Supporting information for:

Insight into the self-assembly of water-soluble perylene bisimide derivatives through a combined computational and experimental approach

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Table S1 *Twist angle (TA), slide angle (SA) and centroid distance (R, in Å) ranges for the different aggregates optimised using PBEh-3c.*

		TA	SA	R
I	2	34°	90°	3.39
	3	32-36°	90°	3.27-3.47
	4	32-36°	90°	3.22-3.47
II	2	49°	72-73°	3.20
	3	48°	71-73°	3.26-3.31
	4	48-49°	71-74°	3.31-3.35
III	2	47°	69°	3.31
	3	47-48°	68-69°/77-78°	3.22-3.38
IV	2	52°	71-73°	3.03
V	2	50°	69°	3.21

Table S2 *PBEh-3c Total energies (U) and the combined vibrational, rotational and translational contribution to the free energies (G_{trv}) as calculated with the RRHO and q-RRHO approximation for PBI-A and class **I-III** aggregates. All values in eV.*

		U	G_{vrt}	
			RRHO	q-RRHO
PBI-A	1	-50656.204936	10.7920	10.8551
I	2	-101313.308695	22.1085	22.3185
	3	-151970.362215	33.5140	33.8797
	4	-202627.390958		
II	2	-101313.341804	22.0577	22.2947
	3	-151970.495910	33.3136	33.7875
	4	-202627.656129		
III	2	-101313.286751	22.0302	22.2824
	3	-151970.391919	33.3269	33.7836
	4	-202627.501794		

Table S3 *PBEh-3c Total energies (U) and the combined vibrational, rotational and translational contribution to the free energies (G_{trv}) as calculated with the RRHO and q-RRHO approximation for doubly-deprotonated PBI-A and class **IV-V** aggregates. All values in eV.*

		U	G_{vrt}	
			RRHO	q-RRHO
PBI-A	1	-50630.650373	10.0922	10.1596
IV	2	-101262.121476	20.6448	20.8828
	3	-151893.468827	31.1819	31.6511
V	2	-101262.160961	20.6134	20.8687
	3	-151893.450194	31.1755	31.6392

Table S4 *B97-3c Total energies (U) and the combined vibrational, rotational and translational contribution to the free energies (G_{trv}) as calculated with the RRHO and q-RRHO approximation for PBI-A and class* ***I-III*** *aggregates. All values in eV.*

		U	G_{vrt}	
			RRHO	q-RRHO
PBI-A	1	-50740.716812	9.8996	10.0133
I	2	-101482.574120	20.4581	20.7379
	3	-152224.418722		
	4	-202966.246776		
II	2	-101482.477680	20.3830	20.7124
	3	-152224.293111		
	4	-202966.094526		
III	2	-101482.434746	20.3452	20.6867
	3	-152224.200039		
	4	-202627.501794		

Table S5 *B97-3c Total energies (U) and the combined vibrational, rotational and translational contribution to the free energies (G_{trv}) as calculated with the RRHO and q-RRHO approximation for doubly-deprotonated PBI-A and class* ***IV-V*** *aggregates. All values in eV.*

		U	G_{vrt}	
			RRHO	q-RRHO
PBI-A	1	-50715.307837	9.2499	9.3527
IV	2	-101431.501151	19.0338	19.3583
	3	-152147.592910		
V	2	-101431.492677	19.0154	19.3389
	3			

Table S6 *PBEh-3c Free energy values in the gas phase (G_{gas}, 1 bar) and solution ($G_{solution}$, 1 mol/L) as calculated with the RRHO and q-RRHO approximation for PBI-A and class* ***I-III*** *aggregates. All values in eV.*

		G_{gas}		$G_{solution}$	
		RRHO	q-RRHO	RRHO	q-RRHO
PBI-A	1	-50645.412896	-50645.349777	-50645.330451	-50645.267333
I	2	-101291.200181	-101290.990097	-101291.117737	-101290.907652
	3	-151936.848197	-151936.482441	-151936.765753	-151936.399996
II	2	-101291.284075	-101291.047147	-101291.201630	-101290.964702
	3	-151937.182338	-151936.708378	-151937.099893	-151936.625934
III	2	-101291.256591	-101291.004324	-101291.174146	-101290.921879
	3	-151937.064977	-151936.608325	-151936.982532	-151936.525881

Table S7 *PBEh-3c Free energy values in the gas phase (G_{gas}, 1 bar) and solution ($G_{solution}$, 1 mol/L) as calculated with the RRHO and q-RRHO approximation for doubly-deprotonated PBI-A and class **IV-V** aggregates. All values in eV.*

		G_{gas}		$G_{solution}$	
		RRHO	q-RRHO	RRHO	q-RRHO
PBI-A	1	-50620.558130	-50620.490783	-50620.475686	-50620.408339
IV	2	-101241.476712	-101241.238644	-101241.394268	-101241.156200
	3	-151862.286882	-151861.817690	-151862.204438	-151861.735246
V	2	-101241.547602	-101241.292225	-101241.465157	-101241.209781
	3	-151862.274674	-151861.810975	-151862.192230	-151861.728531

Table S8 *B97-3c Free energy values in the gas phase (G_{gas}, 1 bar) and solution ($G_{solution}$, 1 mol/L) as calculated with the RRHO and q-RRHO approximation for PBI-A and class **I-III** aggregates. All values in eV.*

		G_{gas}		$G_{solution}$	
		RRHO	q-RRHO	RRHO	q-RRHO
PBI-A	1	-50730.817242	-50730.703473	-50730.734798	-50730.621029
I	2	-101462.116017	-101461.836181	-101462.033573	-101461.753737
II	2	-101462.094719	-101461.765237	-101462.012274	-101461.682793
III	2	-101462.089511	-101461.748007	-101462.007066	-101461.665563

Table S9 *B97-3c Free energy values in the gas phase (G_{gas}, 1 bar) and solution ($G_{solution}$, 1 mol/L) as calculated with the RRHO and q-RRHO approximation for doubly-deprotonated PBI-A and class **IV-V** aggregates. All values in eV.*

		G_{gas}		$G_{solution}$	
		RRHO	q-RRHO	RRHO	q-RRHO
PBI-A	1	-50706.057902	-50705.955088	-50705.975457	-50705.872644
IV	2	-101412.467311	-101412.142805	-101412.384867	-101412.060360
V	2	-101412.477286	-101412.153816	-101412.394841	-101412.071371

Table S10 *Free (energy) binding energy, step-wise equilibrium constants, number average aggregate size (N) and degree of aggregation values (α_{agg}) of a class I dimer with four explicit water molecules hydrogen-bonded to the carboxylic OH groups (2 water molecules as hydrogen-bond donors and two as hydrogen-bond acceptors), as calculated using PBEh-3c. All (free) energies in kJ/mol.*

	$\Delta U_{b,norm}$	$\Delta G_{b,norm}$	β_n	**N**	α_{agg}
Class **I** dimer	-89	-31	2.6×10^5	49	0.9996

Table S11 *Energy difference between the class I and class II dimer calculated using alternative methods than PBEh-3c and B97-3c. All values in kJ/mol.*

MP2	MP2/SCS	MP2/SOS	ωB97XD	RPA
-18	-10	-6	-20	+4

Table S12 *Neutron small angle scattering fit parameters for fits to first and last data sets.*

	First Data Set	**Last Data Set**
Background (cm^{-1})	$0.011 \pm 5.66 \times 10^{-5}$	$0.0095 \pm 8.22 \times 10^{-5}$
Scale	$1.07 \times 10^{-6} \pm 1.63 \times 10^{-7}$	$2.66 \times 10^{-5} \pm 2.43 \times 10^{-6}$
Power Law	2.48±0.03	2.31±0.02
Length (Å)		3000±272
Kuhn Length (Å)		238±15
Radius (Å)		27.9±0.2
Axis ratio		2.7±0.05
χ^2	1.68	2.38

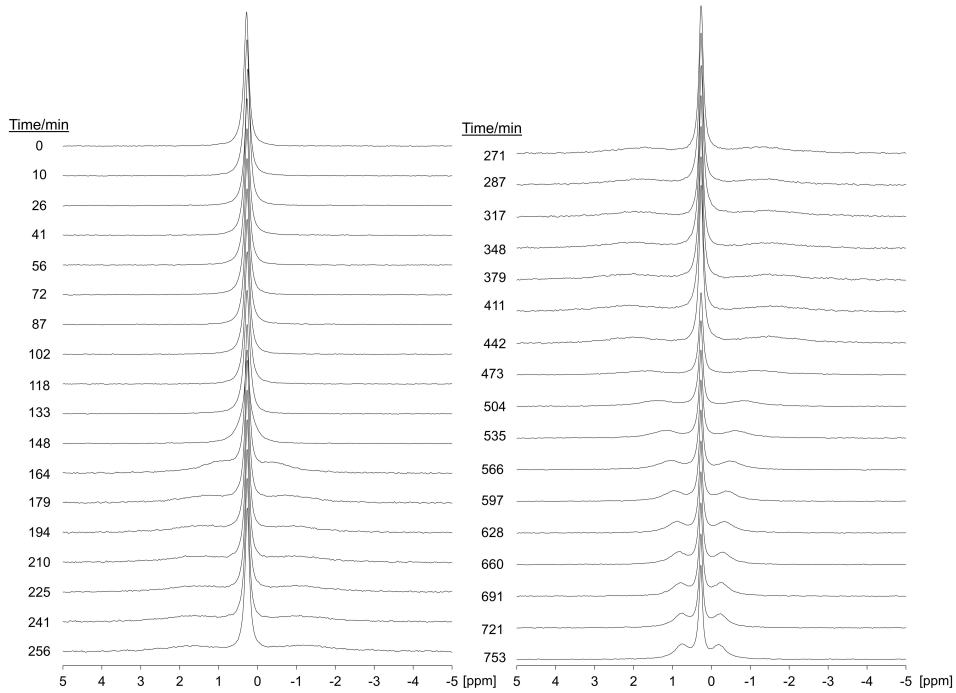

Figure S1 *Example ^{23}Na NMR spectra*

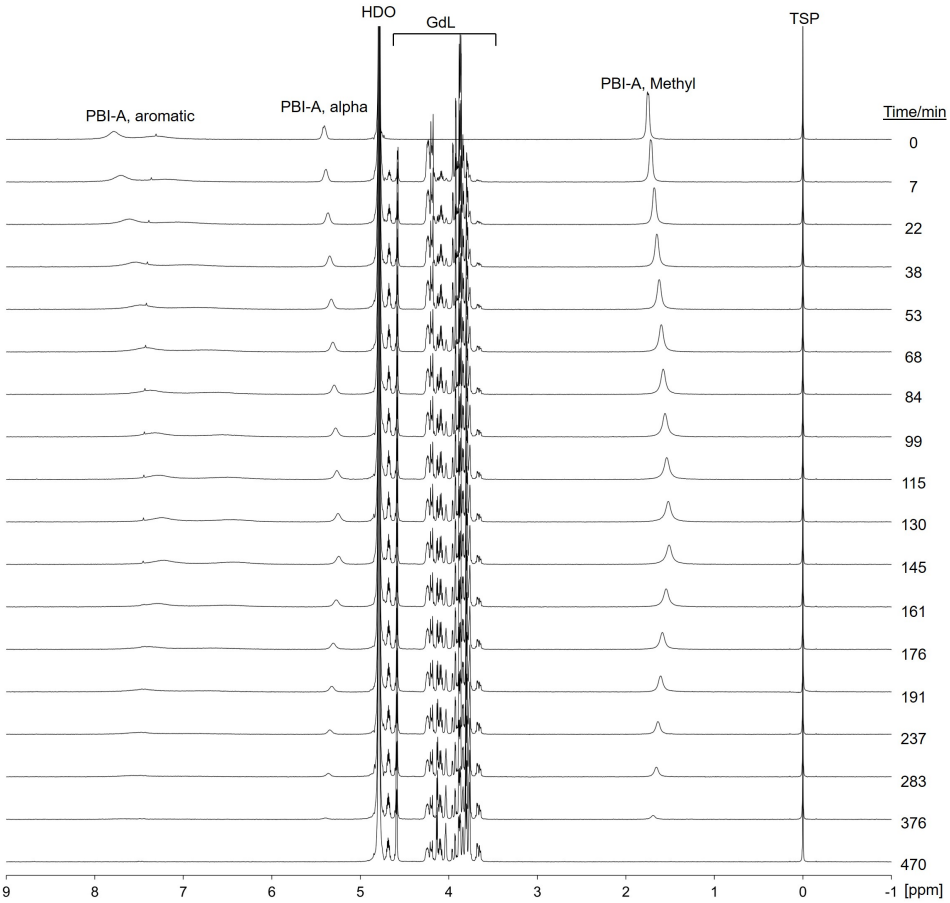

Figure S2 *Example ^{1}H NMR spectra*