Supporting Information for

Molecular Self-Assembly of Substituted Terephthalic Acids at the Liquid/Solid Interface: Investigating the Effect of Solvent

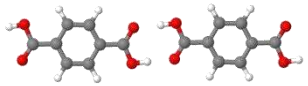
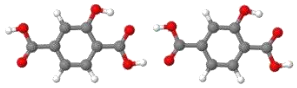
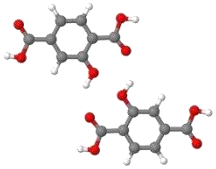
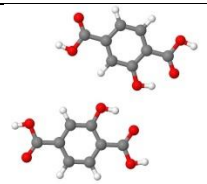
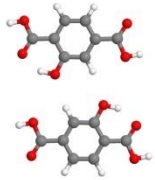
A. Della Pia,[a] D. Luo,[a] R. Blackwell,[b] G. Costantini*[a] and N. Martsinovich*[b]

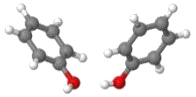
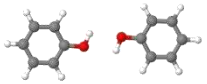
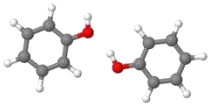
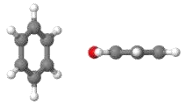
[a] *Department of Chemistry, University of Warwick, Coventry, UK.*

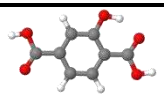
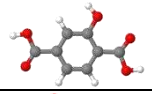
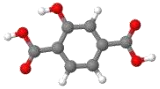
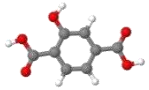
[b] *Department of Chemistry, University of Sheffield, Sheffield, UK.*

Section S1. Comparison of structures and energies calculated using molecular mechanic and quantum mechanics

Table S1. Hydrogen-bonded structures, hydrogen bond distances, interaction energies and isomers' relative energies, calculated using molecular mechanics (MM) (MM3 with fitted hydrogen bond parameters, see main text section 2.2 and Table 2) and quantum mechanics (QM) (MP2 method).

Molecule	Structure (QM)	Interaction	Atom types involved in interaction	Hydrogen bond distances, Å		Energies, kcal mol^{-1}			
				MM	QM (MP2, DZVP basis set)	MM	QM (MP2, DZVP basis set)	QM (MP2, TZVP basis set)	Difference (MM)-(MP2, DZVP)
						Dimer interaction energies			
TPA dimer		COOH...COOH	24-77	1.96	1.76	-15.93	-16.44	-	0.51
2HTPA dimer 1		COOH...COOH	24-77, 73-77	1.96	1.66, 1.72	-16.06	-15.70	-14.74	-0.35
2HTPA dimer 2		2 =O...HO(Ph)	73-77	1.80	2.36	6.40	12.75	-	-6.35
2HTPA dimer 3		1 OH…OH(Ph), 1 CH…OH(Ph)	73-6, 5-6	2.36 (OH…OH), 2.64 (CH…OH)	2.38 (OH…OH), 2.52 (CH…OH)	-3.35	-2.31	-	-1.04
2HTPA dimer 4		2 CH…OH(Ph)	5-6	2.46	2.42	-3.01	-2.47	-	-0.53

Phenol dimer 1 (non-planar)		1 OH…OH	73-6	2.24	2.00	-5.95	-5.44	-	-0.51
Phenol dimer 2		2 OH…OH	73-6	2.45	2.33	-3.14	-3.48	-3.89	0.34
Phenol dimer 3		1 OH…OH, 1 OH…CH	73-6, 5-6	2.24 (OH…OH), 2.66 (CH…OH)	2.00 (OH…OH), 2.72 (CH…OH)	-5.07	-4.76	-5.33	-0.30
Phenol-benzene dimer (non-planar)		2 CH…OH bifurcated	5-6	2.78	2.88	-1.95	-1.70	-	-0.25

								Relative energies of 2HTPA isomers	
2HTPA isomer 1 (OH in)		=O...HO(Ph) intramolecular	73-77	1.72	1.74	0.00	0.00	0.00	
2HTPA isomer 2 (OH out)		=O...O(Ph) repulsion	-	O...O = 2.51	O...O = 2.69	6.77	10.41	10.44	-3.63
2HTPA isomer 3 (OH in)		(H)O...HO(Ph) intramolecular	73-75	1.83	1.80	2.38	3.48	3.88	-1.10
2HTPA isomer 4 (OH out)		(H)O...O(Ph) repulsion	-	O...O = 2.53	O...O = 2.60	6.66	9.66	9.75	-3.00

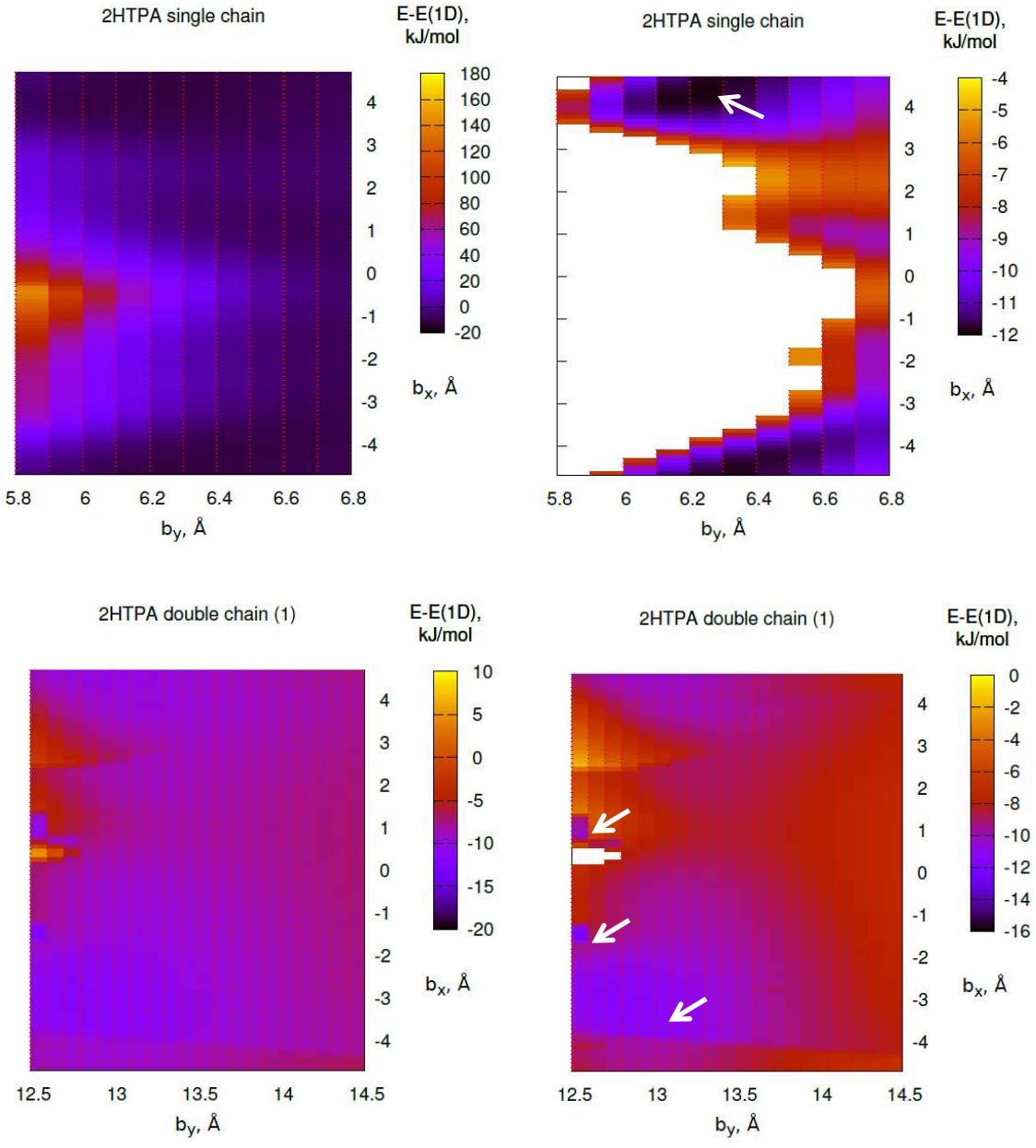
The table shows very good agreement between MP2 and fitted MM3 results, both in energies (differences between the two methods are mostly below 1.1 kcal mol^{-1} = 4.6 kJ mol^{-1}) and in hydrogen bond distances (differences mostly below 0.25 Å). The only exceptions (highlighted in red in the table) are related to the =O...HO(Ph) and (H)O...HO(Ph) hydrogen bonds (interaction between atom types 73-77 and 73-75): 2HTPA isomers 1 and 3 are particularly stable, according to MP2 calculations, thanks to the formation of 6-membered rings involving an intramolecular hydrogen bond. To reproduce these energies in MM, very large energy parameters for these hydrogen bonds would be needed, which would also artificially stabilise 2HTPA dimer 2 (containing *inter*molecular interaction 73-77). Therefore, the values of the MM3 energy and distance parameters for the interaction 73-77 were chosen to be the same as for the interaction 24-77 (=O...HO in carboxylic groups, which involves chemically similar atoms). The parameters for the interaction 73-75 were then fitted to reproduce the difference between 2HTPA isomers 1 and 3.

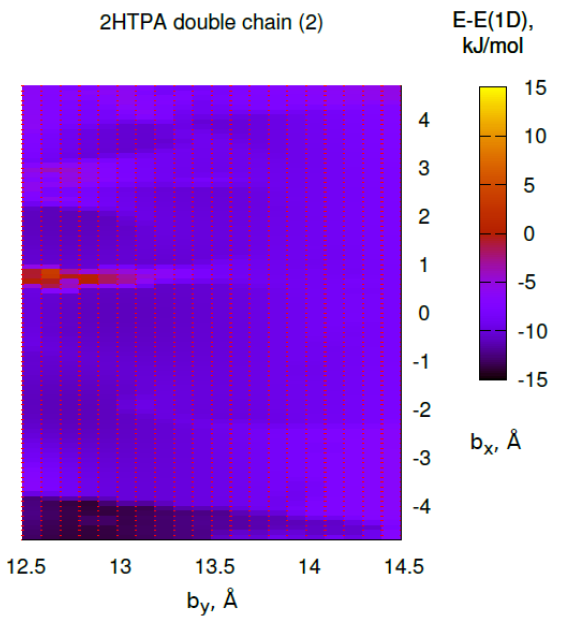
Section S2. Potential energy surfaces for 2D monolayers of 2HTPA and 25DHTPA

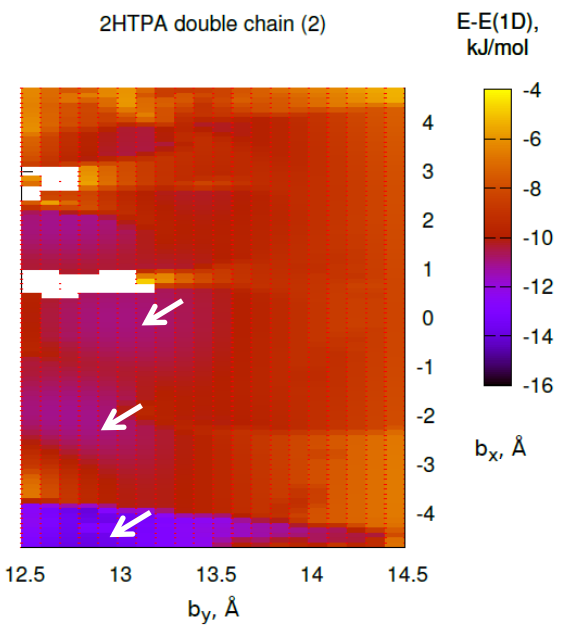
The potential energy surfaces, shown in the figures below, are obtained by simultaneously varying the values of the parameters b_x (shift of the chains relative to each other) and b_y (perpendicular distance between the chains), as described in Section 2.2 of the main text, for either single or double chain 2HTPA and 25DHTPA arrangements.

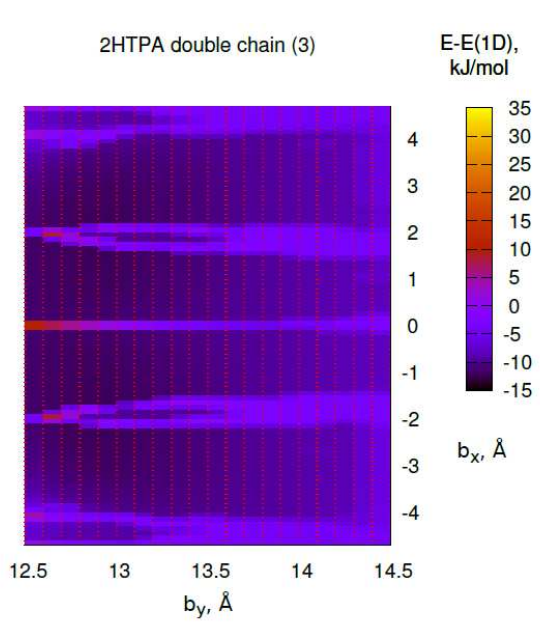
Regions with strong binding (i.e. large negative energies) are shown as dark blue, while regions with repulsion (positive energies) or weak binding (small negative energies) as yellow and red. Figures on the left show full images of the PES, while figures on the right show only the low-energy, binding regions (here repulsive high-energy regions are shown as white).

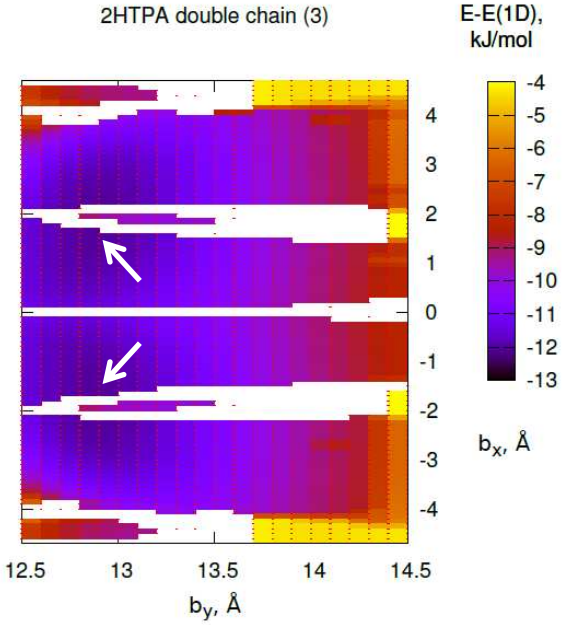
2HTPA and 25DHTPA single chain structures shows clear single minima; while all double chain structures shows multiple minima (marked by arrows).

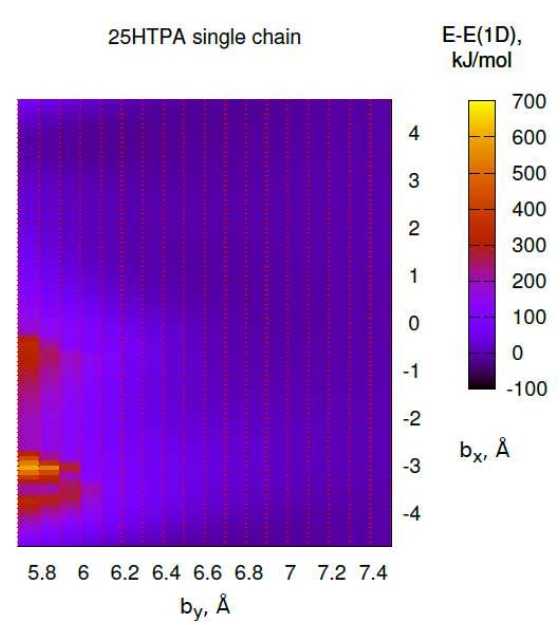


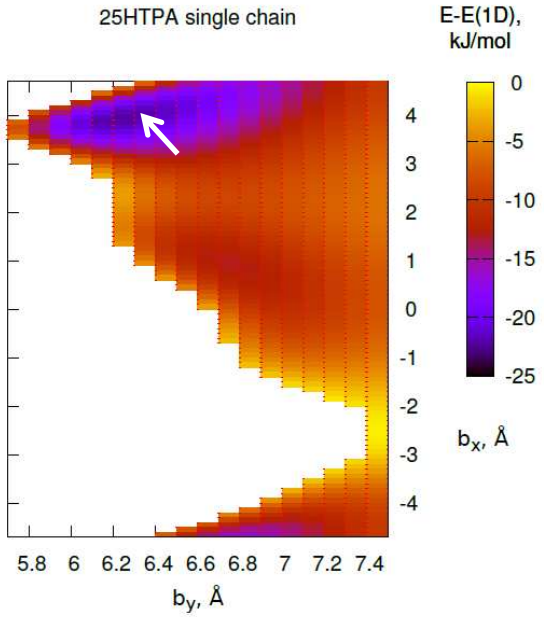

2HTPA double chain (2)
E-E(1D), kJ/mol
15
10
5
0
-5
-10
-15
4
3
2
1
0
-1
-2
-3
-4
12.5
13
13.5
14
14.5
by, Å
bx, Å

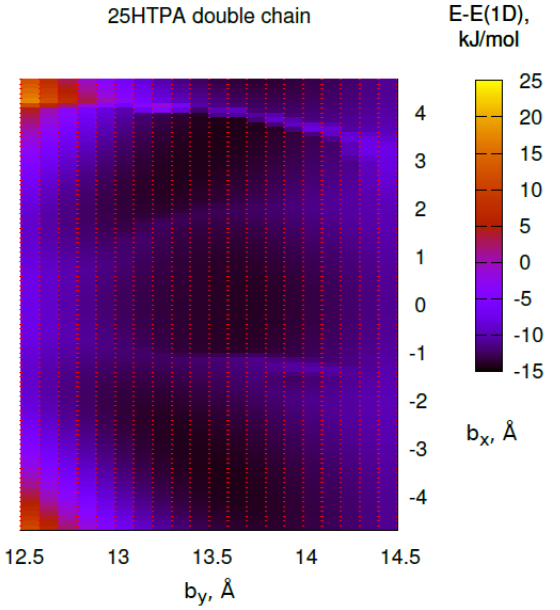

2HTPA double chain (2)
E-E(1D), kJ/mol
-4
-6
-8
-10
-12
-14
-16
4
3
2
1
0
-1
-2
-3
-4
12.5
13
13.5
14
14.5
by, Å
bx, Å

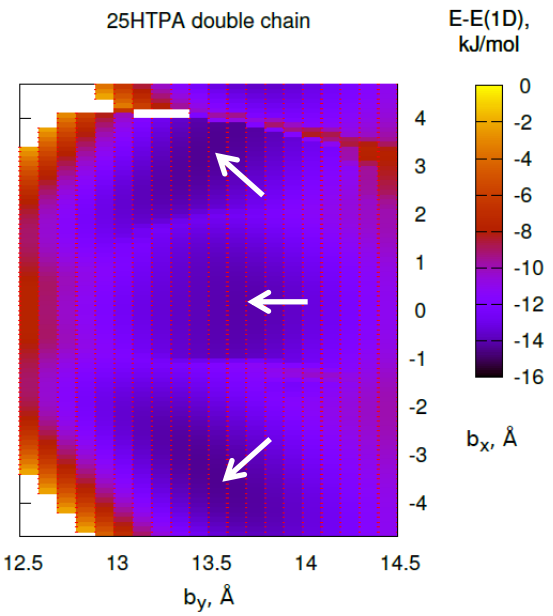

2HTPA double chain (3)
E-E(1D), kJ/mol
35
30
25
20
15
10
5
0
-5
-10
-15
4
3
2
1
0
-1
-2
-3
-4
12.5
13
13.5
14
14.5
by, Å
bx, Å


2HTPA double chain (3)
E-E(1D), kJ/mol
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
4
3
2
1
0
-1
-2
-3
-4
12.5
13
13.5
14
14.5
by, Å
bx, Å


25HTPA single chain
E-E(1D), kJ/mol
700
600
500
400
300
200
100
0
-100
4
3
2
1
0
-1
-2
-3
-4
5.8 6 6.2 6.4 6.6 6.8 7 7.2 7.4
b_y, Å
b_x, Å


25HTPA single chain
E-E(1D), kJ/mol
0
-5
-10
-15
-20
-25
4
3
2
1
0
-1
-2
-3
-4
5.8 6 6.2 6.4 6.6 6.8 7 7.2 7.4
b_y, Å
b_x, Å


25HTPA double chain
E-E(1D), kJ/mol
25
20
15
10
5
0
-5
-10
-15
4
3
2
1
0
-1
-2
-3
-4
12.5 13 13.5 14 14.5
b_y, Å
b_x, Å


25HTPA double chain
E-E(1D), kJ/mol
0
-2
-4
-6
-8
-10
-12
-14
-16
4
3
2
1
0
-1
-2
-3
-4
12.5 13 13.5 14 14.5
b_y, Å
b_x, Å