Supplementary Information

General Criteria for Evaluating Suitable Polymer Ligands for the Synthesis of Aluminum Nanocrystals

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16 Sep 2020
Note added after first publication: This Supplementary Information file replaces that originally published on 26 Nov 2019. The authors regret that Fig. S6B (image of Al nanoparticles) in the original file was incorrect due to errors in image processing. This new version includes the correct image. This correction does not affect the results or conclusions of the article.

1. Materials.

1-methylpyrrolidine (1-MP) (98 %) was purchased from Alfa Aesar. Lithium aluminium hydride ($LiAlH_4$) (98.0 %) was obtained from TCI Shanghai. Titanium (IV) isopropoxide (Ti(*i*-PrO)$_4$) (99 %) was purchased from Amatek Chemical Co., Ltd. (Soochow, China). Styrene (99.0 %) was purchased from Xilong Scientific Co., Ltd. and was purified by passage over a column of basic aluminum oxide (Sinopharm Chemical Reagent Co., Ltd.). Cumyl dithiobenzoate (CDTB) (97 %) and dibenzyl trithiocarbonate (DBTTC) (97 %) were purchased from Chemsoon Co., Ltd. and used as received. Azobisisobutyronitrile (AIBN) (98 %, Aladdin) was recrystallized twice with methanol before use. Tetrahydrofuran (THF) (99.9 %) and aluminium chloride ($AlCl_3$) (99 %) were purchased from Fisher Scientific. Toluene (99.5 %) and methanol (99.5 %) were purchased from Beijing Chemical Work. Toluene, THF and 1-MP was dried prior to use with sodium-potassium alloy (potassium 78 wt. %, sodium 22 wt. %). N-propylamine (98 %) and triphenylphosphine (99.0 %) were purchased from Aladdin.

2. Synthesis of CDTB-PS, HS-PS and TTC-PS

CDTB-PS (1.1 kg/mol, 4.5 kg/mol and 21.4 kg/mol) was synthesized according to previously reported protocols.[1,2]

HS-PS was synthesized through the reaction of CDTB-PS and N-propylamine (Figure S1). Take the synthesis of HS-PS (4.4 kg/mol) for example. Use THF (15 mL) to dissolve CDTB-PS (1.2705 g, 4.5 kg/mol) and triphenylphosphine (0.5232 g). Triphenylphosphine was used to avoid the formation of polystyrene disulfide (PS-S-S-PS). Add 5 mL n-propylamine THF solution (v. 30 %) into the prepared solution under strong stirring. The reaction lasted for half an hour after the addition of n-propylamine. The solvent THF was removed with a rotary evaporator at room temperature. Finally, after being washed in methanol for three cycles, the polymer was vacuumed at 120 ºC for 1 day before use. HS-PS with different molecular weights (M_n=1.0 kg/mol, PDI=1.08) and (M_n=21.0 kg/mol, PDI=1.09) were synthesized by varying in the quantity of reagents and the reaction time with otherwise identical aforementioned conditions from Table S1.

^{1}H NMR of HS-PS (M_n=4.4 kg/mol) ($CDCl_3$): δ 6.37-7.31 (br, 5H, Ph), 1.85 (br, 1H, C*H*CH$_2$), 1.37 (br, 2H, CHC*H*$_2$) (Figure S2).

TTC-PS was synthesized through the thermal-initiation polymerization of styrene (Figure S3). Take the synthesis of TTC-PS (5.0 kg/mol) for example. Add styrene (54.54 g, 0.60 mol) and chain transfer agent DBTTC (0.1450 g, 0.5 mmol) into a Schlenk bottle. After three cycles of freeze-pump-thaw treatment, heat the reaction solution at 110 ºC under stirring. After 4.5 hours, the solution was cooled to room temperature, and then the residual styrene was removed with a rotary evaporator at 50 ºC. Finally, after being washed in methanol for three cycles, the polymer was vacuumed at 120 ºC for 1 day before use. TTC-PS with different molecular weights (M_n =5.0 kg/mol and (M_n =18.0 kg/mol) were synthesized by varying in the quantity of reagents and the reaction time with otherwise identical aforementioned conditions from Table S2. ^{1}H NMR of TTC-PS (M_n=4.4 kg/mol) ($CDCl_3$): δ 6.37-7.31 (br, 5H, Ph), 1.85 (br, 1H, C*H*CH$_2$), 1.37 (br, 2H, CHC*H*$_2$) (Figure S4)

3. Synthesis of Al NCs.

All the syntheses and purification were performed in a glove box under a water- and oxygen-free atmosphere. The precursor $H_3Al(1\text{-}MP)$ was synthesized according to previously reported protocols. In a typical synthesis of Al NCs, take the CDTB-PS (4.5 kg/mol) for example. A mixture of THF (4.325 ml) and CDTB-PS solution (75 µl, 20 mM in THF) were heated to 50 ºC. Under vigorous stirring (500 r.p.m.), a toluene solution of $H_3Al(1\text{-}MP)$ (500 µl, 0.50 M) was added to the mixture, immediately followed by adding a $Ti(i\text{-}PrO)_4$ solution (100 µl, 10 mM in THF) to catalyst the decomposition of $H_3Al(1\text{-}MP)$. The reaction solution was stirred for 2 minutes after the addition of $Ti(i\text{-}PrO)_4$, and then it was incubated at 50 ºC for 4 hours. The solution was cooled down to room temperature and purified by three cycles of centrifugation at 2,000 rcf for 10 min with THF. After the synthesis, an amorphous oxidation layer (4 nm thick) forms on the surface of Al NCs only after exposure to air.[2] No Ti was detected in the Al NC samples by energy-dispersive X-ray spectrometer spectroscopy (EDS) and inductively coupled plasma (ICP) measurements.[2]

4. Characterizations

TEM imaging were carried out with a Hitachi H-800 at 200 kV. The synthesized nanocrystals were dispersed in THF and dropped on a carbon-coated 300 mesh TEM grid under ambient condition. X-Ray diffraction (XRD) measurements of Al NCs drop-coated onto glass substrates were carried out on an Empyrean (Panalytical B.V.) operating at a voltage of 40 kV. Gel permeation chromatography (GPC) measurements were performed in THF using an Agilent 1260 Infinity chromatograph equipped with an Agilent column (PLgel 5-µm Mixed-D, 300 mm × 7.5 mm). An Agilent G1362A refractive index detector (RID) was employed. THF (flow rate of 1.0 mL/min) was used as eluent at 35 ºC. The columns were calibrated with linear polystyrene standards (200-200,000 Da).

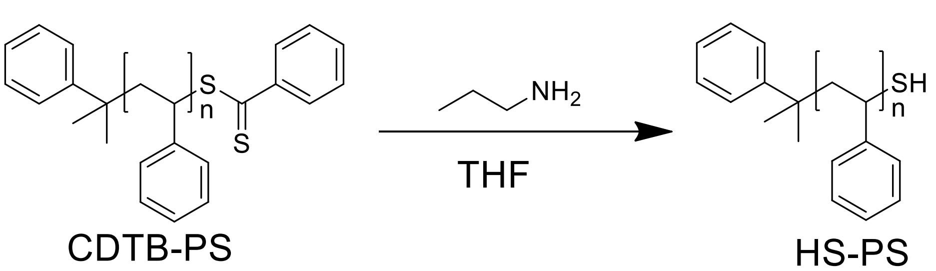


Figure S1 Schematic synthesis of HS-PS.

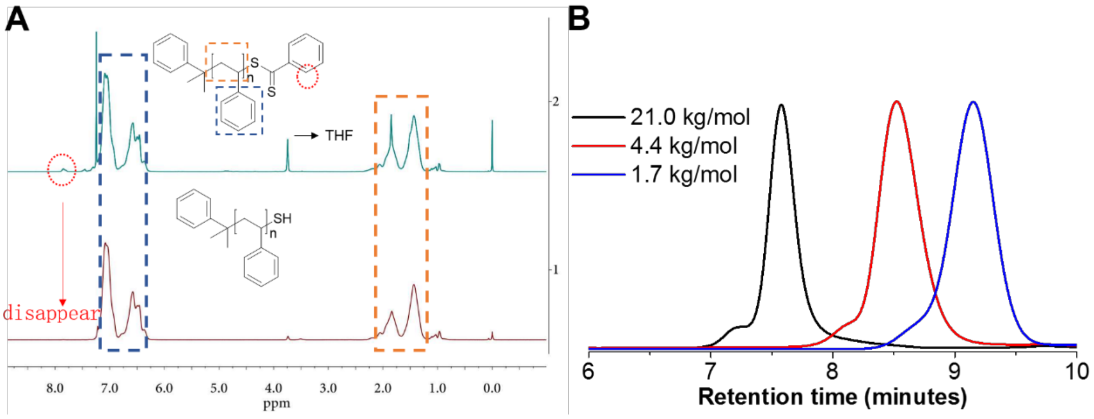


Figure S2. (a) ^{1}H NMR spectrum of CDTB-PS (4.5 kg/mol) (top) HS-PS (4.4 kg/mol) (bottom). The signal of ^{1}H NMR of CDTB-PS at 7.85 (br, -S-CS-C_6H_5) disappear, indicating the formation of HS-PS. (b) Gel permeation chromatography (GPC) elution curves of HS-PS with different molecular weights (blue line: M_n=1.0 kg/mol, red line: M_n=4.4 kg/mol, and black line: M_n=21.5 kg/mol).

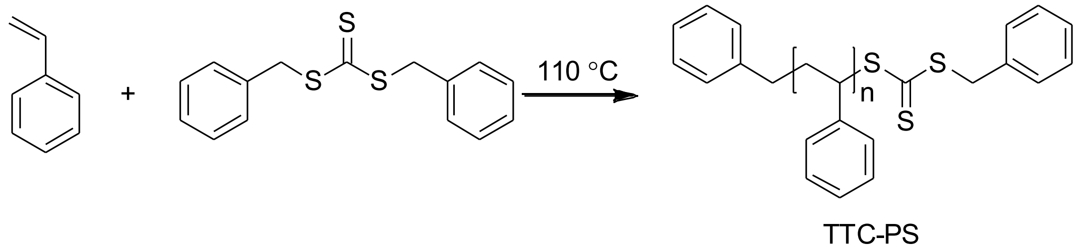


Figure S3 Schematic synthesis of TTC-PS.

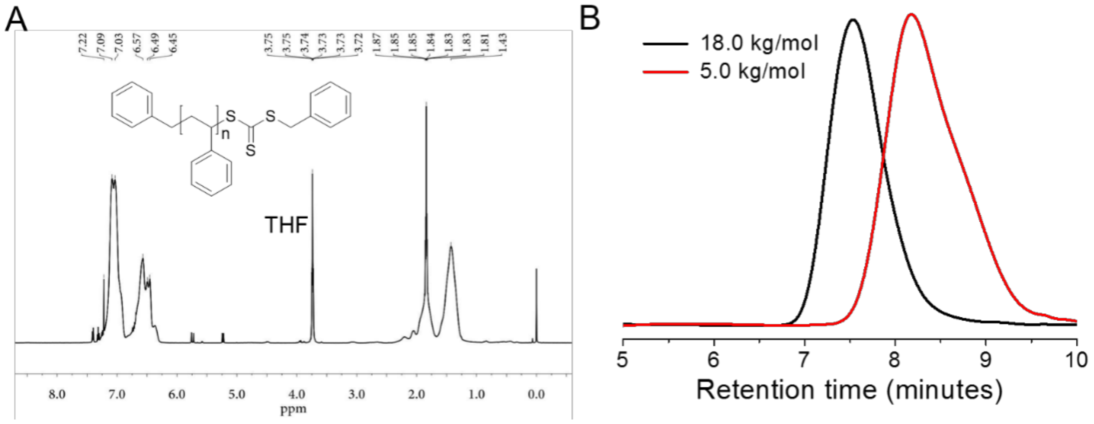


Figure S4 (A) ^{1}H NMR spectrum of TTC-PS (5.0 kg/mol). (B) GPC elution curves of TTC-PS with different molecular weights (red line: M_n=5.0 kg/mol, and black line: M_n=18.0 kg/mol).

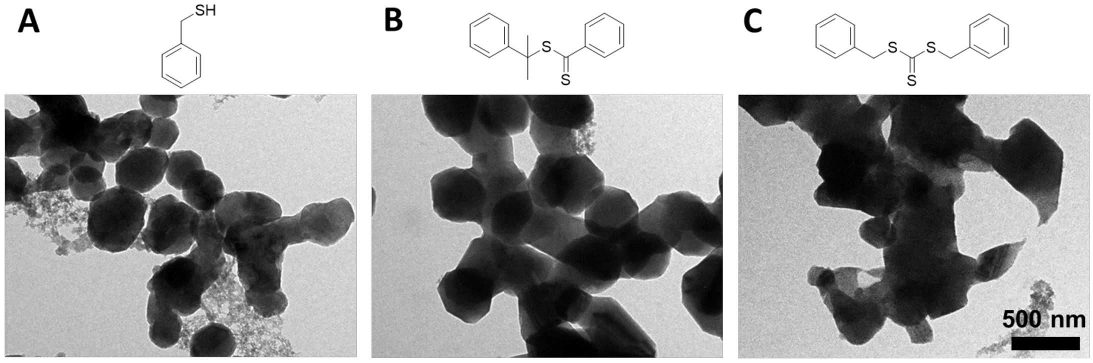


Figure S5 TEM images (A to C) of Al NCs synthesized at 0.30 mM benzyl mercaptan, cumyl dithiobenzonate , and dibenzyl trithiocarbonate, respectively.

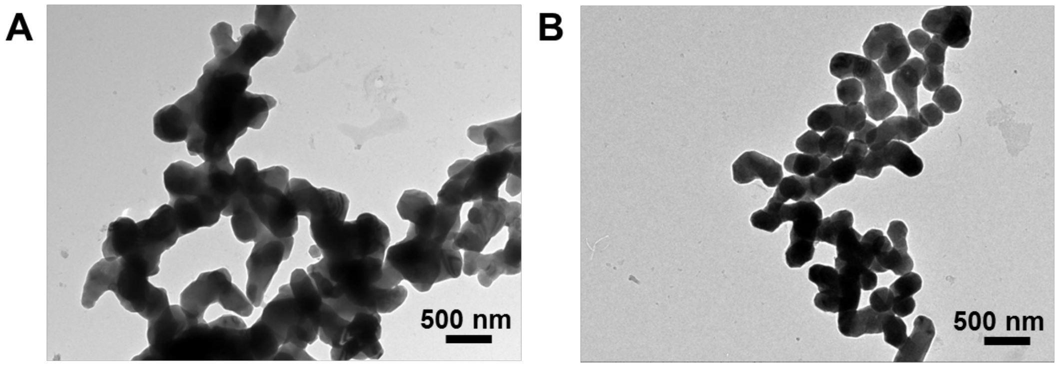


Figure S6 TEM images of Al NCs synthesized with (A) HS-PS (1.0 kg/mol, 0.30 mM) and (B) CDTB-PS (1.1 kg/mol, 0.30 mM).

Table S1 Experimental conditions for synthesis of HS-PS with different molecular weights.

CDTB-PS M_n (kg/mol)	CDTB-PS (g)	N-propy lamine (mL)	Reaction time (minutes)	THF (mL)	HS-PS M_n (kg/mol)	PDI
1.1	1.34	5	15	20	1.0	1.08
4.5	1.27	3	15	21	4.4	1.07
21.5	1.57	2.5	15	15	21.0	1.09

Table S2 Experimental conditions for synthesis of TTC-PS with different molecular weights.

Styrene (g)	DBTTC (g)	Reaction time (hour)	TTC-PS M_n (kg/mol)	PDI
54.54	0.4532	6	5.0	1.51
54.54	0.1450	4.5	18.0	1.32

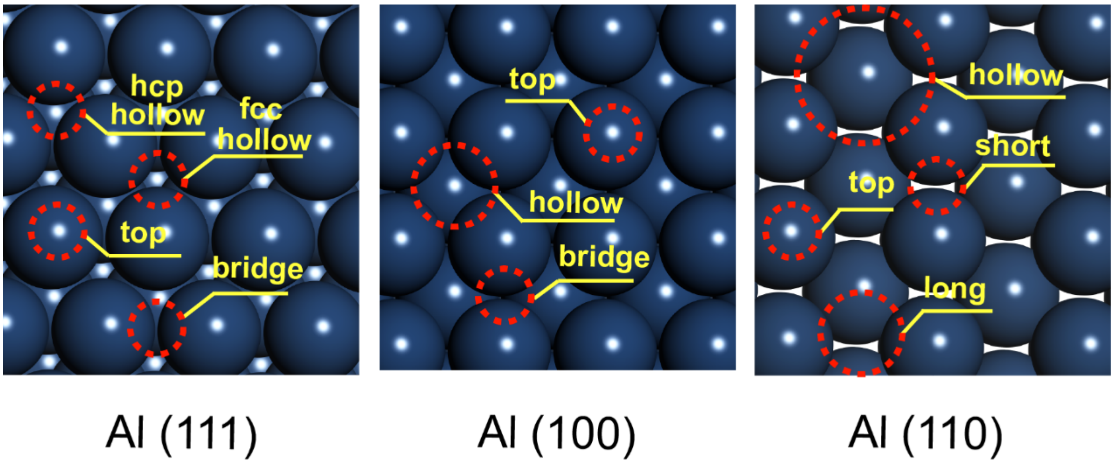
5. Theoretical calculations

All density functional theory (DFT) calculations were performed by the Vienna ab initio simulation package (VASP)[4-7] based on plane-wave basis pseudopotential method. The exchange-correction function was described by the PerdewBurke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA).[8] The electron−ion interactions were treated by Blöchl's all-electron-like projector augmented wave (PAW) method.[9] The plane-wave cutoff for the wave functions was 400 eV throughout. The polymer ligands were modelled for short PS chain with a few repeating units to facilitate the calculations. The Al (111), Al (100) and Al (110) facets were represented by (5 × 5) supercells consisting of repeated four-layer slabs and separated by a vacuum thickness of 20 Å, which was enough to avoid interaction between the surfaces of neighboring slabs. The Brillouin zone integration was performed using a cell size dependent Monkhorst–Pack k point sampling[10] and the k-point mesh was 3 × 3 × 1 for surface reconstruction and single-molecule adsorption. The initial arrangements for the adsorbed polymer ligands on Al surfaces were chosen according to the experimental suggestions, in which the HS-PS molecules were hinted as preferring the standing-up structure on metal surfaces, while CDTB-PS and TTC-PS molecules were supposed to adopt the lying-down structure on metal surfaces. The optimizations of these initial structures were further performed via locating the S atoms of the C=S functional group of ligand molecules on different high-symmetry sites of various Al facets (see Figure S6). During the total energy calculations, the adsorbed ligand molecule and the top three layers of aluminum atoms were allowed to relax in their positions to reach the most stable configuration, whereas the aluminum atoms of the bottom layer were frozen at their bulk positions to simulate the bulk and reduce the computational cost. Ionic relaxation for all stable structures were carried out until all forces were smaller than 0.02 eV $Å^{-1}$.

The adsorption energy for ligand molecules on Al was calculated as follows:

$$\Delta E_{ads/Al} = E_{ligand/Al} - E_{ligand} - E_{Al} \qquad (S1)$$

where $E_{ligand/Al}$ is the total energy of the Al surface together with the adsorbed ligand, E_{ligand} is the total energy of the free ligand, and E_{Al} is the total energy of the bare Al surface. With this method, the negative values of $E_{ads/Al}$ suggest that the adsorptions of free ligands on the aluminum surface are energetically favorable processes. The computed adsorption energies and the optimized configurations for different ligand molecules are listed in Table S3, S4 and S5.



Al (111) Al (100) Al (110)

Figure S7. Top views of Al (111), Al (100) and Al (110) facets as well as the high-symmetry adsorption sites.

Table S3. Computational results on the structures and energies for HS-PS molecules with the standing-up geometry adsorbed at the high-symmetry sites of Al (111), Al (100) and Al (110).

Crystal face	**Initial site**[a]	**Optimized site**[a]	$d_{\text{S-Al}}$ **(nm)**[b]	E_{Al} **(eV)**	$E_{\text{HS-PS}}$ **(eV)**	$E_{\text{HS-PS/Al}}$ **(eV)**	$\Delta E_{\text{ads/Al}}$ **(eV)**	$\Delta E_{\text{ads/Al}}$ **(kcal/mol)**
Al (111)	top	bridge-fcc	0.230	-355.524	-514.406	-872.038	-2.108	-48.612
	hcp	hcp	0.240	-355.524	-514.406	-872.033	-2.104	-48.515
	fcc	hcp	0.244	-355.524	-514.406	-872.190	-2.260	-52.123
	bridge	bridge-fcc	0.241	-355.524	-514.406	-872.190	-2.260	-52.111
Al (100)	top	bridge-hollow	0.228	-346.319	-514.406	-867.180	-6.455	-148.857
	hollow	hollow	0.237	-346.319	-514.406	-867.357	-6.632	-152.947
	bridge	bridge-hollow	0.240	-346.319	-514.406	-867.418	-6.693	-154.355
Al (110)	top	top-hollow	0.228	-341.058	-514.406	-857.939	-2.474	-57.061
	hollow	hollow-short	0.235	-341.058	-514.406	-857.753	-2.288	-52.769
	long	long	0.229	-341.058	-514.406	-857.517	-2.053	-47.341
	short	short	0.238	-341.058	-514.406	-857.774	-2.310	-53.270

[a] The adsorption site in the initial and optimized structures, respectively.

[b] The distance between the S atom of the C-S functional group and the nearest neighboring Al atom on the surface.

Table S4. Computational results on the structures and energies for CDTB-PS molecules with the lying-down geometry adsorbed at the high-symmetry sites of Al (111), Al (100) and Al (110).[2]

Crystal face	Initial site[a]	Optimized site[a]	$d_{\text{S-Al}}$ (nm)[b]	E_{Al} (eV)	$E_{\text{CDTB-PS}}$ (eV)	$E_{\text{CDTB-PS/Al}}$ (eV)	$\Delta E_{\text{ads/Al}}$ (eV)	$\Delta E_{\text{ads/Al}}$ (kcal/mol)
Al (111)	top	top	0.234	-355.524	-295.487	-651.522	-0.512	-11.797
	hcp	hcp	0.244	-355.524	-295.487	-651.672	-0.662	-15.260
	fcc	fcc	0.238	-355.524	-295.487	-651.639	-0.628	-14.482
	bridge	bridge	0.241	-355.524	-295.487	-651.608	-0.597	-13.769
Al (100)	top	bridge	0.238	-346.319	-295.487	-646.542	-4.736	-109.226
	hollow	hollow	0.250	-346.319	-295.487	-646.834	-5.028	-115.959
	bridge	hollow	0.246	-346.319	-295.487	-646.745	-4.940	-113.910
Al (110)	top	hollow	0.238	-341.058	-295.487	-636.991	-0.446	-10.285
	hollow	short	0.238	-341.058	-295.487	-637.071	-0.526	-12.125
	long	long	0.276	-341.058	-295.487	-637.070	-0.525	-12.107
	short	short	0.236	-341.058	-295.487	-637.084	-0.538	-12.416

[a] The adsorption site in the initial and optimized structures, respectively.

[b] The distance between the S atom of the C=S functional group and the nearest neighboring Al atom on the surface.

Table S5. Computational results on the structures and energies for TTC-PS molecules with the lying-down geometry adsorbed at the high-symmetry sites of Al (111), Al (100) and Al (110).

Crystal face	Initial site[a]	Optimized site[a]	$d_{\text{C-Al}}$ (nm)[b]	$d_{\text{S-Al}}$ (nm)[b]	E_{Al} (eV)	$E_{\text{DBCBTT-PS}}$ (eV)	$E_{\text{DBCBTT-PS/Al}}$ (eV)	$\Delta E_{\text{ads/Al}}$ (eV)	$\Delta E_{\text{ads/Al}}$ (kcal/mol)
Al (111)	top	top	2.141	2.443	-355.524	-315.541	-672.613	-1.548	-35.697
	hcp	hcp	2.133	2.506	-355.524	-315.541	-672.589	-1.524	-35.144
	fcc	fcc	2.132	2.508	-355.524	-315.541	-672.526	-1.461	-33.691
	bridge	bridge	2.133	2.554	-355.524	-315.541	-672.504	-1.439	-33.184
Al (100)	top	top	2.124	2.296	-346.319	-315.541	-667.377	-5.517	-127.224
	hollow	hollow	2.100	2.487	-346.319	-315.541	-666.823	-4.963	-114.449
	bridge	bridge	2.099	2.538	-346.319	-315.541	-667.102	-5.242	-120.882
Al (110)	top	top	2.140	2.441	-341.058	-315.541	-657.983	-1.384	-31.916
	hollow	short	2.133	2.506	-341.058	-315.541	-657.404	-0.805	-18.564
	long	long	2.132	2.508	-341.058	-315.541	-657.538	-0.939	-21.654
	short	short	2.133	2.527	-341.058	-315.541	-657.778	-1.179	-27.18818

[a] The adsorption site in the initial and optimized structures, respectively.

[b] The distance between the C or S atom of the C=S functional group and the nearest neighboring Al atom on the surface.

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