

SUPPLEMENTARY MATERIAL

When Catchers meet – a computational study on the dimerization of the Buckycatcher

Filipe Menezes,^{a*} and Grzegorz Maria Popowicz^{b*}

S1: Additional Tables and Figures

Table S1: Binding energies according to different methods (in kcal/mol).

Dimer	GFN2-xTB	M06-2X		R2SCAN-3C		PBE-D3BJ	PBE-D3BJ (ATM)
		def2-TZVP	6-31G*	6-31G*	cc-pVTZ	def2-TZVP	def2-TZVP
1	45.1	28.4	35.1	35.8	29.1	32.6	26.5
2	24.6	18.9	22.4	27.7	24.1	27.1	24.5
3	36.4	17.7	24.4	28.5	22.4	25.6	21.0
4	23.7	8.5	11.2	18.2	15.9	16.7	14.7
5A	25.3	14.6	17.9	18.9	15.8	16.6	14.7
5B	22.7	10.2	13.6	17.5	14.6	17.5	14.6
6	35.1	17.6	22.4	24.9	20.1	22.5	18.4
7A	24.1	12.1	15.1	18.8	16.1	17.1	15.2
7B	21.1	6.3	9.4	14.0	11.5	13.3	11.2
8A	18.1	12.3	15.5	17.5	14.6	16.5	14.8
8B	18.2	12.5	16.4	18.9	15.5	19.0	16.1
9	16.2	-0.2	2.4	7.2	5.4	5.6	4.2
10	37.6	19.7	25.4	28.3	22.8	26.1	20.9
11	34.8	18.2	23.1	25.4	20.6	23.5	19.1
12	33.5	19.1	23.9	24.3	19.6	21.1	17.4
13	24.2	8.7	12.2	18.7	15.7	16.9	14.5
14	23.3	17.9	22.2	27.8	23.7	28.5	25.0
15	28.1	15.8	19.6	22.3	18.7	20.0	17.6
16	23.9	11.3	14.3	18.3	15.7	16.8	14.9

Dimer	PM6-D3H4X	M06-2X	R2SCAN-3C		PBE-D3BJ	PBE-D3BJ (ATM)
		6-31G*	6-31G*	cc-pVTZ	def2-TZVP	def2-TZVP
1	42.1	38.8	42.1	36.2	39.4	34.0
2	28.8	24.0	28.8	24.8	27.6	25.2
3	29.2	25.7	32.3	27.4	31.1	27.1
4	18.4	13.8	19.9	18.5	20.0	18.2
5A	20.5	15.3	18.1	15.6	18.4	16.3
5B	20.1	13.7	17.5	14.7	18.4	15.7
6	30.2	25.3	29.5	25.7	28.3	24.5
7A	20.3	17.5	21.0	18.6	20.0	18.2
7B	18.1	13.0	17.5	15.0	16.9	15.2
8A	19.9	8.9	11.4	8.7	12.6	10.8
8B	21.1	17.6	19.9	16.8	20.1	17.4
9	6.7	5.8	9.1	8.3	8.6	7.7
10	35.2	31.0	34.8	30.0	32.9	28.4
11	36.5	31.7	35.1	29.5	33.3	28.3
12	27.0	23.4	27.1	23.5	25.7	22.3
13	23.5	20.6	23.5	20.2	22.5	19.9
14	28.8	23.1	28.0	23.6	27.8	24.7
15	22.8	21.6	25.1	22.2	23.8	21.5
16	20.3	17.2	21.1	18.7	20.1	18.3

Dimer	GFN2-xTB	GFN1-xTB	GFN0-xTB	PM6-D3H4X	PM6-D3H+
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1	45.1	47.4	52.0	42.1	45.8
2	24.6	27.9	32.1	28.8	30.9
3	36.4	37.4	43.7	29.2	30.6
4	23.7	22.3	25.3	18.4	20.0
5A	25.3	23.6	25.1	20.5	22.7
5B	22.7	25.1	27.3	20.1	22.4
6	35.1	33.8	36.8	30.2	32.2
7A	24.1	21.8	22.5	20.3	21.7
7B	21.1	20.9	21.8	18.1	16.3
8A	18.1	19.7	21.2	19.9	22.2
8B	18.2	24.0	25.2	21.1	23.8
9	16.2	13.7	17.6	6.7	7.6
10	37.6	40.3	44.4	35.2	38.6
11	34.8	35.9	43.8	36.5	40.1
12	33.5	31.3	34.8	27.0	29.7
13	24.2	23.4	26.6	23.5	26.3
14	23.3	31.9	35.6	28.8	31.9
15	28.1	26.9	28.5	22.8	25.0
16	23.9	22.3	22.9	20.3	21.7

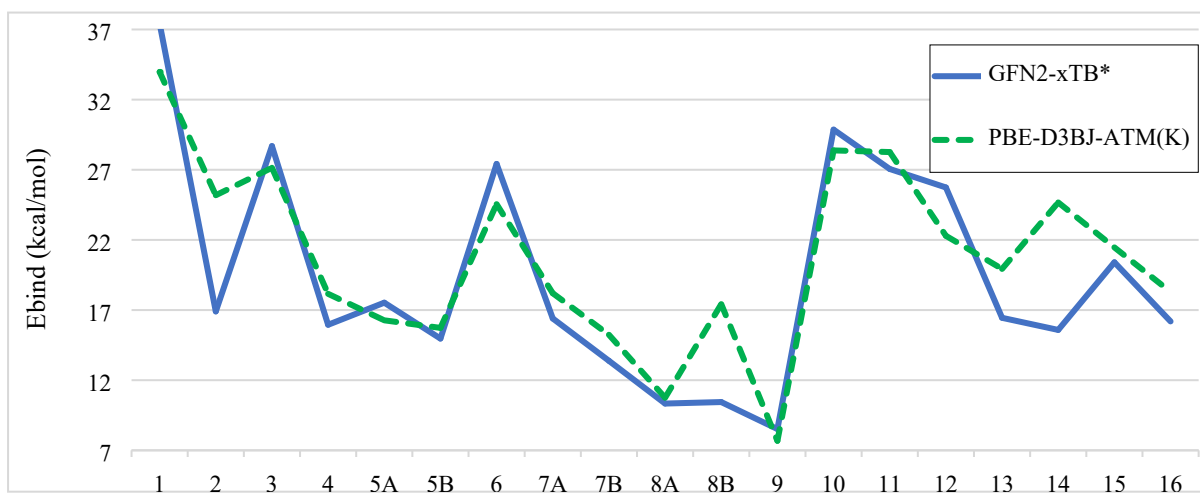


Figure S1: Shifted GFN2-xTB curve where dimerization energies for species 2, 8B and 15 are treated as outliers. Standard deviation with respect to PBE-D3BJ (ATM) data is 1.98 kcal/mol. Shift on the GFN2-xTB curve amounts to 7.7 kcal/mol, which reflects the overall error in binding energies. The standard deviation reflects errors in relative binding energies.

Table S2: Gibbs free energies for the formation of catcher's dimers. Gas phase data at 300 K.

Dimer	GFN2-xTB	PM6-D3H4X	M06-2X	r ² SCAN-3c	PBE-D3BJ	PBE-D3BJ (ATM)
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			6-31G*	6-31G*	cc-pVTZ	def2-TZVP	def2-TZVP
1	-26.3	-23.3	-20.1	-17.1	-17.5	-20.6	-15.2
2	-8.6	-11.9	-7.1	-10.8	-7.9	-10.7	-8.3
3	-15.1	-10.2	-6.7	-9.5	-8.4	-12.1	-8.1
4	-8.7	-2.5	2.1	-2.3	-2.6	-4.1	-2.3
5A	-9.1	-4.2	1.1	-2.5	0.8	-2.0	0.1
5B	-7.8	-4.6	1.8	-2.1	0.8	-2.9	-0.2
6	-16.9	-12.4	-7.5	-7.1	-8.0	-10.5	-6.8
7A	-8.1	-3.7	-0.9	-2.2	-2.0	-3.4	-1.6
7B	-6.7	-2.0	3.1	2.1	1.1	-0.8	0.9
8A	-1.7	-3.1	7.9	-0.7	8.2	4.2	6.1
8B	-2.4	-5.4	-1.9	-3.1	-1.0	-4.4	-1.7
9	-0.3	8.6	9.4	8.0	7.0	6.7	7.6
10	-19.3	-17.5	-13.2	-10.6	-12.3	-15.2	-10.7
11	-17.5	-17.7	-12.9	-6.6	-10.7	-14.5	-9.5
12	-16.0	-10.5	-6.9	-7.9	-7.0	-9.3	-5.8
13	-7.5	-7.5	-4.6	-2.8	-4.3	-6.5	-4.0
14	-6.0	-11.9	-6.2	-10.9	-6.7	-10.9	-7.8
15	-12.4	-7.2	-6.0	-6.7	-6.6	-8.3	-5.9
16	-9.4	-4.5	-1.4	-2.6	-3.0	-4.3	-2.5

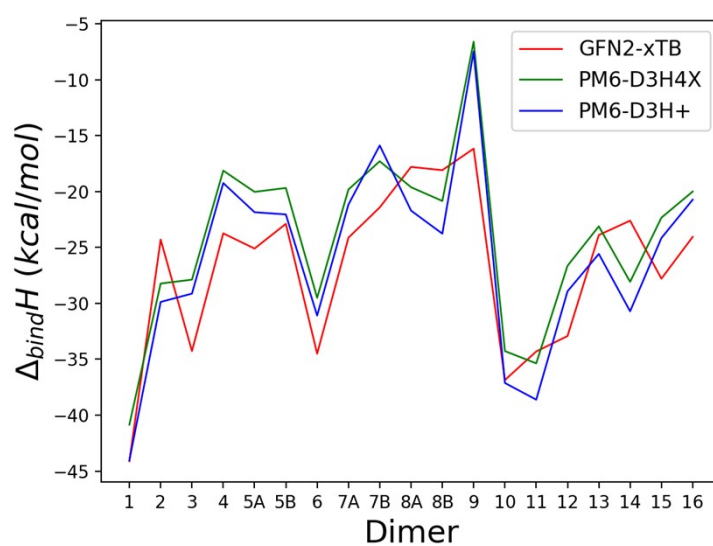


Figure S2: Enthalpies of binding for the formation of the dimers in gas phase. Data given in units of kcal/mol.

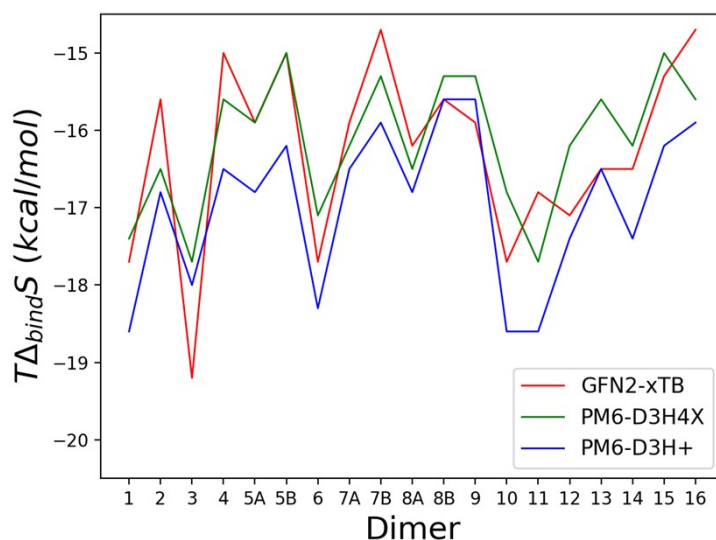


Figure S3: Change in entropy associated with the dimerization of the buckycatcher in gas phase at 300 K. Data represented as $T\Delta_{\text{bind}}S$ and given in units of kcal/mol.

Table S3: Gibbs free energies for the formation of catcher's dimers. Toluene data at 300 K. Solvation with ALPB.

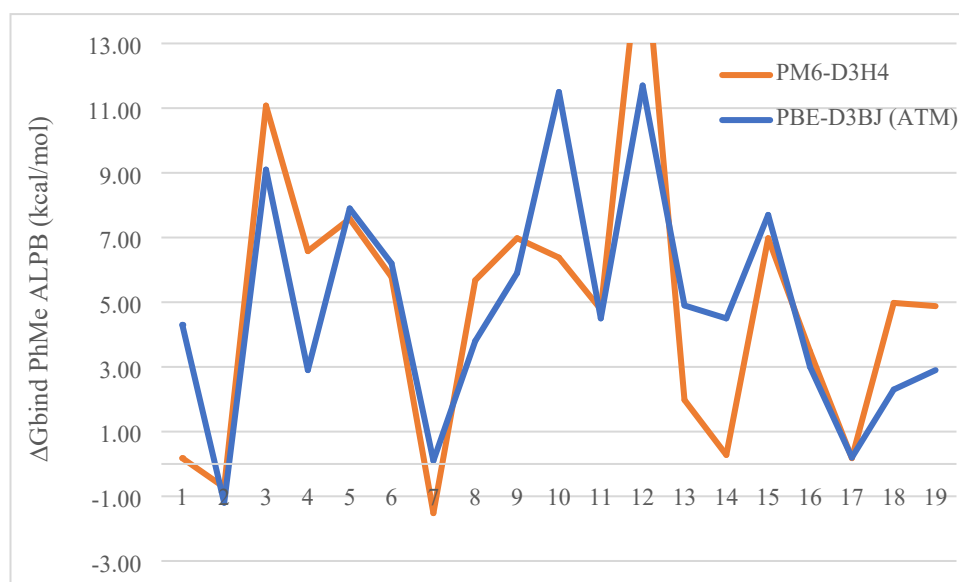
Dimer	GFN2-xTB	PM6-D3H4X	M06-2X	R2SCAN-3C		PBE-D3BJ	PBE-D3BJ (ATM)
			6-31G*	6-31G*	cc-pVTZ	def2-TZVP	def2-TZVP
1	-9.1	-6.2	-2.9	0.0	-0.4	-3.5	1.9
2	-1.0	-4.3	0.4	-3.2	-0.4	-3.1	-0.7
3	-2.1	2.8	6.3	3.5	4.6	0.9	4.9
4	-5.1	1.0	5.7	1.3	0.9	-0.5	1.3
5A	-2.8	2.1	7.4	3.8	7.1	4.3	6.4
5B	-1.6	1.6	8.0	4.1	7.0	3.3	5.9
6	-9.9	-5.4	-0.5	-0.1	-1.0	-3.5	0.2
7A	-3.5	1.0	3.8	2.5	2.6	1.3	3.1
7B	-2.3	2.4	7.5	6.5	5.5	3.6	5.3
8A	4.0	2.6	13.6	5.0	13.9	9.9	11.8
8B	3.8	0.8	4.3	3.0	5.1	1.8	4.4
9	1.2	10.0	10.9	9.5	8.4	8.1	9.0
10	-5.9	-4.1	0.2	2.9	1.1	-1.8	2.8
11	-2.5	-2.7	2.1	8.4	4.3	0.5	5.6
12	-5.4	0.0	3.6	2.6	3.5	1.3	4.7
13	-0.4	-0.4	2.5	4.3	2.8	0.6	3.1
14	2.2	-3.6	2.1	-2.6	1.5	-2.7	0.5
15	-5.3	-0.2	1.0	0.3	0.4	-1.2	1.2
16	-4.7	0.2	3.3	2.1	1.7	0.4	2.2

Table S4: Gibbs free energies for the formation of catcher's dimers. Toluene data at 300 K. Solvation with COSMO ($\epsilon=7.0$).

Dimer	GFN2-xTB	PM6-D3H4X	M06-2X	R2SCAN-3C		PBE-D3BJ	PBE-D3BJ (ATM)
			6-31G*	6-31G*	cc-pVTZ	def2-TZVP	def2-TZVP
1	-19.2	-16.3	-13.0	-10.1	-10.5	-13.6	-8.2
2	-5.0	-8.3	-3.6	-7.3	-4.4	-7.1	-4.8
3	-9.5	-4.6	-1.1	-3.9	-2.8	-6.5	-2.5
4	-4.2	2.0	6.6	2.2	1.9	0.4	2.2
5A	-6.6	-1.7	3.5	-0.1	3.2	0.5	2.5
5B	-3.9	-0.8	5.7	1.8	4.7	0.9	3.6
6	-13.9	-9.4	-4.5	-4.1	-5.0	-7.5	-3.8
7A	-5.2	-0.7	2.1	0.8	1.0	-0.4	1.4
7B	-3.3	1.3	6.4	5.5	4.4	2.6	4.2
8A	0.8	-0.6	10.4	1.7	10.6	6.6	8.5
8B	0.6	-2.4	1.2	-0.1	2.0	-1.4	1.3
9	0.2	9.0	9.9	8.5	7.4	7.1	8.0
10	-13.7	-12.0	-7.7	-5.0	-6.8	-9.6	-5.1
11	-10.8	-11.0	-6.2	0.1	-4.0	-7.8	-2.7
12	-11.0	-5.6	-2.0	-3.0	-2.1	-4.3	-0.9
13	-4.8	-4.8	-1.9	-0.1	-1.6	-3.9	-1.3
14	-2.6	-8.4	-2.8	-7.5	-3.3	-7.5	-4.4
15	-9.9	-4.8	-3.6	-4.3	-4.2	-5.8	-3.4
16	-6.3	-1.4	1.7	0.6	0.1	-1.2	0.6

Table S5: Gibbs free energies for the formation of catcher's dimers. Toluene data at 300 K. Solvation with COSMO ($\epsilon=2.38$).

Dimer	GFN2-xTB	PM6-D3H4X	M06-2X	R2SCAN-3C		PBE-D3BJ	PBE-D3BJ (ATM)
			6-31G*	6-31G*	cc-pVTZ	def2-TZVP	def2-TZVP
1	-22.4	-19.5	-16.2	-13.2	-13.6	-16.8	-11.4
2	-6.6	-9.9	-5.2	-8.9	-6.0	-8.7	-6.4
3	-12.1	-7.2	-3.7	-6.5	-5.4	-9.1	-5.1
4	-6.4	-0.2	4.4	0.0	-0.3	-1.8	0.1
5A	-7.8	-2.9	2.4	-1.3	2.1	-0.7	1.4
5B	-5.8	-2.7	3.8	-0.1	2.8	-0.9	1.7
6	-16.4	-11.9	-7.0	-6.6	-7.5	-10.0	-6.3
7A	-6.6	-2.1	0.7	-0.6	-0.5	-1.8	-0.1
7B	-5.0	-0.4	4.7	3.8	2.7	0.9	2.5
8A	-0.4	-1.8	9.2	0.6	9.5	5.5	7.4
8B	-0.8	-3.8	-0.3	-1.6	0.5	-2.8	-0.1
9	0.0	8.9	9.7	8.3	7.3	7.0	7.8
10	-16.3	-14.5	-10.3	-7.6	-9.3	-12.2	-7.7
11	-13.9	-14.1	-9.3	-3.0	-7.1	-10.9	-5.8
12	-13.3	-7.9	-4.3	-5.3	-4.4	-6.6	-3.2
13	-6.0	-6.1	-3.2	-1.4	-2.9	-5.1	-2.6
14	-4.2	-10.0	-4.3	-9.1	-4.9	-9.1	-5.9
15	-11.0	-5.9	-4.7	-5.4	-5.3	-6.9	-4.6
16	-7.8	-2.9	0.2	-0.9	-1.3	-2.7	-0.9



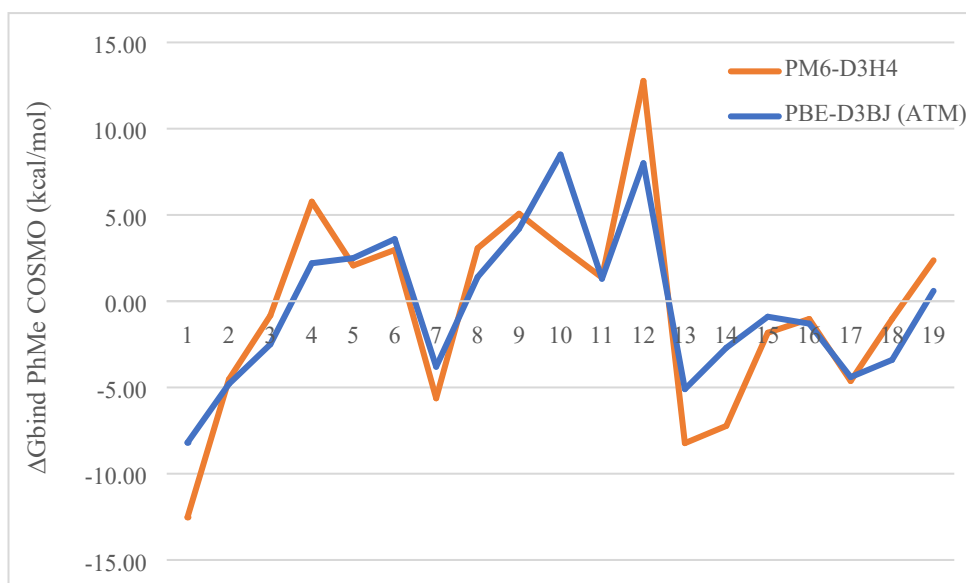


Figure S4: Gibbs free energies of dimerization using shifted PM6-D3H4 data. Shifts used are -4.0 and -3.8 kcal/mol for ALPB and COSMO, respectively.

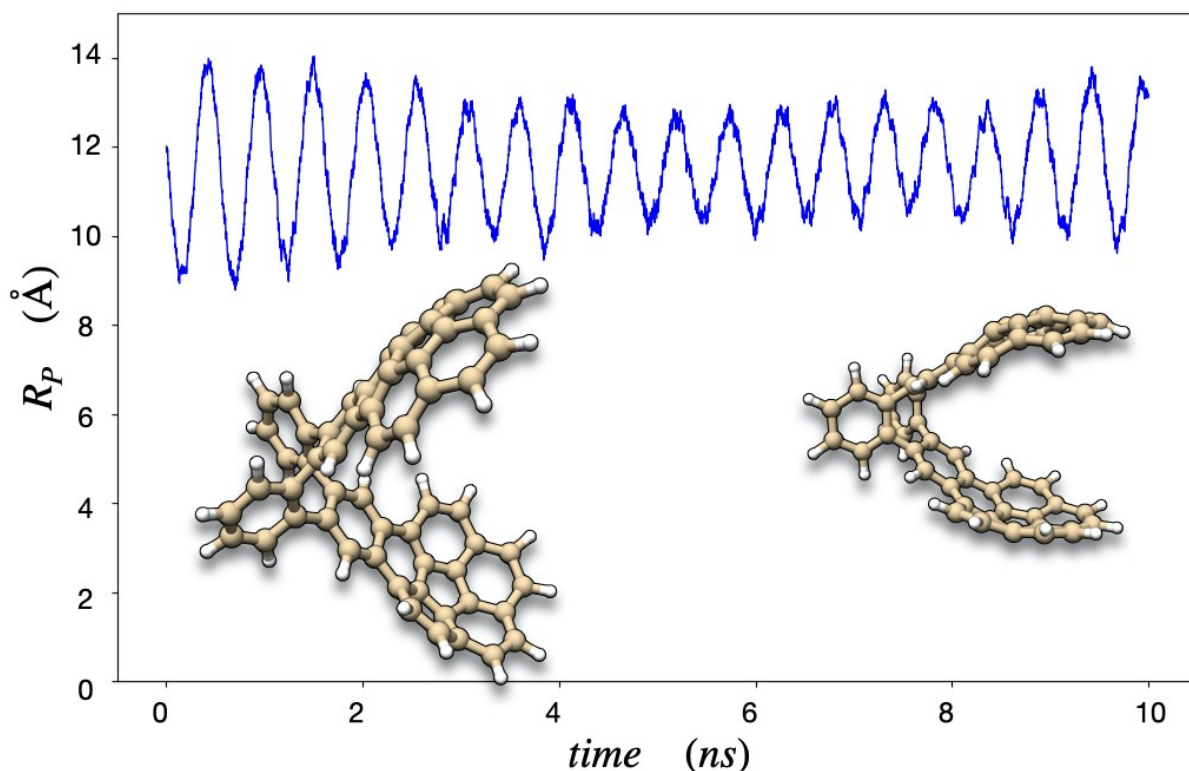


Figure S5: Evolution of the RP parameter as a function of time for a reference dynamics simulation of the buckycatcher alone. The oscillation movement corresponds to the opening and closing of the catcher's pocket.

S2: Choosing a Reference for the Benchmark

The buckycatcher-fullerene has been the subject of countless studies. For a brief overview, we refer the reader to the introduction of another work of ours, which provides a more extensive account of studies on the system.¹ Several reference values have been proposed in the literature for the binding energy of this complex. Perhaps we start with the value we chose as reference, the data of Sure and Grimme.² The main advantage of the method is the

fact that these binding energies are derived (back corrected) from experimental data.³ This is indeed a unique selling point since no other value reported in the literature has such support. However, the accuracy of the back-corrected electronic binding energies relies on the errors of several other evaluations. Firstly, the effect of solvent is estimated using a solvation model. For this end, Sure and Grimme relied on COSMO-RS⁴ solvation energies, which are acknowledged to be among the highest quality predictions of solvation effects.⁵ Additionally, there are translational, rotational, and vibrational contributions to enthalpy and entropy, estimated using standard statistical mechanical models with corrections for low-frequency modes.⁶ Several accounts in the literature attest however the quality of the predictions using standard models.⁷

Besides the reference values proposed by Sure and Grimme, there are theoretical calculations using *ab initio* theory. The most recent values, proposed by Villot and coworkers,⁸ were obtained using a linear-scaling variant of quantum chemistry's gold standard, CCSD(T). Undoubtedly, the main advantage of these calculations is that they yield electronic binding energies, which can be directly compared with the results of other theoretical calculations. There is no requirement for back-correcting solvation or thermal effects, present in the experimental data. However, several are the concerns that can be raised from such calculations. Firstly, DLPNO-CCSD(T),⁹ the linear scaling variant of CCSD(T) used for the calculations, is not CCSD(T): several layers of approximations are required to render the calculations feasible. Further, CCSD(T) calculations are currently feasible for extremely small systems. This means that the behavior of the DLPNO approximations for large systems is not yet truly validated against actual CCSD(T) calculations. In fact, some studies already indicate that errors in DLPNO-CCSD(T) do indeed increase with system size.¹⁰ Additionally, Diffusion Monte Carlo calculations¹⁰ disagree with DLPNO-CCSD(T) by almost 15 kcal/mol and are significantly closer to the experimentally back-corrected values of Sure and Grimme.

Given the advantages and disadvantages of both reference values, we are convinced that experimentally back-corrected values are of higher accuracy and chose these as reference.

S3: Imaginary Frequencies inverted for Calculation of Thermodynamic Data

Dimer	Imaginary Frequencies (cm ⁻¹)	Dimer	Imaginary Frequencies (cm ⁻¹)
1	---	16	---
2	---	17	8.3
3	---	18	---
4	---	19	---
5	A: 0.98 B: 1.53	20	A: -8.7 B: ---
6	---	21	---
7	A: 10.9 B: ---	22	A: 11.3 B: ---
8	A: 6.3 B: 13.2	23	A: 16.1 B: ---
9	11.6	24	36.5
10	---	25	---
11	20.95, 9.56	26	---
12	11.3, 3.6	27	---
13	6.5	28	---
14	---	29	---
15	---	30	6.0

S4: Validating use of Gas-Phase Geometries instead of geometries optimized in the Dielectric of Solvents

Geometries reoptimized using PM6-D3H4/COSMO in the dielectric of toluene.

Dimer	RMSD(gas,toluene) (Å)	Dimer	RMSD(gas,toluene) (Å)
1	0.0066	8B	0.0044
2	0.0033	9	0.0032
3	0.0026	10	0.0022
4	0.0170	11	0.0085
5A	0.0200	12	0.0017
5B	0.032	13	0.0034
6	0.0080	14	0.0053
7A	0.0018	15	0.026
7B	0.0015	16	0.0032
8A	0.020	----	

Geometries reoptimized using GFN2-xTB/ALB in the dielectric of toluene.

Dimer	RMSD(gas,toluene) (Å)	Dimer	RMSD(gas,toluene) (Å)
1	0.034	8B	0.058
2	0.030	9	0.024
3	0.032	10	0.075
4	0.069	11	0.049
5A	0.063	12	0.026
5B	0.044	13	0.056
6	0.047	14	0.031
7A	0.051	15	0.027
7B	0.042	16	0.018
8A	0.030	----	

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