Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Formation Mechanism of Ultra Porous Framework Materials

Supporting Information

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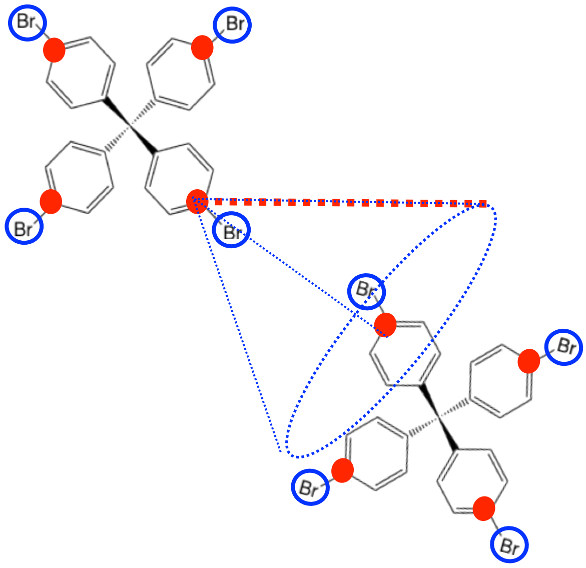
Contents

1. Bonding Criteria



2. Generation mechanisms

Mechanism 1.

Seed a simulation cell with solvent*

Remove solvent

Seed PAF build unit

Bonding test

Optimisation

MD

Loop 88 times

*either 1511 DMF molecules or 1175 DCM molecules. The solvent molecules are treated as rigid bodies in the simulation.

Mechanism 2.

Seed a simulation cell with one PAF build unit

Grow PAF build unit

Bonding test

Optimisation

MD

Loop x times

Mechanism 3.

Seed a simulation cell with x PAF build unit

Grow PAF build unit

Seed solvent*

Bonding test

Optimisation

MD

Remove solvent

Loop x times

* 1511 DMF molecules. The solvent molecules are treated as rigid bodies in the simulation.

3. Model generation descriptions

Model	Simulation cell length (Å)	Generation mechanism	Solvent	MD loops	Total MD time (ns)	AMBUILD steps	Bond distance (Å)	Bond angle (°)	Final wt% Br	Final density (g cm^{-3})
1	50	1	DMF	1	4.4	88	10	70	12.00	0.42
2	50	1	DMF	10	4.4	88	10	70	10.60	0.42
3	50	1	DMF	50	22.0	88	10	70	11.10	0.42
4	50	1	DMF	10	4.4	88	10	50	16.60	0.42
5	50	1	DCM	10	4.4	88	10	50	14.10	0.36
6	50	1	DMF	10	4.4	88	3	70	40.80	0.63
7	50	1	DMF	10	4.4	88	6.5	70	21.80	0.48
8	50	1	DMF	10	4.4	88	10	70	10.60	0.42
9	50	1	DMF	10	4.4	88	12	70	8.30	0.41
10	50	1	DMF	10	4.4	88	15	70	4.80	0.39
11	50	1	DMF	1	4.4	88	10	10	49.70	0.74
12	50	1	DMF	1	4.4	88	10	30	41.00	0.63
13	50	1	DMF	1	4.4	88	10	50	21.90	0.48
14	50	1	DMF	1	4.4	88	10	70	12.00	0.42
15	50	1	DMF	1	4.4	88	10	90	7.40	0.40
16	50	1	DMF	1	4.4	88	10	100	5.30	0.39
17	300	2	None	1	24.4	488	8	70	11.80	0.01
18	300	2	None	1	36.6	733	8	90	11.50	0.01
19	300	2	None	1	29.8	596	8	100	13.80	0.01
20	300	2	None	1	17.6	7352	12	70	10.60	0.01
21	300	2	None	1	28.7	574	12	90	9.50	0.01
22	300	2	None	1	45.7	914	12	100	5.96	0.01
23	50	3	DMF	1	1	200	10	100	2.01	0.74
									1.71	0.73
									2.25	0.75
24	50	2	None	1	1	200	10	100	2.00	0.61
									2.71	0.70
									2.67	0.72
25	50	3	DMF	1	1	200	12	100	2.07	0.72
									1.68	0.76
									2.22	0.76
26	50	2	None	1	1	200	12	100	2.51	0.68
									1.72	0.62
									2.73	0.62
27	75	3	None	1	1	200	12	100	4.56	0.51
28	100	3	None	1	1	200	12	100	5.47	0.47
29	100	2	None	1	1.53	306	12	100	2.75	0.68
30	100	2	None	1	0.575	115	12	100	1.93	0.62
31	100	2	None	1	0.575	115	12	100	2.41	0.63
32	100	2	None	1	0.59	118	12	100	2.10	0.67
33	100	2	None	1	0.555	115	12	100	2.34	0.65

Table S1. The network generation process details for each Model system.

4. Radial Distribution Function

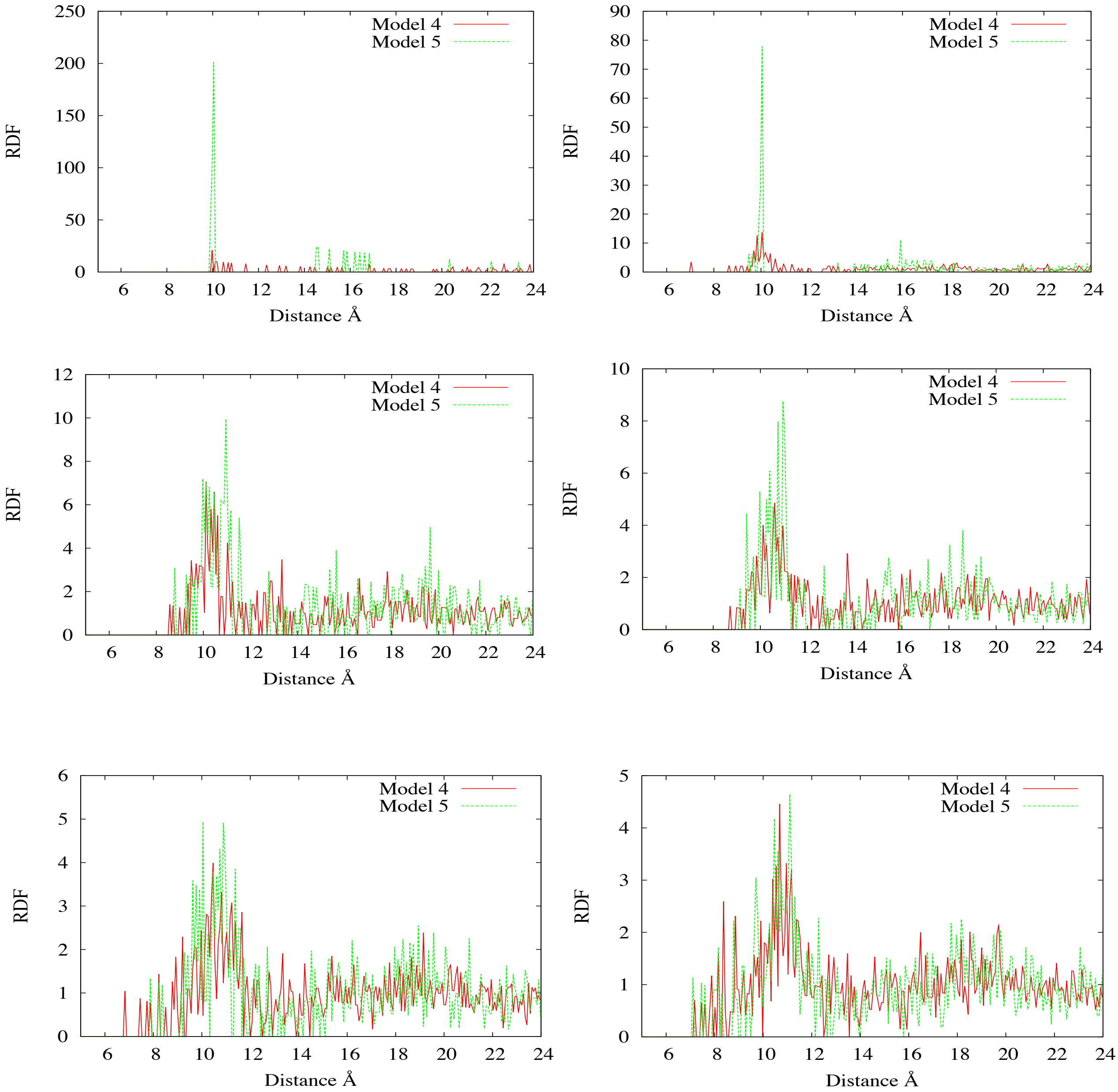


Fig. S2. Radial distribution for Model-4 and Model-5. The solvent used during the generation of Model-4 is DMF and the solvent used during the generation of Model-5 is DCM. central carbon (a) step 18 (b) step 42 (c) step 54 (d) step 66 (e) step 78 (f) step 90

5. Distance AMBUILD criteria

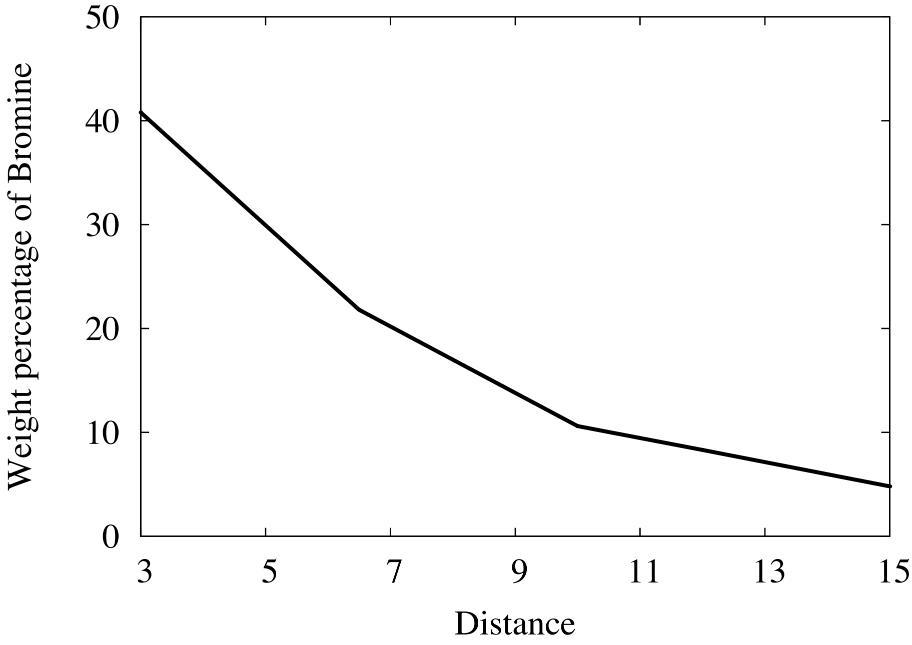


Fig. S3. The final weight percentage of bromine as a function of the distance criteria between the end groups used during the AMBUILD network generation process. Models -6, -7, -8, -9, and -10.

6. Angle AMBUILD criteria

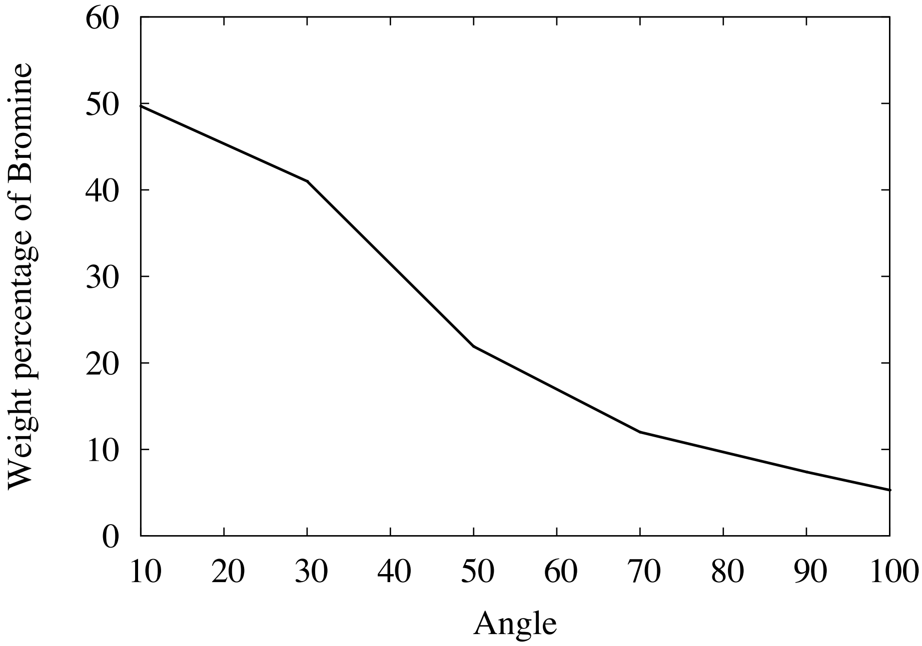


Fig. S4. The final weight percentage of bromine as a function of the angle criteria between the end groups used during the AMBUILD network generation process. Models -11, -12, -13, -14, and -15.

7. Cluster generation

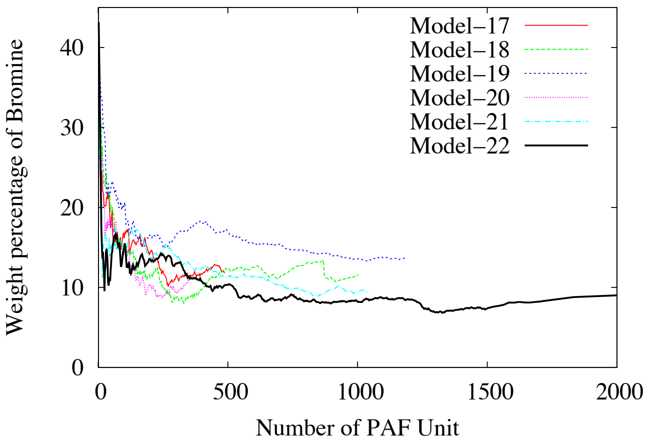


Fig. S5. Weight percentage of Br as a function of the number of PAF build units for Models-17-22.

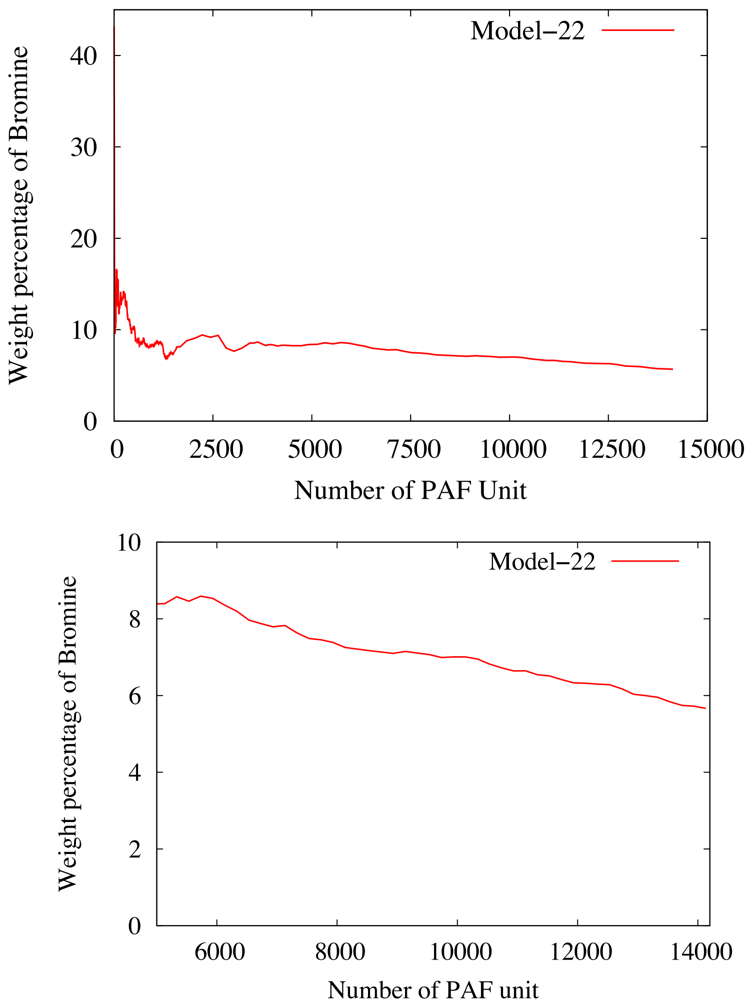


Fig. S6. Weight percentage of Br as a function of the number of PAF build units for Model-22; (a) total run (b) for the region after which the periodic boundary is crossed (at approximately 6000 PAF build units).

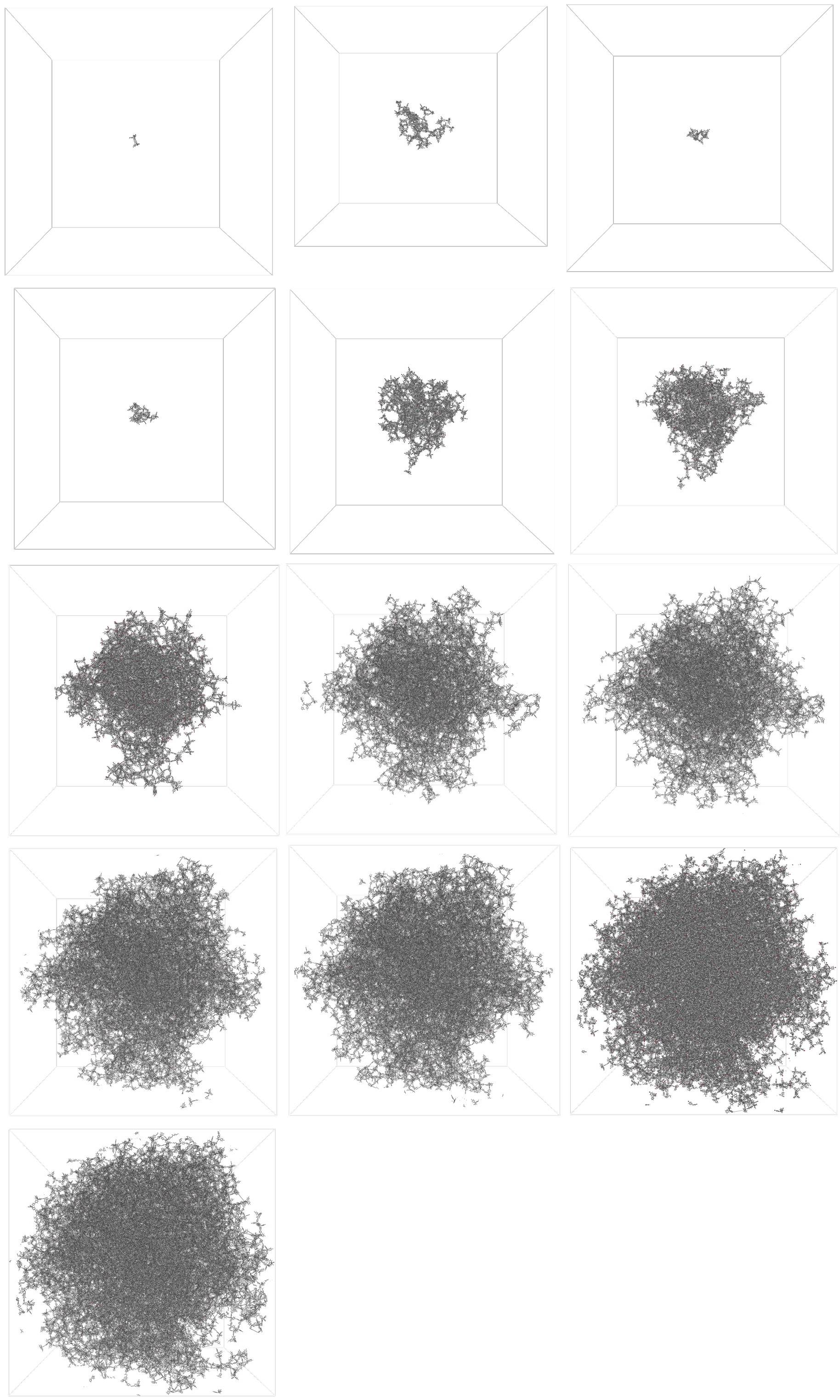


Fig. S7. Snap shots of the resulting cluster structure for Model-22 during the cluster generation process.

8. Small Cluster generation

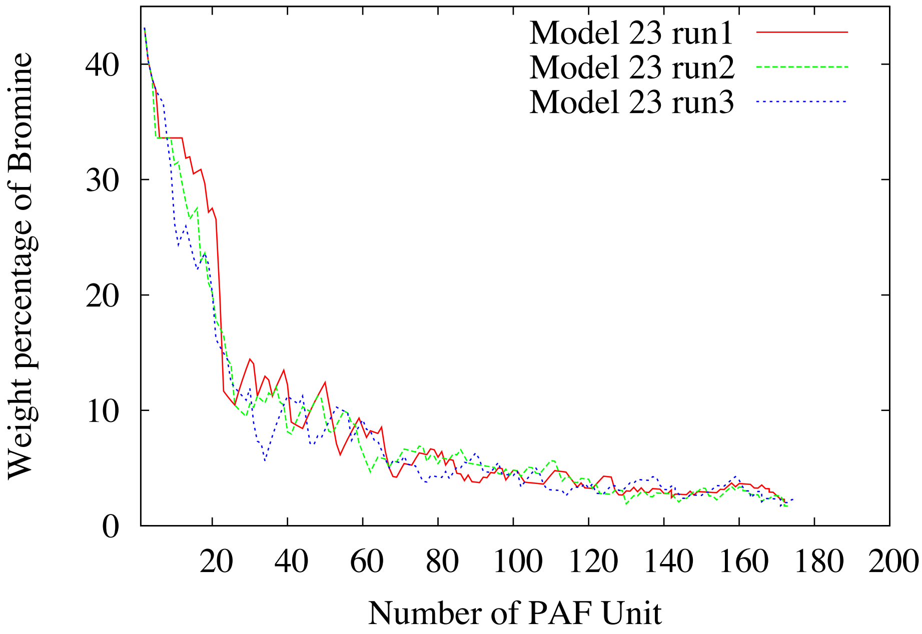


Fig. S8. Weight percentage of Br as a function of the number of PAF build units for Model-23, generated with DMF solvent and end group distance of 10 Å.

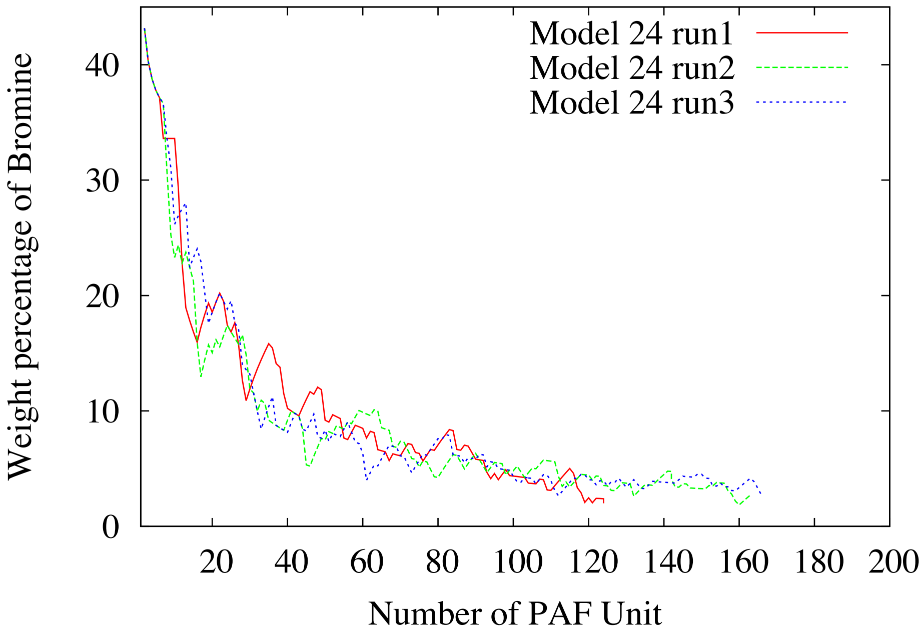


Fig. S9. Weight percentage of Br as a function of the number of PAF build units for Model-24, generated with no DMF solvent and end group distance of 10 Å.

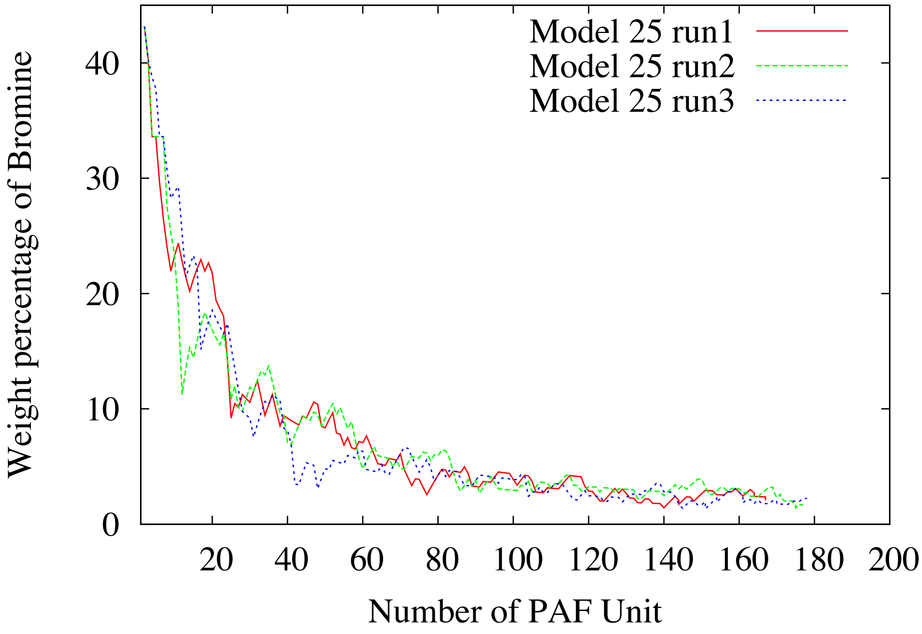


Fig. S10. Weight percentage of Br as a function of the number of PAF build units for Model-25, generated with DMF solvent and end group distance of 12 Å.

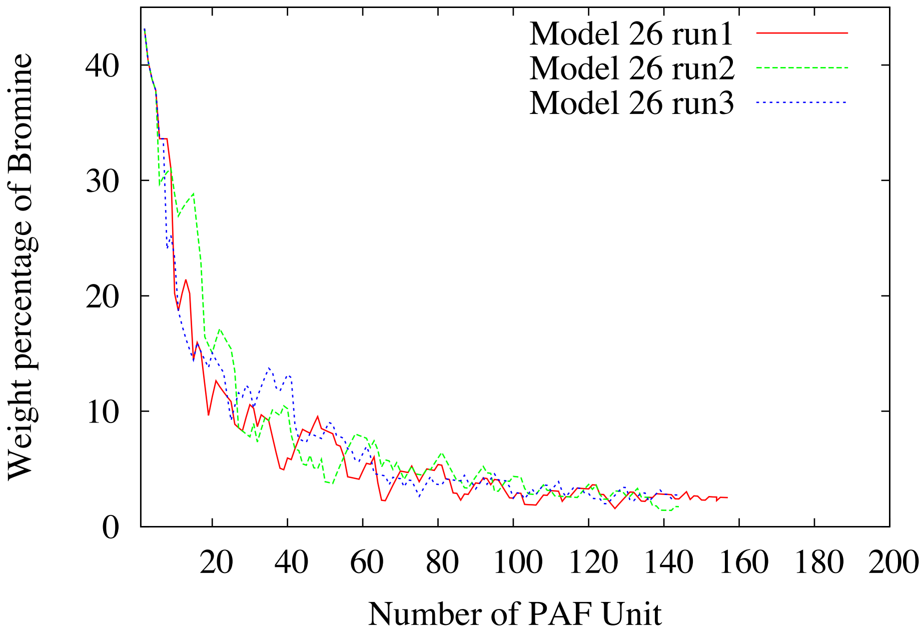


Fig. S11. Weight percentage of Br as a function of the number of PAF build units for Model-26, generated with no DMF solvent and end group distance of 12 Å.

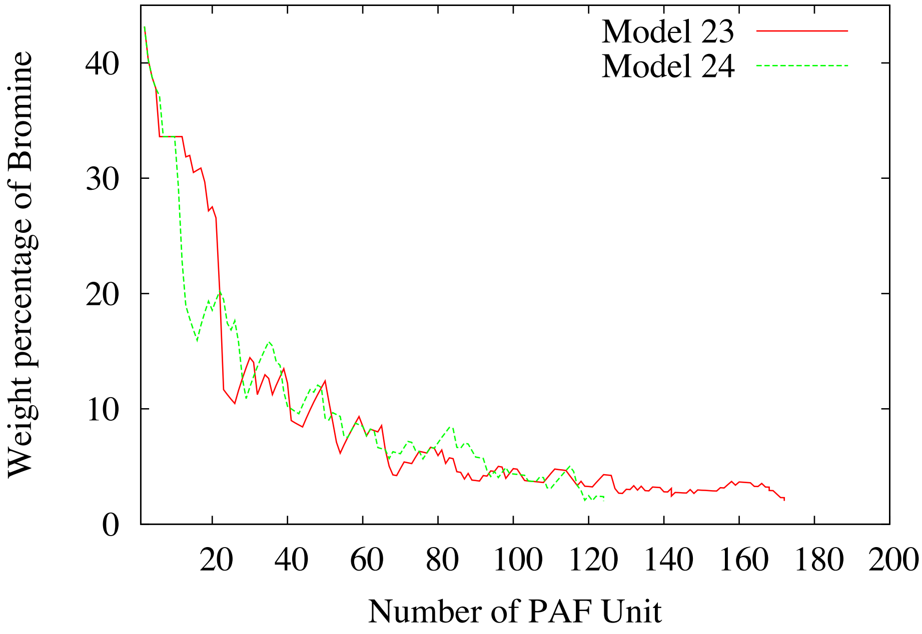


Fig. S12. Weight percentage of Br as a function of the number of PAF build units for Model-23 (with DMF solvent) and -24 (No solvent).

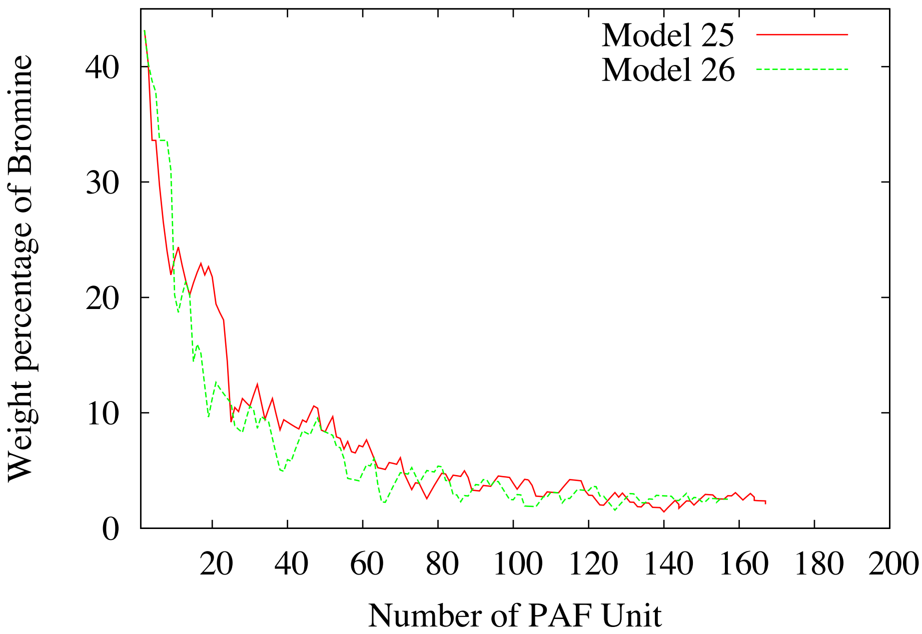


Fig. S13. Weight percentage of Br as a function of the number of PAF build units for Model-25 (with DMF solvent) and -26 (No solvent).

9. Cluster cell size

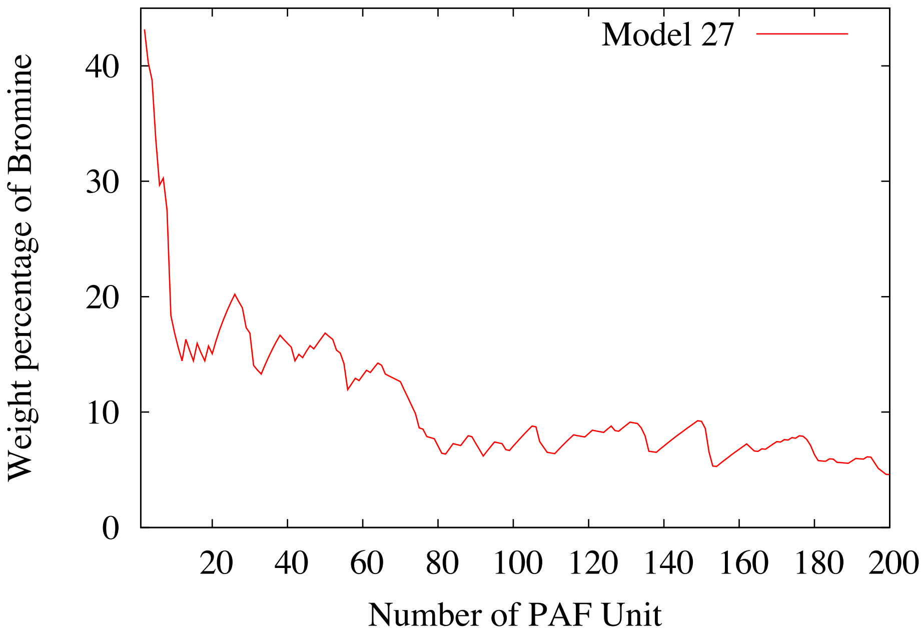


Fig. S14. Weight percentage of Br as a function of the number of PAF build units for Model-27 (cell size of 75 Å)

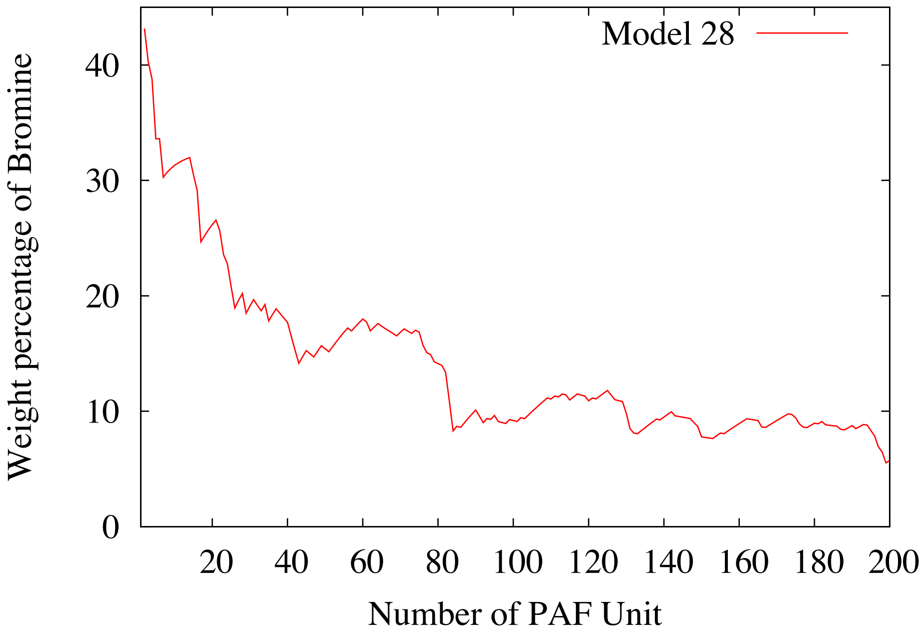


Fig. S15. Weight percentage of Br as a function of the number of PAF build units for Model-28 (cell size of 100 Å)

10. Multiple Cluster Seed

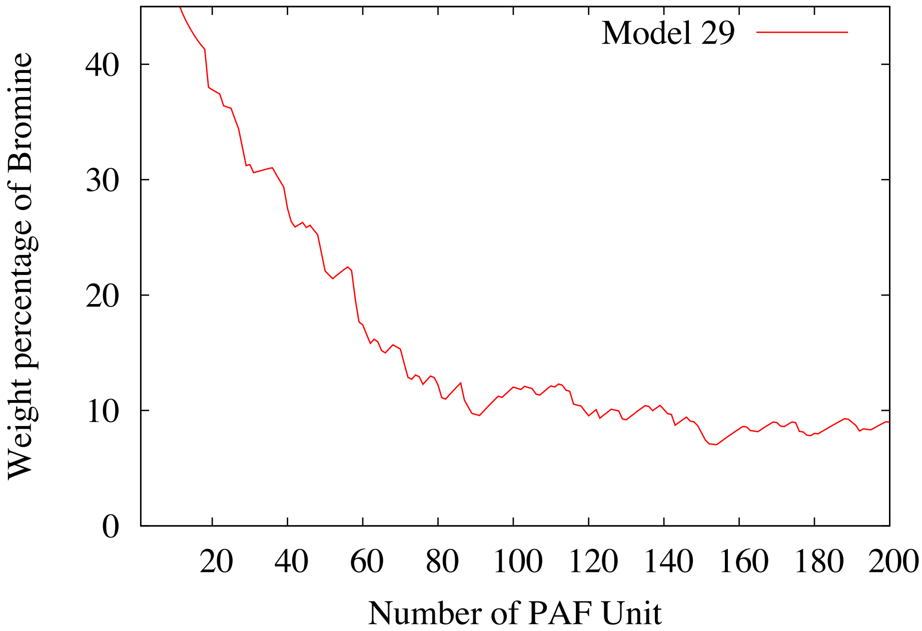


Fig. S14. Weight percentage of Br as a function of the number of PAF build units for Model-29 (cell size of 100 Å with multiple (10) initial seeds of PAF build units)