Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

Work Function Modification of the (111) Gold Surface Covered by Long Alkanethiol-Based Self-Assembled Monolayers

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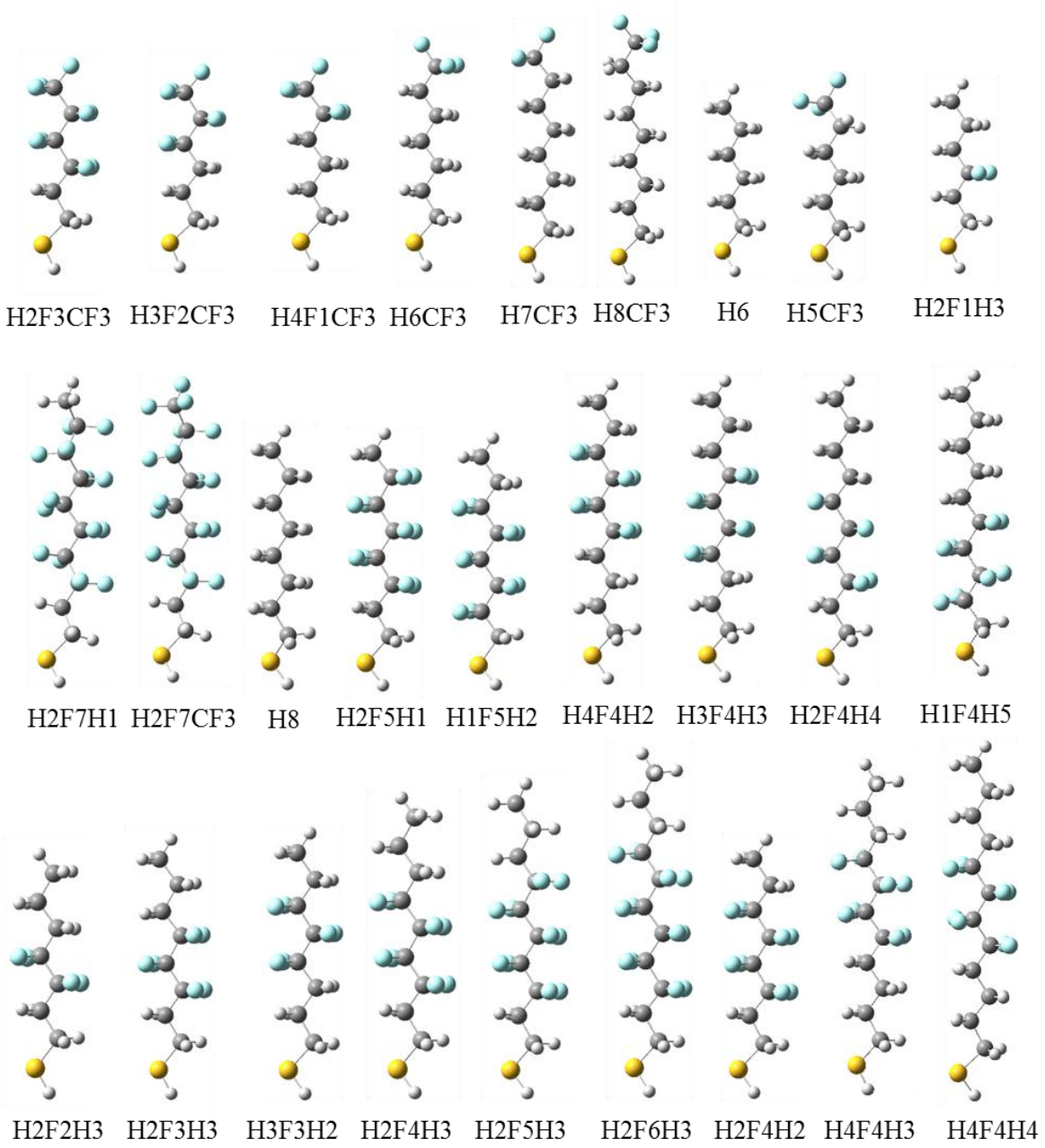

Figure S1. Chemical structures of the neutral alkanethiols under study. The colors refer to the following atoms: white → hydrogen, grey → carbon, yellow → sulphur and pale blue → fluorine.

LDA	H6	H2F3H3	H2F4H3	H2F7CF3	H3F4H3	H4F4H2
α-tilt	15.4	11	18.1	9.8	7.3	7.6
β-twist	27	19.8	9.5	86.2	33	37.7

VDW	H6	H2F3H3	H2F4H3	H2F7CF3	H3F4H3	H4F4H2
α-tilt	15.3	10.8	17.5	9.6	7	7.5
β-twist	30.4	21.9	10.3	86.7	30	37

Table 1. Geometrical parameters calculated for selected molecules with two different functionals. The top part of the table reports data obtained with LDA functional, while the second half yields the results with explicit vdW interactions treated within the Grimme approach.

	H6	**H5CF3**	**H2F7H1**	**H2F7CF3**	**H8**	**H2F5H1**	**H1F5H2**
α-tilt	15.4	26.5	9.8	9.8	11.6	10.7	12.8
β-twist	27	25.8	84.9	86.2	46.7	20.3	13.8

	H6CF3	**H7CF3**	**H8CF3**	**H2F3CF3**	**H3F2CF3**	**H4F1CF3**
α-tilt	24.35	11.1	18.72	13.15	13.22	14.5
β-twist	12.23	24.2	4.13	20.3	18.64	20.33

	H4F4H2	**H3F4H3**	**H2F4H4**	**H1F4H5**	**H2F1H3**	**H2F2H3**	**H2F3H3**
α-tilt	7.6	7.3	7.6	7.5	12.8	24.3	11
β-twist	37.7	33	37.3	35.1	20.2	14.3	19.8

	H3F3H2	**H2F4H3**	**H2F5H3**	**H2F6H3**	**H2F4H2**	**H4F4H3**	**H4F4H4**
α-tilt	11.2	18.1	10.1	13.4	11.1	13.3	13
β-twist	6.2	9.5	3	4.5	18.7	6	0.3

Table 2. Geometrical parameters calculated for all molecules analyzed in the paper, as obtained at the LDA level.