Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Impact of fluorination on the energy level alignment of F_nZnPc/$MAPbI_3$ interface

Elham Oleiki,[a] Saqib Javaid,[a,b] Geunsik Lee*[a]

[a] *Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea.*

[b] *MMSG, Theoretical Physics Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan*

Email: gslee@unist.ac.kr

Table S1. Adsorption energies (eV) of F_nZnPc for different adsorption sites with reference to the position of Zn atom on $MAPbI_3$ surface.

	I top	**bridge**	**Pb top**
F_4ZnPC	-2.50	-2.36	-2.37
F_8ZnPC	-2.40	-2.39	-1.98
F_{12}ZnPc	-2.62	-2.59	-1.94
F_{16}ZnPc	-2.46	-2.44	-1.81

Table S2. Substrate and molecular distortion energies for ZnPc/$MAPbI_3$ and F_{16}ZnPc/$MAPbI_3$.

	ZnPc/$MAPbI_3$	**F_{16}ZnPc/$MAPbI_3$**
Molecular distortion energy (eV)	0.18	0.29
Substrate distortion energy (eV)	0.02	0.17
Total distortion energy (eV)	0.20	0.46

We define the distortion energy as following:

(Eq. S1): $E_{distortion}$ (molecule/$MAPbI_3$) = [$E_{distorted}$ ($MAPbI_3$) - E_{ideal} ($MAPbI_3$)]

+ [$E_{distorted}$ (molecule) - E_{ideal} (molecule)]

Here, $E_{distorted}$ ($MAPbI_3$) is the total energy of substrate distorted by molecule adsorption, E_{ideal} ($MAPbI_3$) is total energy of bare $MAPbI_3$ surface optimized, $E_{distorted}$ (molecule) is the total energy of molecule distorted after adsorption on the substrate and E_{ideal} (molecule) is the total energy of a single molecule in gas phase.

Table S3. Calculated quadrupole moments by PBE method for molecular structures shown in Fig. S3. Q_{xx} and Q_{yy} are in-plane components and Q_{zz} is the component perpendicular to the molecular plane. Values for two F_4ZnPc isomers in Fig. S3 are almost the same, thus the mean values are presented. The molecular models considered in Fig. S1 are denoted by F_n*ZnPc (*n* = 4,8,12).

	ZnPc	F_4*ZnPc	F_4ZnPc	F_8*ZnPc	F_8ZnPc	F_{12}*ZnPc	F_{12}ZnPc	F_{16}ZnPC
Q_{xx} (a.u.)	12.80	9.87	2.10	-0.70	-7.97	-2.81	-2.61	-12.92
Q_{yy} (a.u.)	12.80	9.88	2.09	-0.69	-7.96	-2.81	-3.02	-12.92
Q_{zz} (a.u.)	-25.60	-19.96	-4.19	1.40	15.93	5.62	5.63	25.84

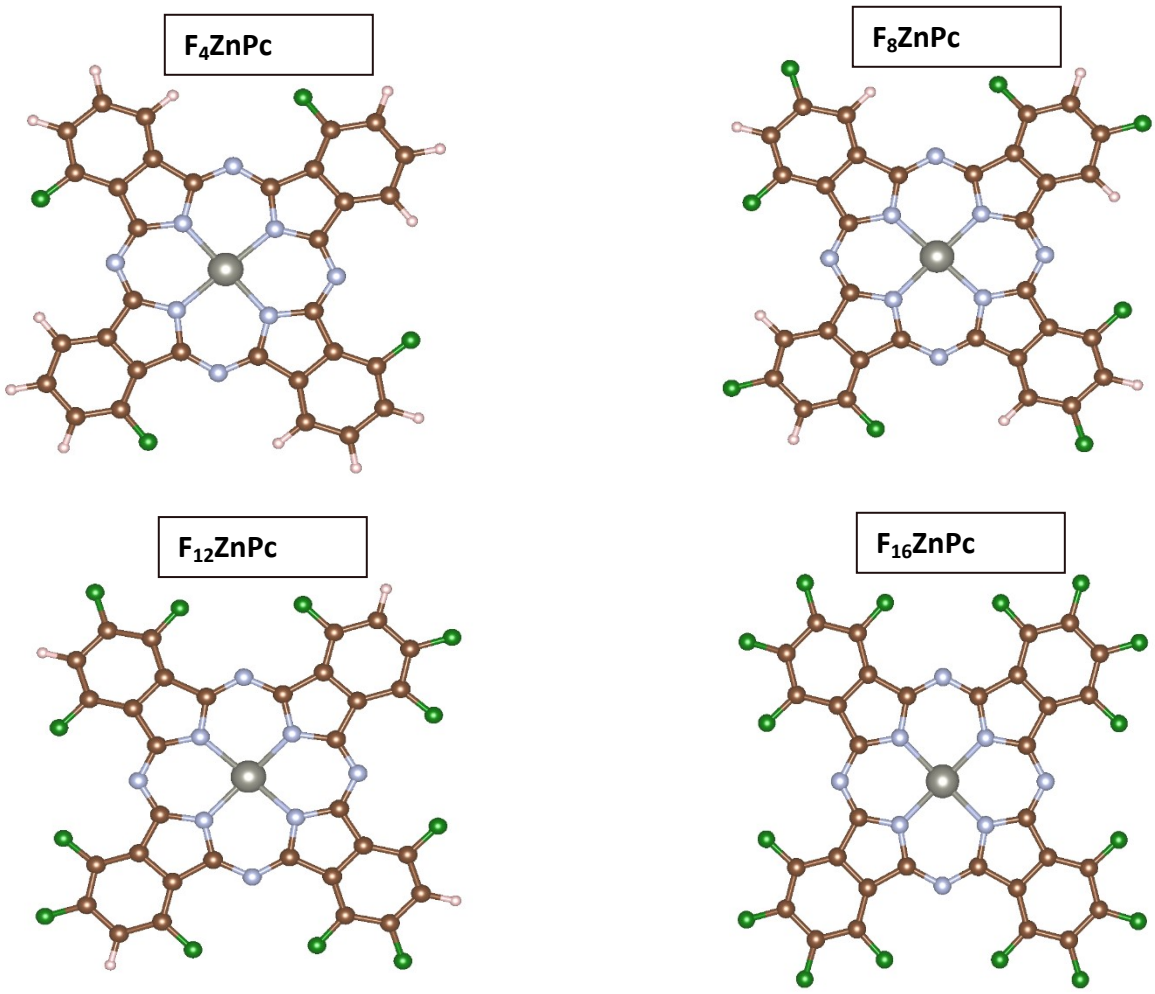

Fig. S1 Optimum molecular structures of F_nZnPc considered in this study. Atomic color scheme: N (light blue), C (brown), H (pink), Zn (grey) and F (green).

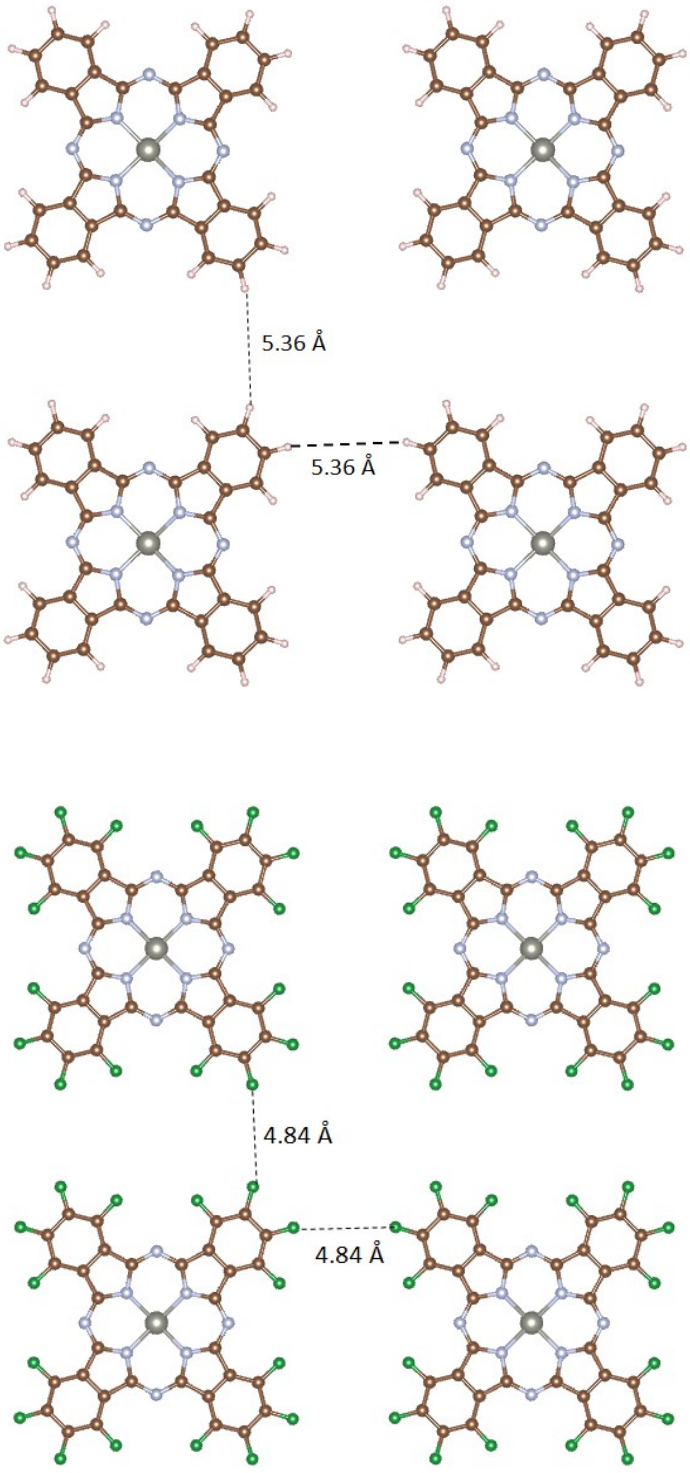

Fig. S2 Top view of relative molecular positions in square lattice of ZnPc and F_{16}ZnPc. Atomic color scheme: N (light blue), C (brown), H (pink), Zn (grey) and F (green).

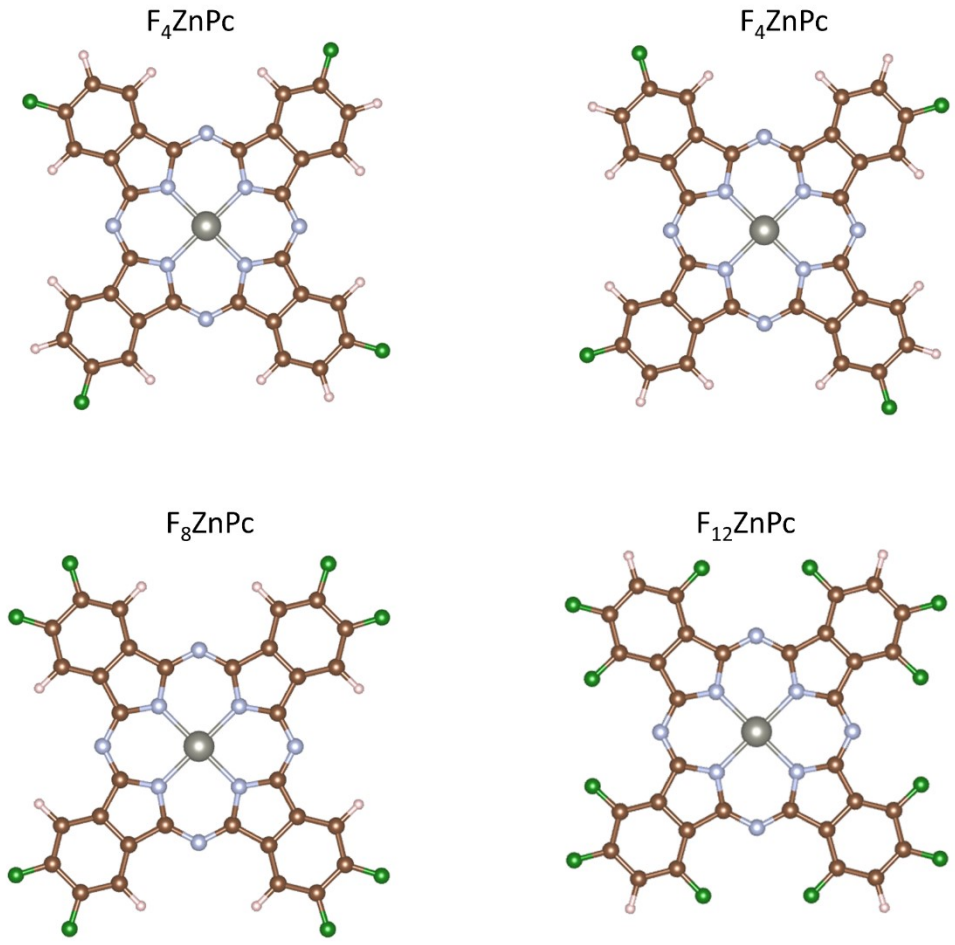

Fig. S3 Optimum molecular structures of F_nZnPc considered for calculation of quadrupole moments whose results are listed in Table. S3, and molecular ionization energy presented in Fig. S4. Atomic color scheme: N (light blue), C (brown), H (white), Zn (grey), and F (green).

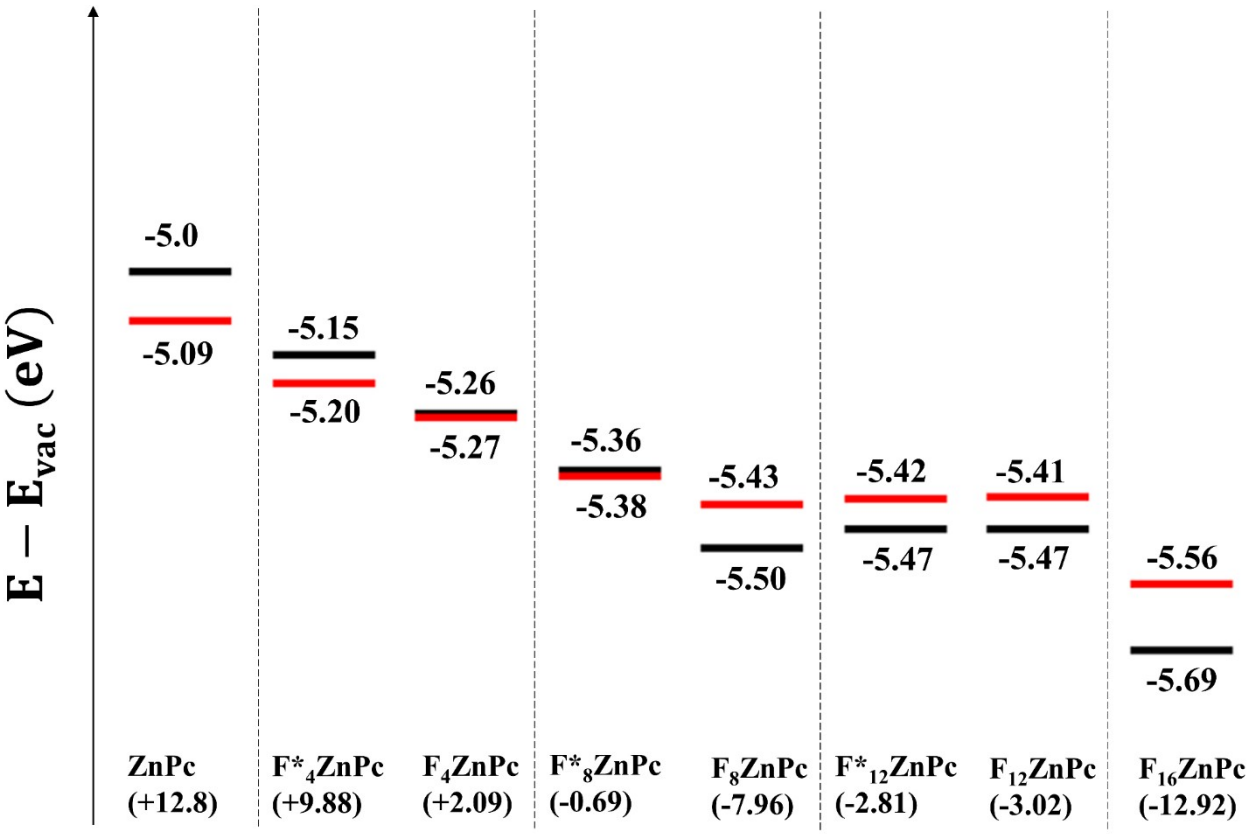

Fig. S4 Molecular ionization energy for different F_nZnPc isomers. The ionization energy of an isolated gas phase molecule is shown in black color. Red color shows the effect of intermolecular interaction on ionization energy (gas phase molecules are arranged in a square lattice in which intermolecular distance is ~ 5 Å). Values in parenthesis are molecular quadrupole moments in a.u.

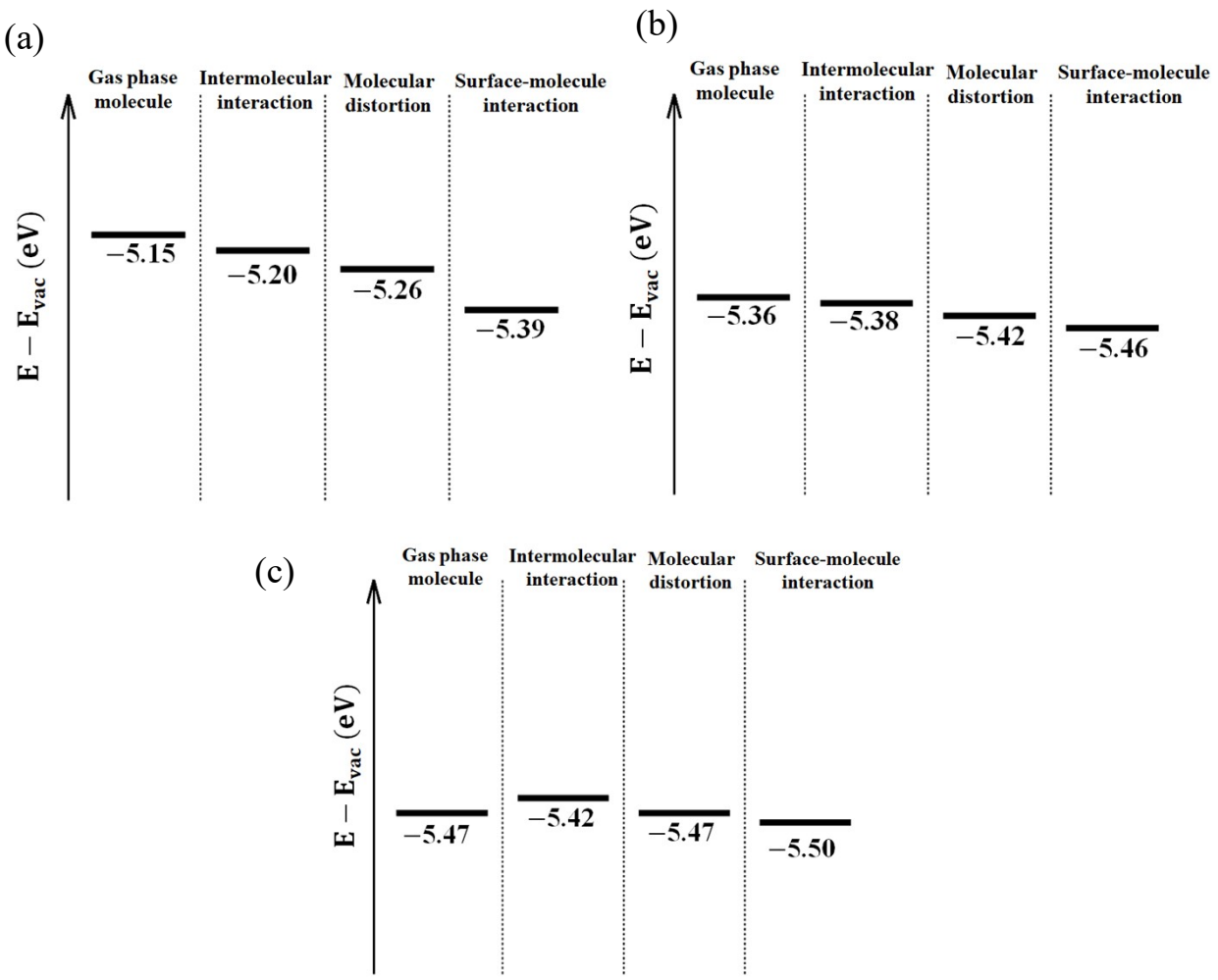

Fig. S5 (a) F_4ZnPc, (b) F_8ZnPc and (c) F_{12}ZnPc HOMO energy levels relative to the vacuum level for equilibrium structures of an isolated gas phase molecule (left most), and an adsorbed molecule (rightest). The effect of intermolecular interaction and molecular distortion on HOMO is shown in the middle left and middle right, respectively. In the middle left, the gas molecules are arranged into a square lattice, and in the middle right, the non-planar distortion by the interaction with substrate is additionally included.

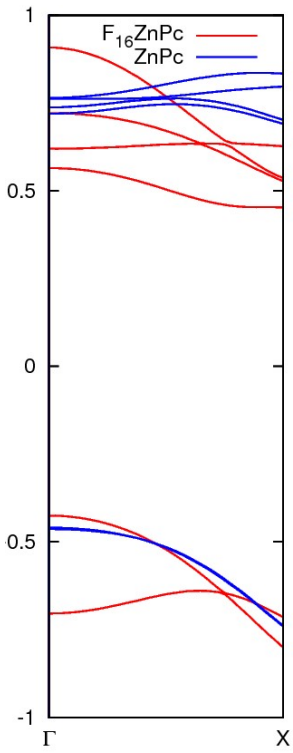

Fig. S6 Band structures of F_{16}ZnPc and ZnPc with the crystallographic data from Ref. [1] and [2] for ZnPc and F_{16}ZnPc, respectively.

References

1 H. Jiang, P. Hu, J. Ye, R. Ganguly, Y. Li, Y. Long, D. Fichou, W. Hu and C. Kloc, *Angew. Chemie Int. Ed.*, 2018, **57**, 10112–10117.

2 H. Jiang, J. Ye, P. Hu, F. Wei, K. Du, N. Wang, T. Ba, S. Feng and C. Kloc, *Sci. Rep.*, 2015, **4**, 7573.