Supporting Information

Atomistic simulations of the aggregation of small aromatic molecules in homogenous and heterogenous mixtures

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System	Temperature (K)	Number of Clusters	Average Cluster Size	Max Cluster Size
60 Benzene, 0 Naphthalene, 0 Anthracene	100	7.4	8.3	15.6
	200	3.4	15.9	27.2
	300	4.2	2.2	2.6
	400	2.6	2.0	2.2
	500	2.2	2.4	2.4
0 Benzene, 40 Naphthalene, 0 Anthracene	100	7.2	5.5	11.4
	200	4.8	8.6	12.4
	300	4.0	6.5	14.0
	400	3.6	2.1	2.4
	500	2.0	1.7	1.8
0 Benzene, 0 Naphthalene, 30 Anthracene	100	6.2	4.7	9.2
	200	5.4	5.8	9.4
	300	3.8	7.9	13.0
	400	3.2	5.8	11.2
	500	2.8	2.5	3.2
30 Benzene, 20 Naphthalene, 0 Anthracene	100	8.2	6.3	12.2
	200	5.0	9.6	18.6
	300	4.2	3.6	7.2
	400	2.2	2.3	2.8
	500	2.4	2.1	2.2
30 Benzene, 0 Naphthalene, 15 Anthracene	100	7.8	6.0	11.2
	200	4.6	9.6	14.8
	300	3.4	5.8	9.0
	400	3.4	2.4	3.0
	500	2.6	1.6	1.6
0 Benzene, 20 Naphthalene, 15 Anthracene	100	7.2	4.8	9.0
	200	5.0	7.6	15.2
	300	3.4	8.8	13.0
	400	2.8	4.4	7.6
	500	1.8	2.3	2.6
20 Benzene, 13 Naphthalene, 10 Anthracene	100	7.0	6.1	13.8
	200	4.4	9.7	13.4
	300	4.2	5.6	11.4
	400	2.8	2.5	3.2
	500	2.4	1.7	1.8

Table S1: The averages values over five replicates of number of clusters, average cluster size and maximum cluster size for each system and temperature at the end of the 10 ns simulations.

Table S2: The simulation time of each replicate of each system at 200K. Time is in nanoseconds.

System	Replicate	Time (ns)
60 Benzene, 0 Naphthalene, 0 Anthracene	1	201
	2	138
	3	139
	4	138
	5	137
0 Benzene, 40 Naphthalene, 0 Anthracene	1	179
	2	174
	3	108
	4	109
	5	314
0 Benzene, 0 Naphthalene, 30 Anthracene	1	109
	2	110
	3	170
	4	107
	5	245
30 Benzene, 20 Naphthalene, 0 Anthracene	1	200
	2	170
	3	234
	4	173
	5	169
30 Benzene, 0 Naphthalene, 15 Anthracene	1	140
	2	208
	3	170
	4	135
	5	135
0 Benzene, 20 Naphthalene, 15 Anthracene	1	251
	2	225
	3	141
	4	139
	5	140
20 Benzene, 13 Naphthalene, 10 Anthracene	1	154
	2	118
	3	152
	4	163
	5	231

Benzene: 60, Naphthalene: 0, Anthracene: 0

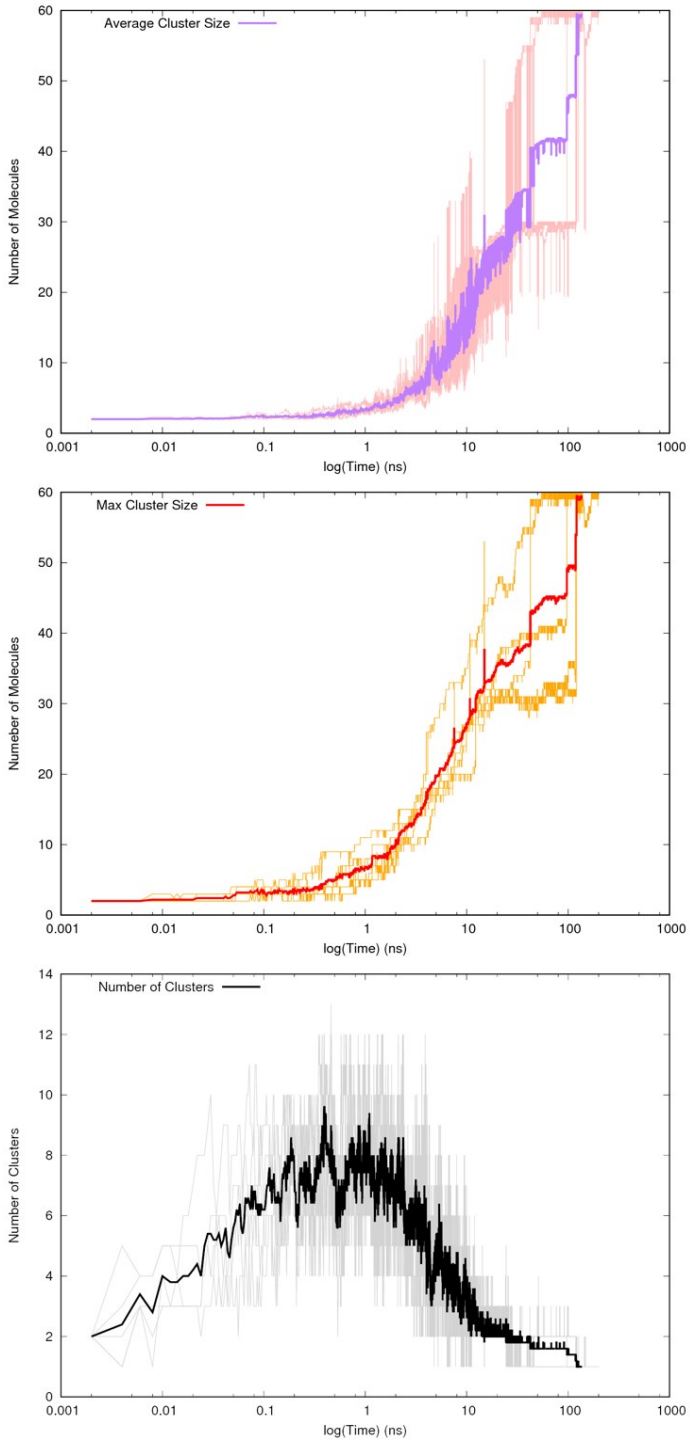

Figure S1: Variation across the five replicates for the system consisting of 60 benzene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

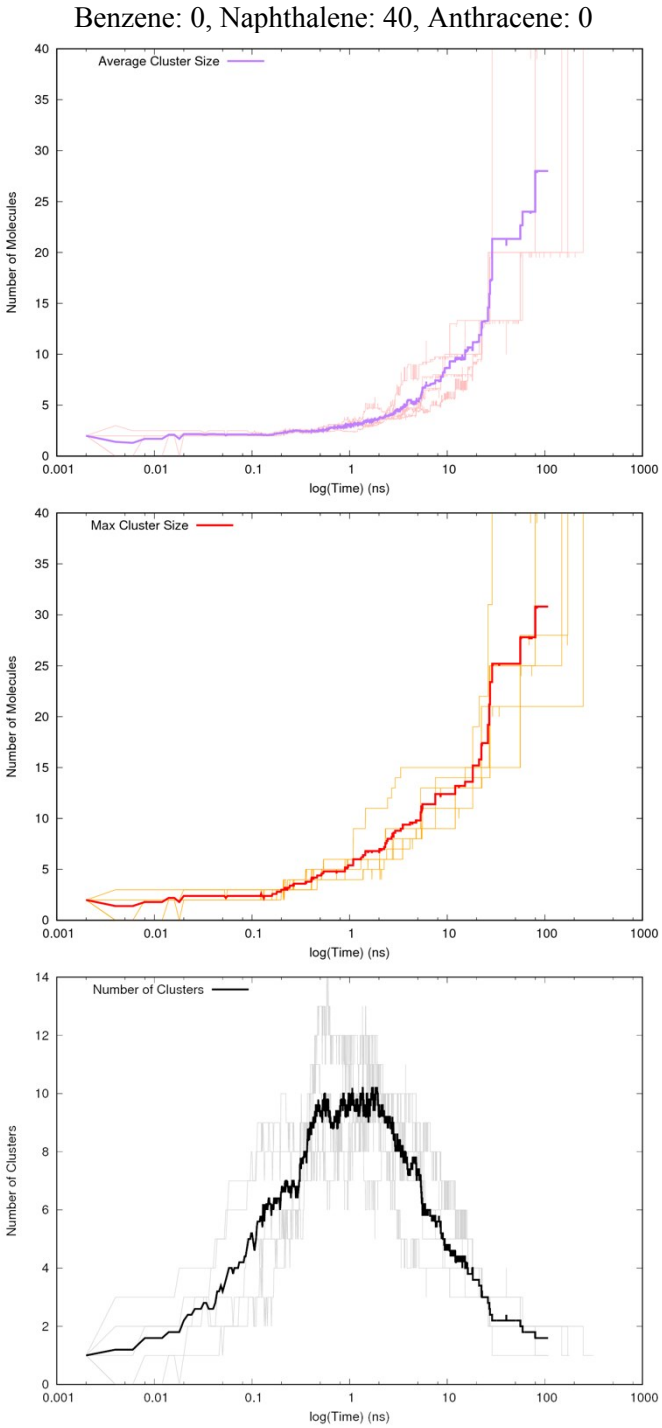

Figure S2: Variation across the five replicates for the system consisting of 40 naphthalene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

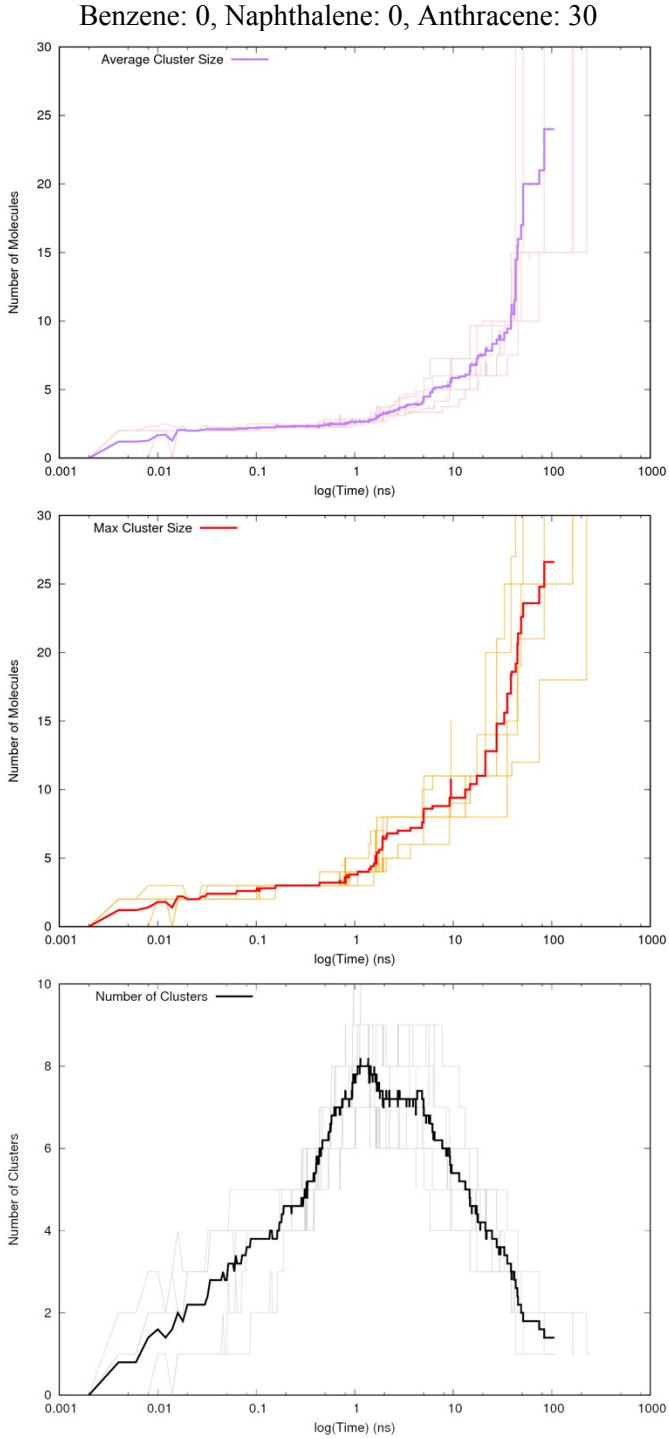

Figure S3: Variation across the five replicates for the system consisting of 30 anthracene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

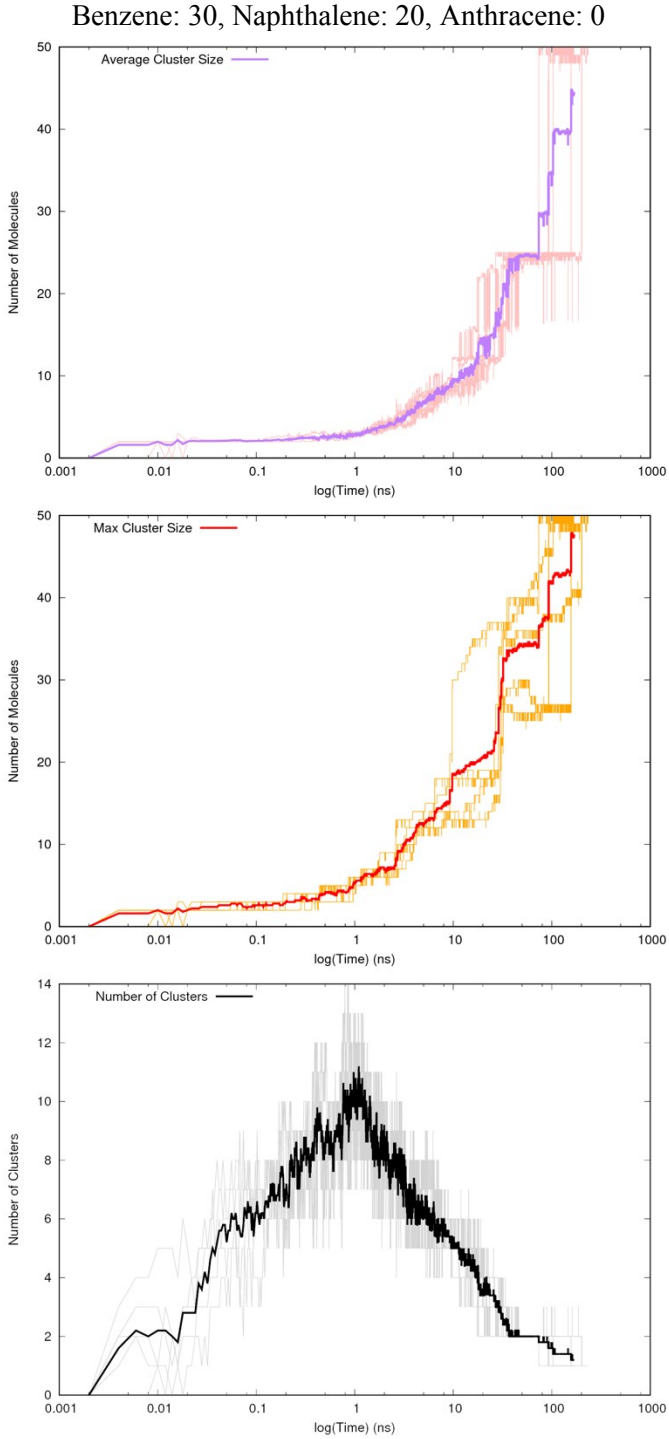

Figure S4: Variation across the five replicates for the system consisting of 30 benzene and 20 naphthalene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

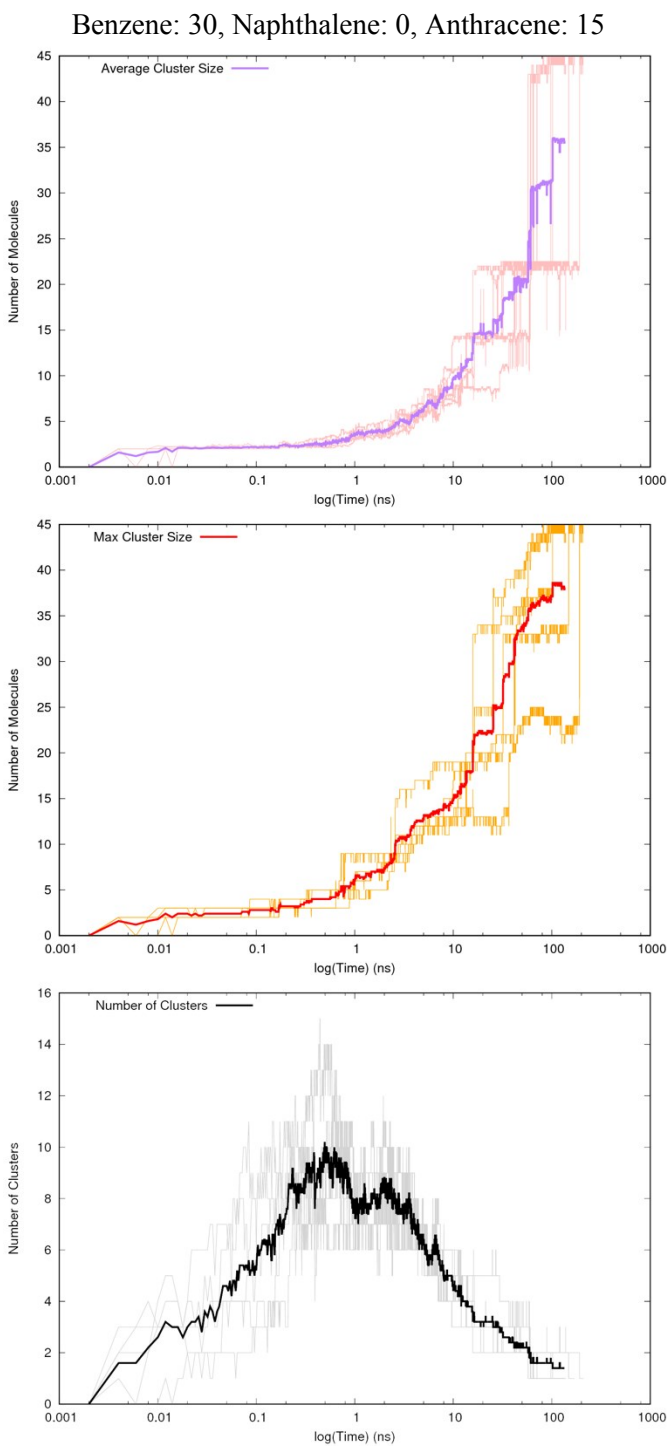

Figure S5: Variation across the five replicates for the system consisting of 30 benzene and 15 anthracene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

Benzene: 0, Naphthalene: 20, Anthracene: 15

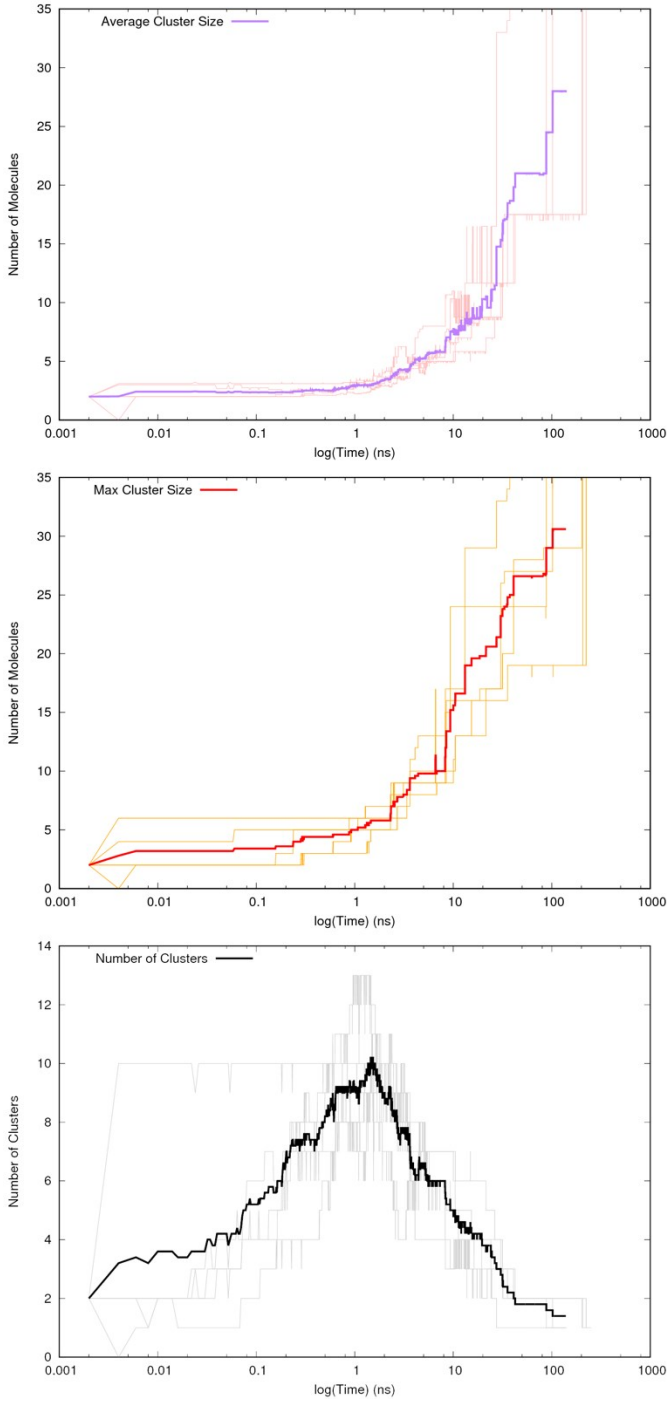

Figure S6: Variation across the five replicates for the system consisting of 20 naphthalene and 15 anthracene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

Benzene: 20, Naphthalene: 13, Anthracene: 10

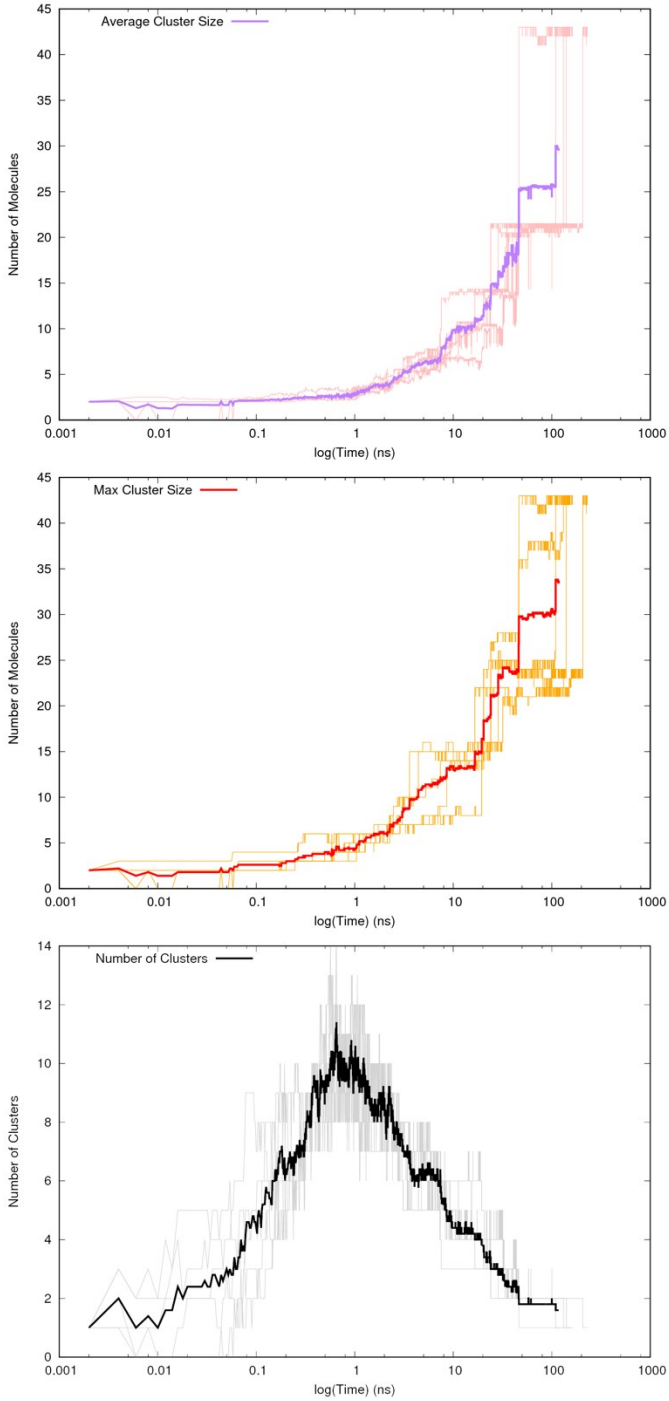

Figure S7: Variation across the five replicates for the system consisting of 20 benzene, 13 naphthalene and 10 anthracene molecules. (Top) The average cluster size in each replicate (pink lines), and the average across all replicates of the average cluster size (purple line). (Middle) The maximum cluster size in each replicate (orange lines), and the average across all replicates of the maximum cluster size (red line). (Bottom) The number of clusters in each replicate (grey lines), and the average across all replicates of the number of clusters (black line).

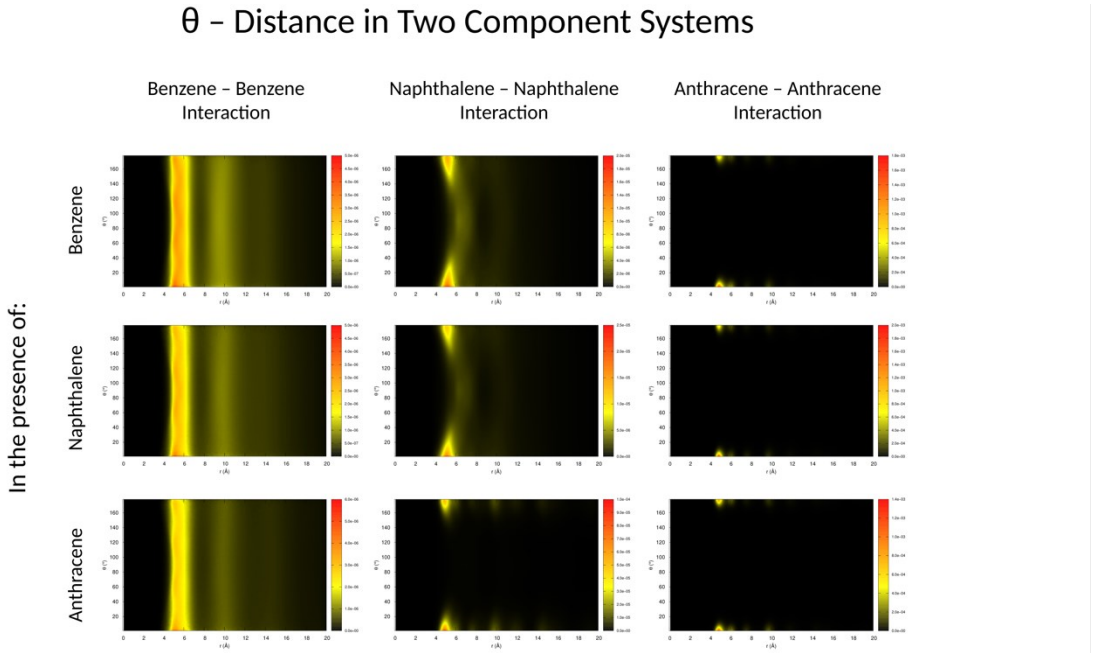

Figure S8: Structural analysis of the orientation of molecules within a cluster for heterogenous systems as defined by θ angle as a function of distance, r. Benzene-benzene, naphthalene-naphthalene and anthracene-anthracene interactions described in the presence of a) benzene, b) naphthalene and c) anthracene interactions

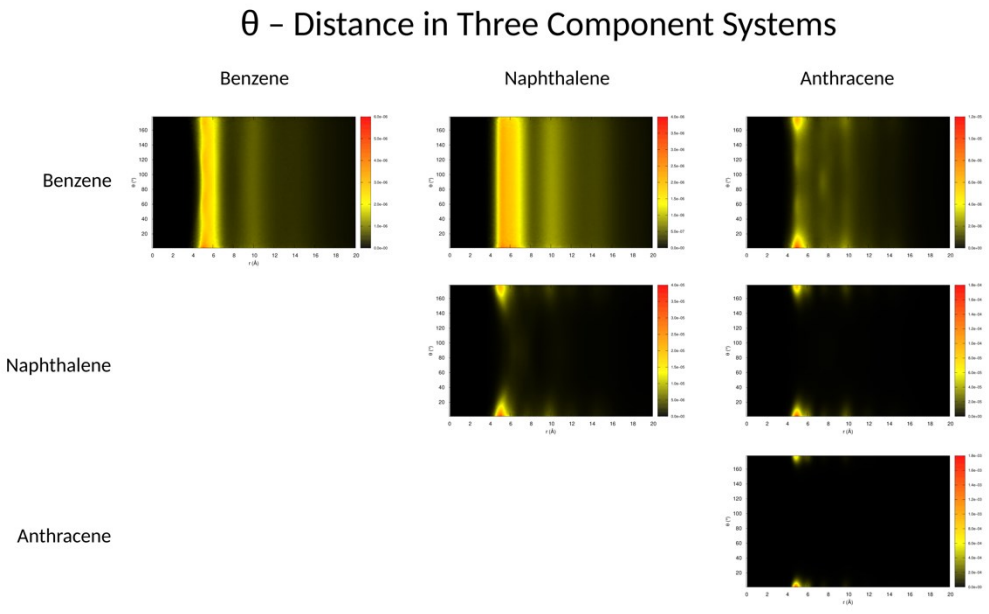

Figure S9: Structural analysis of the orientation of molecules within a cluster for heterogenous systems as defined by θ angle as a function of distance, r, for benzene-naphthalene, benzene-anthracene and naphthalene-anthracene interactions. The colours provide a measure of the number of molecules observed in the various configurations, with black indicating none and red indicating many interactions at that configuration with graduations from yellow to orange

Table S3. Interaction energies (ΔE, PWPB95-D3BJ/QZVPP//M06L/6-31G(2df,p), in kJ mol^{-1}) for the T- shaped and parallel-displaced (PD) structures at equilibrium distances (R, in Å) for the dimers and trimers shown in Figure 8.

Species	T-shaped		PD-Fixed[b]		PD-Opt[c]	
	ΔE	R[h]	ΔE	R_1[i]	ΔE	R_1
C_6H_6 ••• C_6H_6	11.0,[a] 11.3,[d] 10.2[e]	2.56	11.9,[a] 11.7,[d] 8.9,[e] 11.1[f]	3.620	11.4	3.450
$C_{10}H_8$ ••• C_6H_6	13.1[a], 11.2[g]	2.52	19.3,[a] 16.5[g]	3.610	20.4	3.425
$C_{14}H_{10}$ ••• C_6H_6	16.7	2.49	23.9	3.370	25.1	3.408
C_6H_6 ••• C_6H_6••• C_6H_6	21.7	2.56	24.5	3.620	N/A	
C_6H_6 ••• $C_{10}H_8$ ••• C_6H_6	26.5	2.52	39.7	3.540	N/A	
C_6H_6 ••• $C_{14}H_{10}$ ••• C_6H_6	32.2	2.50	48.9	3.380	N/A	
$C_{10}H_8$ ••• $C_{10}H_8$	20.6	2.55	27.8	3.470	N/A	
$C_{14}H_{10}$ ••• $C_{10}H_8$	23.4	2.52	34.5	3.370	N/A	

[a]This work.
[b]Using the optimized geometries of the monomers (C_6H_6, $C_{10}H_8$, and $C_{14}H_{10}$) at M06L/6-31G(2df,p) level of theory.
[c]Fully optimized dimers(C_6H_6•••C_6H_6, C_6H_6•••$C_{10}H_8$, and C_6H_6•••$C_{14}H_{10}$) at M06L/6-31G(2df,p) level of theory.
[d]Calculated the estimated CBS binding energies at MP2-R12/A+ΔCCSD(T)/aug-cc-pVDZ level of theory, see Ref. 1.
[e]Calculated the approximated CBS binding energies at MP2/aug-cc-pV{T,Q}Z + ΔCCSD/aug-cc-pVTZ level of theory, see Ref. 2.
[f]Calculated at the CCSD(T)/cc-pV{Q,5}Z level of theory, see Ref. 3.
[g]Calculated at the MP2/6-31+G* level of theory, see Ref. 4.
[h]C–H to ring centre distance R for T-shaped dimers and trimers.
[i]Ring-to-ring vertical distance R_1 and ring centre to ring centre distance R_2 for PD dimers and trimers.

References

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