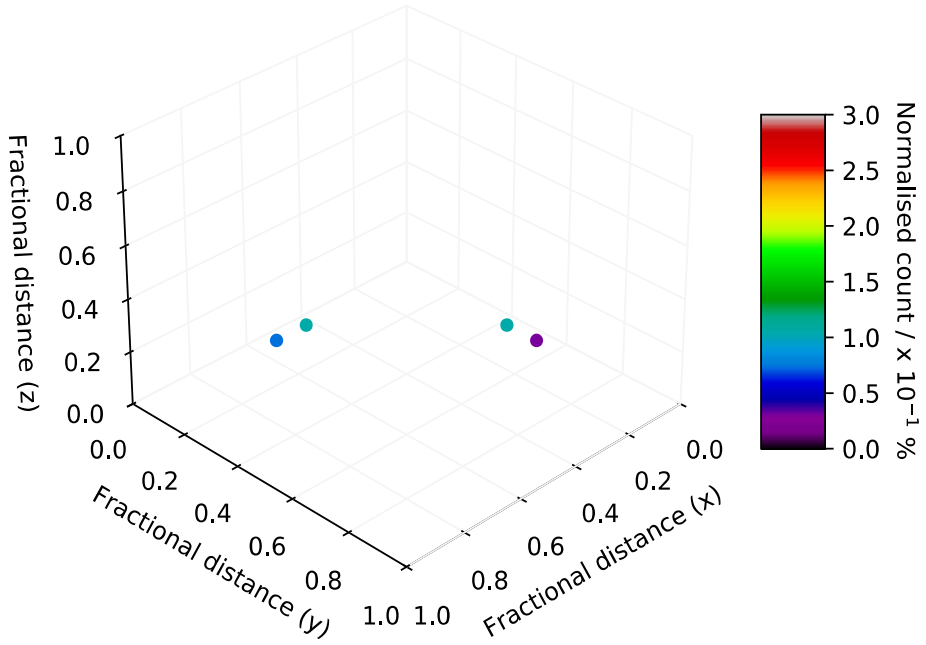


Figure SI.15. Plot of the four-dimensional concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in toluene solvent.

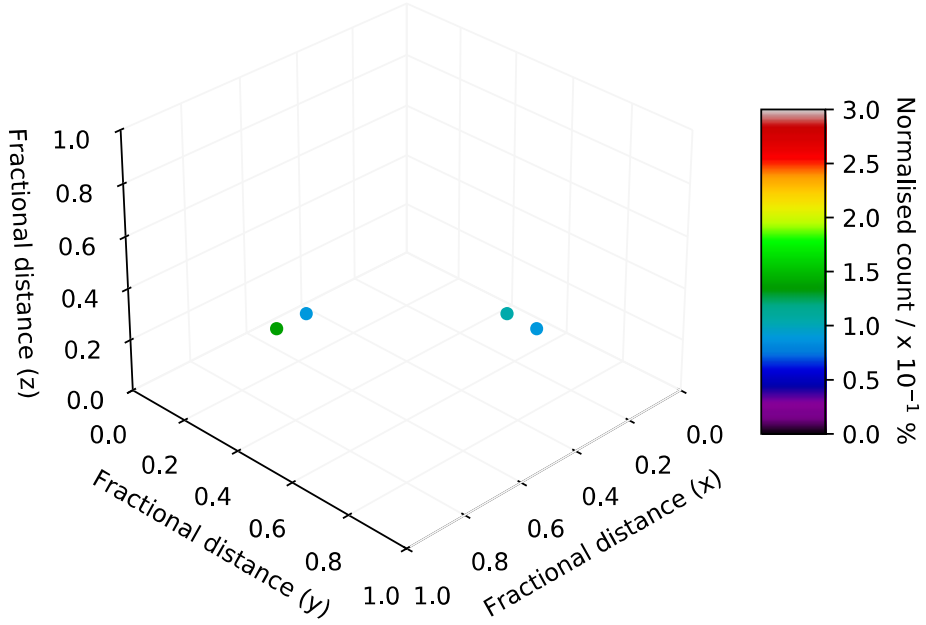


Figure SI.16. Plot of the four-dimensional concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in THF solvent.

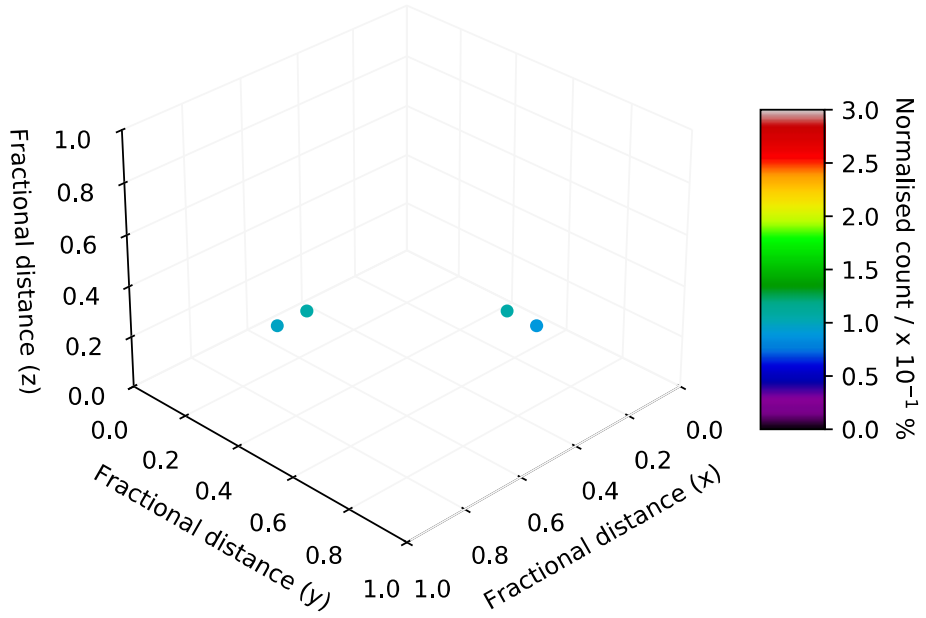


Figure SI.17. Plot of the four-dimensional concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in 1,4-dioxane solvent.

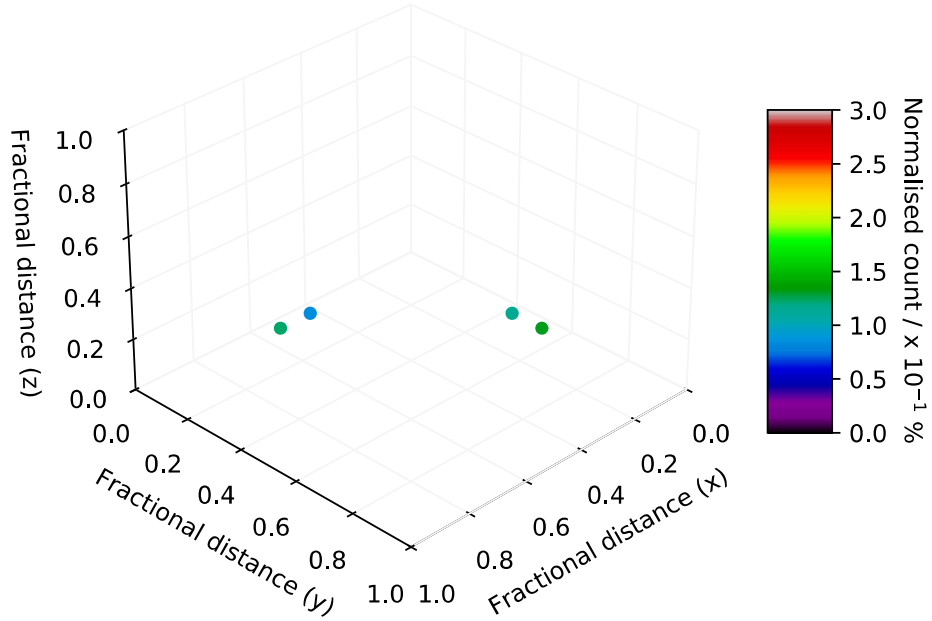


Figure SI.18. Plot of the four-dimensional concentration profile of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated in DMF solvent.

Based on the concentration profiles, we then calculated the fractional distances associated with the largest normalised count for each slice in each model. The plot of fractional distance against solvent polarity index[4] is shown in Figure SI.19.

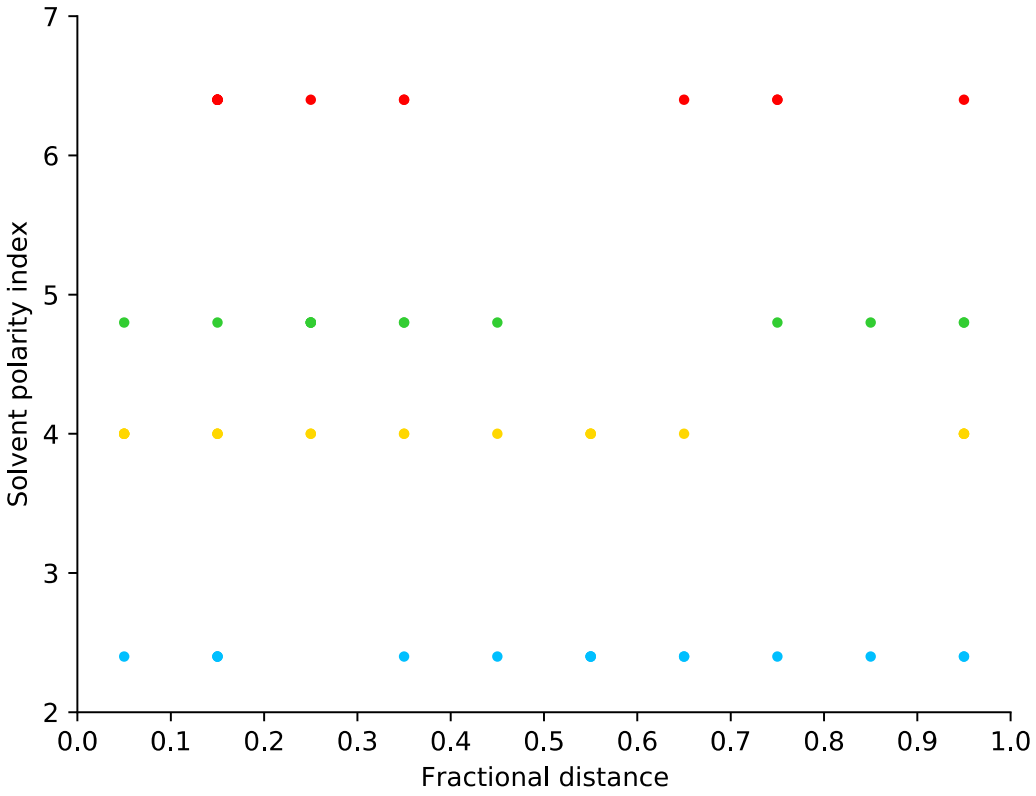


Figure SI.19. Plot of the fractional distances corresponding to the largest normalised count for each slice in each of the CMP-1 Solvent/Monomer Phase Interface Systems potential energy diffusion models generated. Key: toluene – blue, THF – yellow, 1,4-dioxane – green, DMF – red.

Degree of solvent diffusion – post network formation and desolvation

The Solvent/Monomer Phase Interface Systems were analysed after both network generation (once the polymer framework had completely formed) and after the desolvation protocol using Materials Studio 5.0. Slices were taken through the centre of each model using the lattice parameters of a: 0.45–0.55, b: 0–1 and c: 0–1 (slice A) and a: 0–1, b: 0.45–0.55 and c: 0–1 (slice B). For the slices taken after the network generation, this equated to a slice of 20 Å x 200 Å x 200 Å (slice A) or 200 Å x 20 Å x 200 Å (slice B). The slices taken after desolvation were smaller due to a reduction in the unit cell size during the NPT MD stages of the desolvation protocol, however the percentage size of the slice relative to the entire model remained consistent. Then, fragments of the slice were collected and sampled to calculate their density and surface area, and the findings from slices A and B were averaged. The lattice ranges of each fragment are given in Table SI.21.

Table SI.21. Lattice ranges of the fragments sampled as part of the Solvent/Monomer Phase Interface Systems analysis.

Fragment	Slice A lattice range / Å			Slice B lattice range / Å		
	a	b	c	a	b	c
0	0.00–1.00	-0.05–0.05	0.45–0.55	-0.05–0.05	0.00–1.00	0.45–0.55
1	0.00–1.00	0.00–0.10	0.45–0.55	0.00–0.10	0.00–1.00	0.45–0.55
2	0.00–1.00	0.10–0.20	0.45–0.55	0.10–0.20	0.00–1.00	0.45–0.55
3	0.00–1.00	0.20–0.30	0.45–0.55	0.20–0.30	0.00–1.00	0.45–0.55
4	0.00–1.00	0.30–0.40	0.45–0.55	0.30–0.40	0.00–1.00	0.45–0.55
5	0.00–1.00	0.40–0.50	0.45–0.55	0.40–0.50	0.00–1.00	0.45–0.55
6	0.00–1.00	0.45–0.55	0.45–0.55	0.45–0.55	0.00–1.00	0.45–0.55

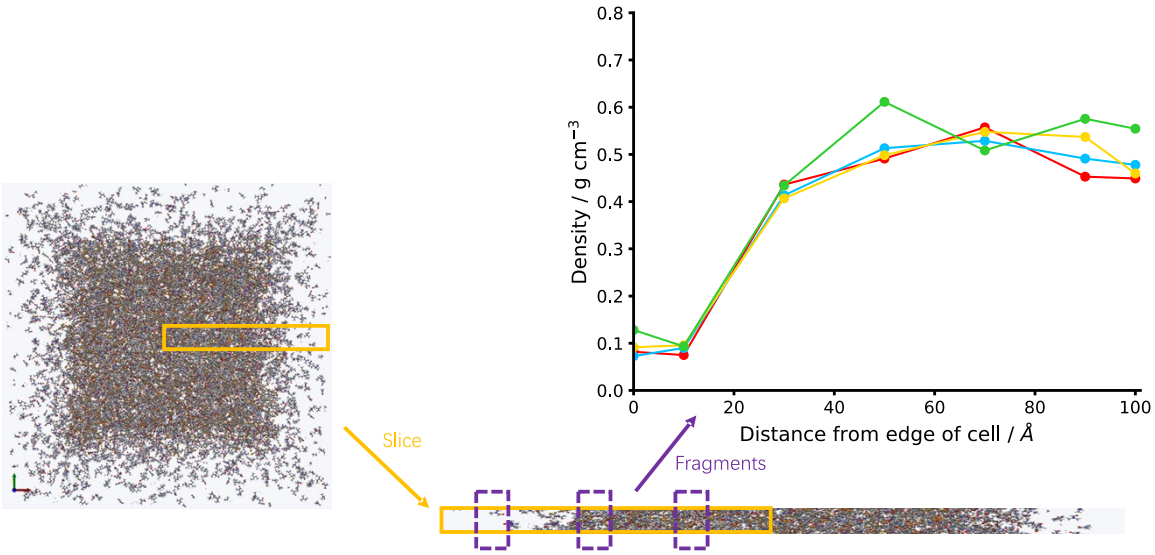


Figure SI.20. Example of a slice through a CMP-1 Solvent/Monomer Phase Interface System model and the resulting fragments that were analysed, along with the plot of the average density of the CMP-1 Solvent/Monomer Phase Interface Systems (including solvent) after network generation but before desolvation against the distance from the edge of the simulation cell. Key: toluene – blue, THF – yellow, 1,4-dioxane – green, DMF – red.

Table SI.22. Average surface areas across slices A and B of the CMP-1 Solvent/Monomer Phase Interface Systems artificially synthesised in each solvent after network generation. Key – Connolly: Connolly surface area, SSA – smoothed solvent surface area, SASA – smoothed solvent accessible surface area.

Solvent	Surface Area / m^2 g^{-1}	Fragment ID						
		0	1	2	3	4	5	6
Toluene	Connolly	9104	9058	4732	4139	4120	4521	4577
	SSA	21857	19096	5789	4338	3888	4478	4603
	SASA	21857	19095	5776	4330	3868	4466	5750
THF	Connolly	8668	8300	4494	4514	4059	4128	4503
	SSA	20886	20316	5464	4522	3885	4116	4868
	SASA	20879	20309	5453	4497	3855	4108	4851
Dioxane	Connolly	7711	7659	4487	3794	4372	3932	4206
	SSA	16430	18593	5279	3362	4472	3694	3661
	SASA	16428	18592	5275	3351	4458	3684	3654
DMF	Connolly	8403	9110	4666	4709	4180	4415	4403
	SSA	19313	24633	5270	4503	3589	4846	5192
	SASA	19309	24631	5264	4488	3570	4837	5181

Table SI.23. Average surface areas across slices A and B of the CMP-1 Solvent/Monomer Phase Interface Systems synthesised in each solvent after desolvation. Key – Connolly: Connolly surface area, SSA – smoothed solvent surface area, SASA – smoothed solvent accessible surface area.

Solvent	Surface Area / m^2 g^{-1}	Fragment ID						
		0	1	2	3	4	5	6
Toluene	Connolly	3840	3078	3516	5347	2683	3467	3792
	SSA	567	397	92	606	738	248	107
	SASA	560	390	12	338	737	163	102
THF	Connolly	2477	1892	1101	1252	3244	2712	3094
	SSA	183	93	123	57	1070	64	1615
	SASA	177	47	122	52	1067	26	1609
Dioxane	Connolly	2052	2323	2465	4220	2117	3397	3126
	SSA	219	121	53	1413	243	247	39
	SASA	219	111	45	1368	201	192	2
DMF	Connolly	2644	3830	2599	2413	3509	2900	1297
	SSA	264	469	251	96	572	443	241
	SASA	234	446	212	88	534	380	241

Pore size distribution analysis

Pore size distributions were obtained for each of the Solvent/Monomer Phase Interface Systems after the full artificial synthesis (network generation followed by desolvation) protocol. This was done by running each of fragments 0–6 obtained through the Materials Studio slicing procedure for slices A and B (fragment ranges given in Table SI.21) through the Poreblazer 4.0 code.[14] This resulted in 8 structures per fragment per solvent, as there were 4 models generated of each structure, and each was sliced in two directions, A and B. For each fragment and solvent, the respective pore size distribution functions of each of the 8 structures were combined to produce one plot, where the pore widths (x axis) were averaged, as these differed slightly from one model to the next due to different final simulation cell sizes, and the pore intensities were summed to generate the total contribution of pores to each fragment for each solvent. The resulting plots are shown in Figure 7.

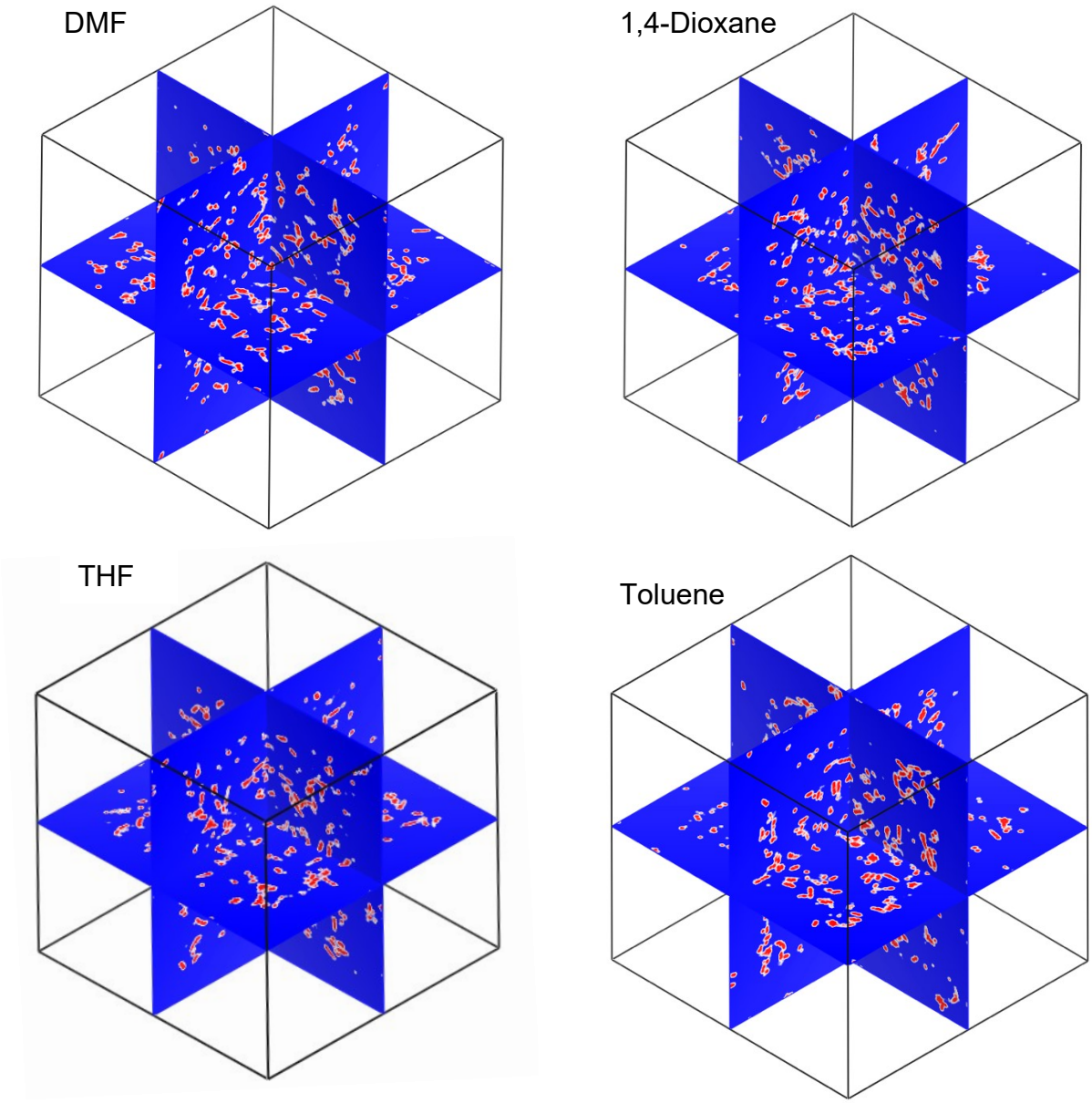


Figure SI.21. Cell density slices in the xy, yz, and xz planes through Model 1 for each of the Solvent/Monomer Phase Interface Systems after network generation and before desolvation or homocoupling. Blue regions represent solvent volume and red/white regions represent the CMP-1 framework.

7. References

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