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SUPPORTING INFORMATION

First-Principles Investigation of the Lewis Acid-Base Adduct Formation at the Methylammonium Lead Iodide Surface

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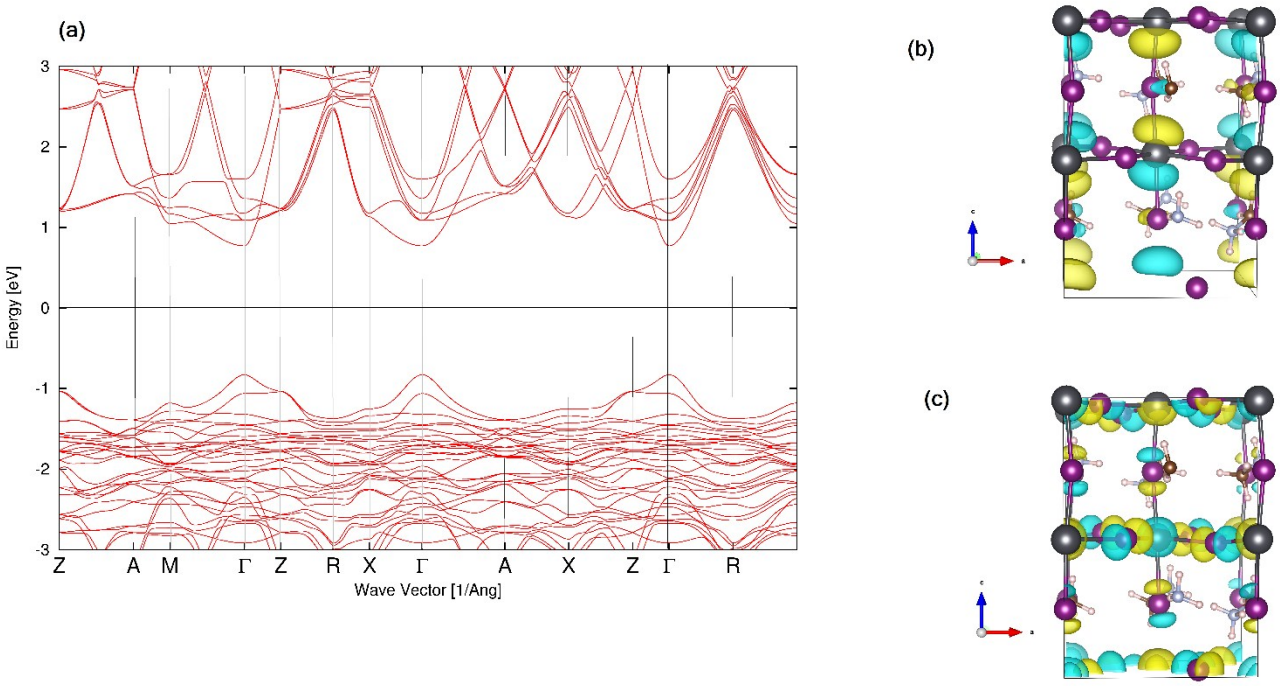

Figure 1S: DFT calculated (a) Bandstructure of bulk *t*–$MAPbI_3$. (b) Valence band maximum and (c) conduction band minimum wavefunction (Isosurface level 0.08 eV/Å^3).

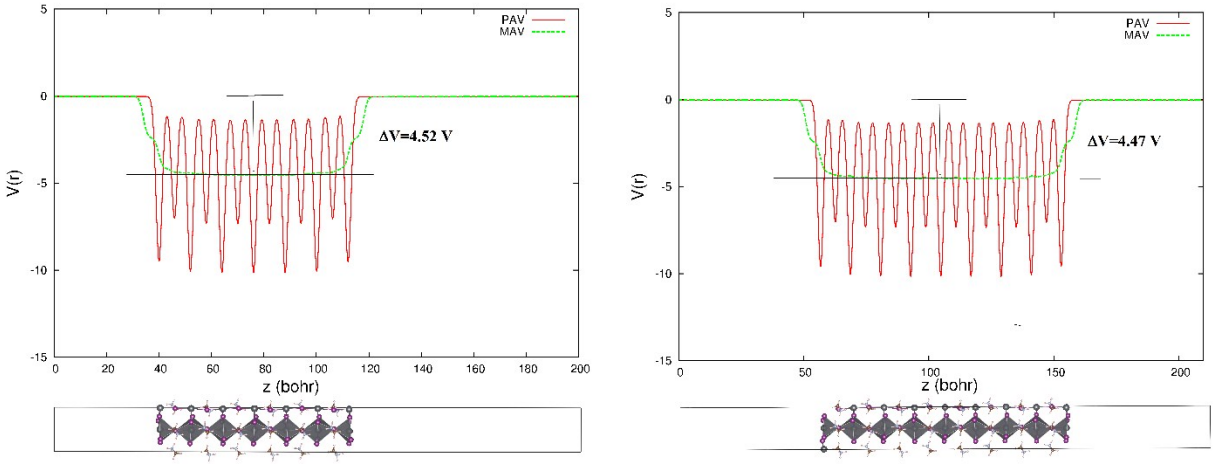

Figure 2S: DFT calculated Nanosmoothed (MAV) and planar averaged (PAV) electrostatic potential for (left) (1×1×3) and (right) (1×1×4) slab. The zero is the vacuum electrostatic potential

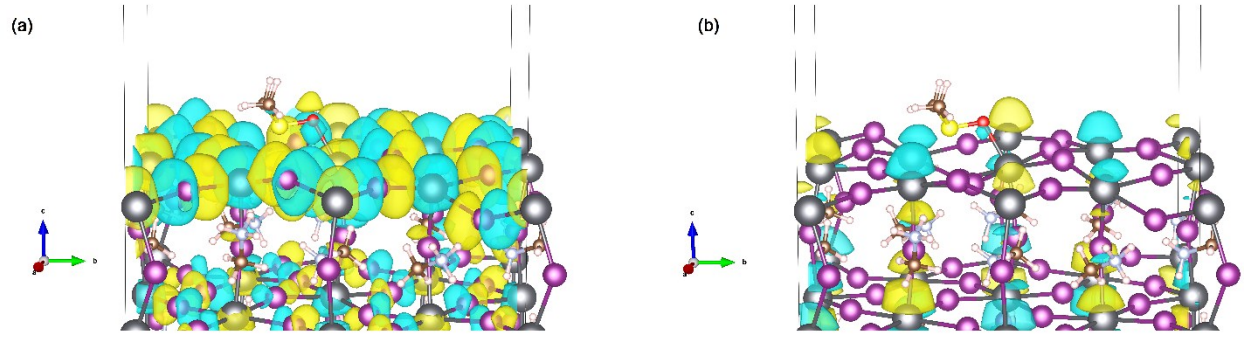

Figure 3S: DFT calculated (a) VBM and (b) CBM wavefunction for **$DMSO_1$** (isosurface level 0.02 eV/Å^3).

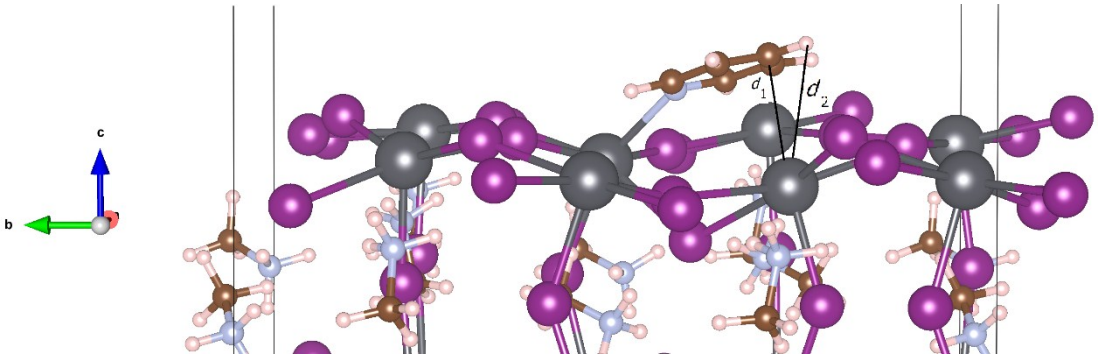

Figure 4S: Geometrical details of the vdW-DF2 calculated **Py_2** adduct

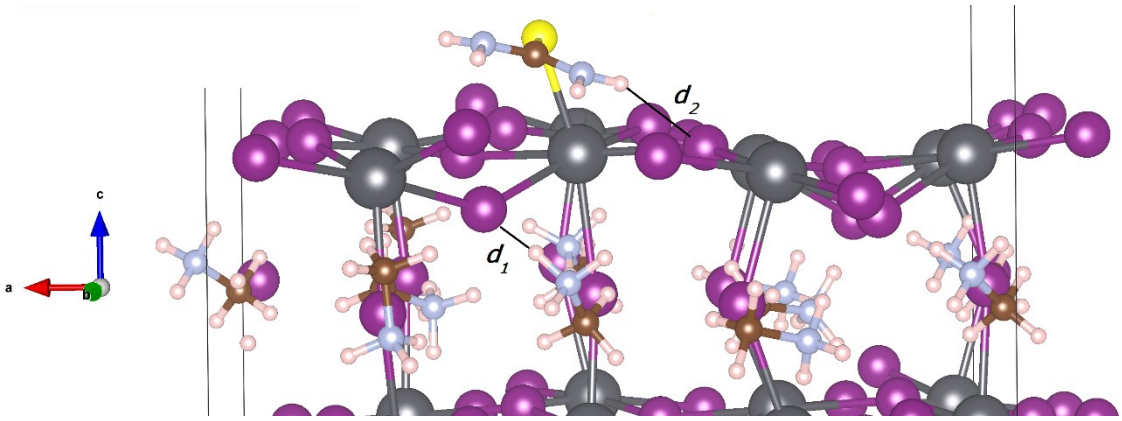

Figure 5S: Geometrical details of the vdW-DF2 calculated **Thu** adduct

Table 1S. Main geometrical parameters for the optimized structures of the bases here investigated at different level of theory. ([a]PAW/PBE VASP code [1-5]; [b]b3lyp/ 6-311++g(d,p) G09 code [6])

	Py				**DMSO**			**Thu**	
	PAO/ PAO (+vdW-DF2)	**PW[a]**	**G09[b]**	**PAO/ PAO (+vdW-DF2)**	**PW[a]**	**G09[b]**	**PAO/ PAO (+vdW-DF2)**	**PW[a]**	**G09[b]**
1	1.352/1.366	1.330	1.337	1.543/1.559	1.495	1.514	1.690/1.690	1.667	1.676
2	1.352/1.366	1.330	1.337	1.846/1.889	1.821	1.835	1.372/1.371	1.362	1.359
3	1.411/1.421	1.418	1.394	1.846/1.889	1.821	1.835	1.372/1.371	1.362	1.359
4	1.411/1.421	1.418	1.394	----	----	-----	------	----	----
5	1.408/1.418	1.370	1.392	----	----	-----	------	----	----
6	1.408/1.418	1.370	1.392	----	----	-----	------	----	----
α	116.4/116.3	118.9	117.3	106.4/106.0	97.0	96.6	122.4/122.4	122.2	122.3
β	124.2/124.1	122.9	123.6	96.5/95.5	106.8	106.8	115.3/115.3	115.5	115.5
γ	118.5/118.6	116.0	118.5	----	----	----	-----	----	----
δ	118.2/118.2	123.2	118.5	-----	----	----	-----	----	----
ε	118.5/118.6	116.0	118.5	-----	----	----	-----	----	----
ζ	124.2/124.1	122.9	123.6	-----	----	----	----	----	----

Table 2S. Bondlengths of the formed adduct between Lewis bases and MAPI (001) flat surface.

Adduct	**Pb-X bondlength**	**DFT/PBE/PAO (Å)**	**vdW-DF2 (Å)**
Py_1	X=N	2.57	2.62
Py_2	X=N	2.72	2.80
$DMSO_1$	X=O	2.47	2.52
Thu_1	X=S	2.97	2.85

References

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[6] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams–Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.