Electronic Supplementary Information (ESI) for

Tuning the liquid-phase exfoliation of arsenic nanosheets by the interaction with various solvents

Zheng-Hang Qi,† Yi Hu,† Zhong Jin* and Jing Ma*

Table of Contents

Computational methods

All DFT calculations were performed by using the plane-wave technique as implemented in Vienna Ab-initio Simulation Package.[1,2] The projector-augmented wave method for the ion–electron interaction were employed. The exchange-correlation potential and long-range dispersion interaction was described by optPBE-vdW functional.[3] The cutoff energy for the plain waves was set to be 500 eV, and the convergence for the total energy was 10^{-5} eV. A vacuum layer of 30 Å was used in the simulation, which is sufficient for excluding the repeated image interactions. The Monkhorst–Pack (MP) set of 7 × 7 × 1 *k*-points for the geometry relaxation and 14 × 14 × 1 for electronic structures were used to sample the Brillouin zone. The isolated solvent molecule was calculated in a unit cell of 20 × 20 × 20 $Å^3$, with an 11 × 11 × 11 MP *k*-points mesh. All atoms in the unit cell were fully relaxed until the total energy convergence of 10^{-5} eV was met and the force on each atom was less than 0.02 eV $Å^{-1}$. The adsorption energy is defined by the formula: $E_{ads} = E_{total} - E_{As} - E_{sol}$, where E_{total} is the total energy of arsenene with adsorbed solvent and E_{As} and E_{sol} are individual energies of pristine arsenene and isolated solvent respectively. The charge transfer was estimated by Bader charge analysis.[4]

Experimental methods

Exfoliation of arsenic crystals: the exfoliation of arsenic crystals in organic solvents were performed via a sonication process. Firstly, 100 mg of gray arsenic powder (Aladdin Aldrich) were added into 10 mL of chloroform, tetrahydrofuran (THF) and cyclohexane in glass vials, respectively. All solvents were >98% pure, purchased from Aladdin Aldrich and used as supplied. Additionally, the O_2 in the glass vials were exhausted by Ar gas injection. The three kinds of mixtures were then sonicated in batch using a Shanghai Kunshan Corp sonic bath (60 W, 40 kHz) for 300 min at a constant temperature of 20 °C. Subsequently, the resulting dispersions were centrifuged at a speed of 1000 r.p.m. (90*g*, g = 9.8 m/s^2) for 5 min to separate large size particles and arsenic nanosheets. The top 8 mL of suspensions were collected by pipette, followed by centrifuging at a speed of 8000 r.p.m. (5760*g*, g = 9.8 m/s^2) for 10 min. The radius of the centrifuge rotor is 8 cm. Finally, the supernatants were discarded and the sediments were dried in a vacuum drying oven. To define the concentration of exfoliated arsenic nanosheets, each suspension was vacuum filtered on AAO membranes with a pore size of ~50 nm. The concentration of the exfoliated arsenic nanosheets were determined by the weight difference of the dried AAO membrane before and after vacuum filtration.

Characterizations of arsenic nanosheets: For the transmission electron microscope (TEM) characterizations and size distributions analyses, the arsenic nanosheets were re-dispersed in ethyl alcohol solvent. The TEM characterizations were performed on a JEM-2100 system with an operating voltage of 200 kV. The size distributions of arsenic nanosheets were determined by a dynamic laser scattering (DLS, Bruker BI-200SM) with a laser of 640 nm wavelength at 25 °C. Atomic Force Microscope (AFM) characterizations were performed using a Bruker Dimension Icon instrument with scanAsyst model and Sharp Nitride Lever (SNL) probes. X-ray photoelectron spectroscopy (XPS) were collected on a UIVAC VersaProbe PHI-5000 instrument with monochromatic AI-Kα X-ray radiation.

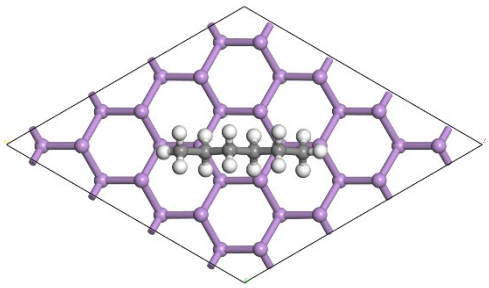
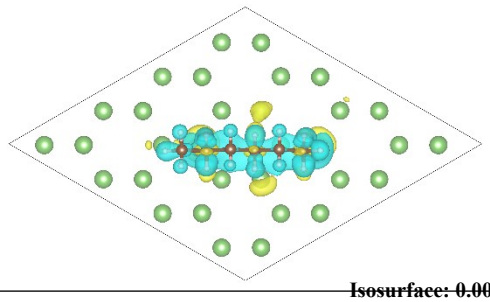
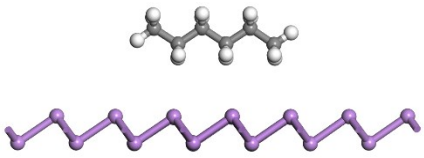
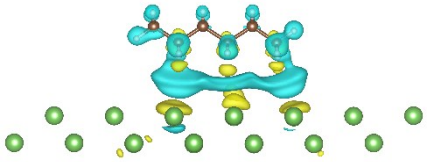
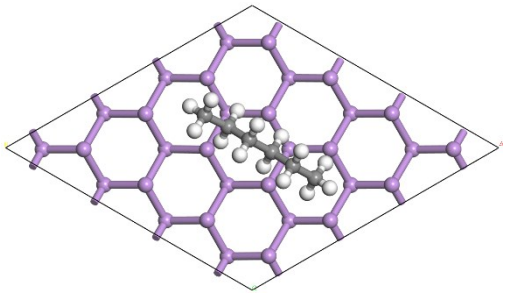
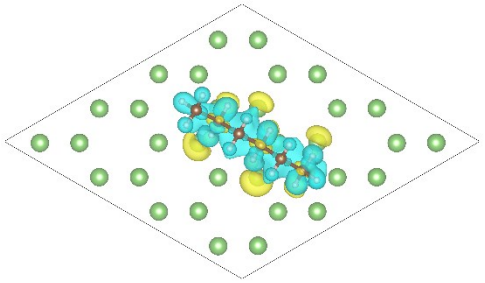
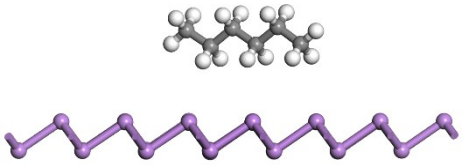
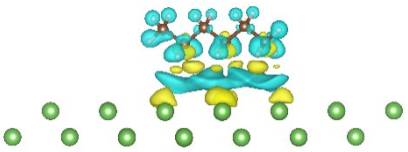
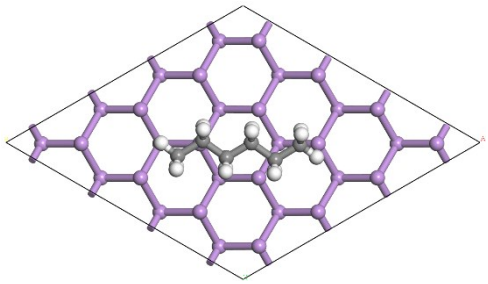
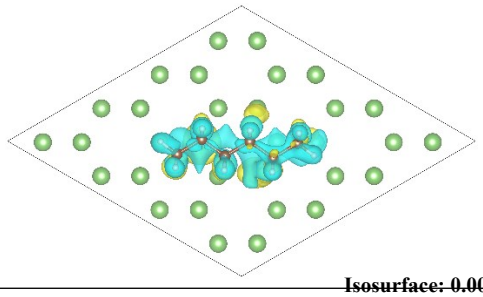
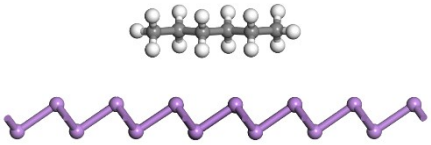
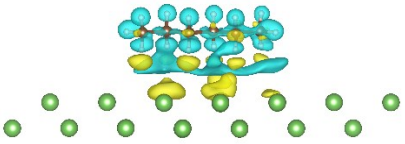
Cell viability assay: The cytotoxicity of different arsenic nanosheets exfoliated in different solvents (cyclohexane, tetrahydrofuran and chloroform) was determined by the CCK-8 assay. Cells cultured in 96-well plates were grown to confluence. The cells were first incubated for 16–24 h at 37 °C under 5% CO_2, then incubated for additional 24 h after mixing with arsenic nanosheets. Thereafter, 100 μL fresh culture medium (5% FBS) and 10 μL CKK-8 was added to each well and incubating for additional 2 h. An enzyme-linked immune sorbent assay (ELISA) reader was used to measure the absorbance value of each well with background substraction at 450 nm. The following formula was used to calculate the viability of the cell growth.

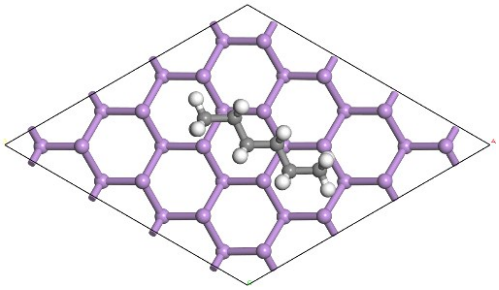
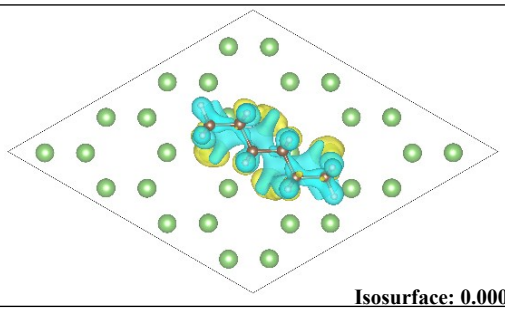
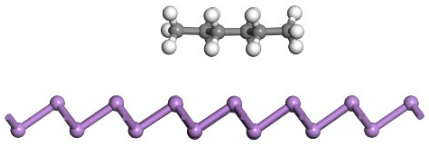
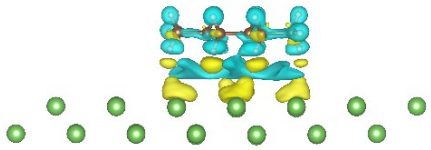
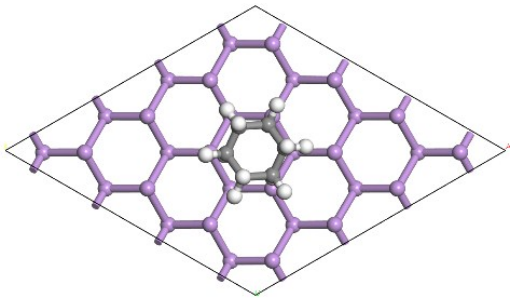
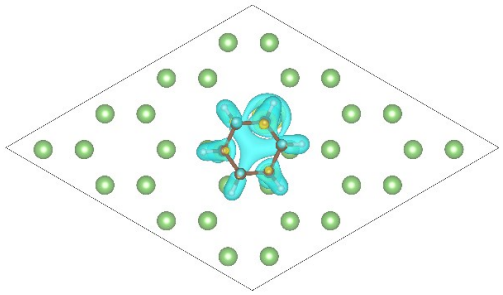
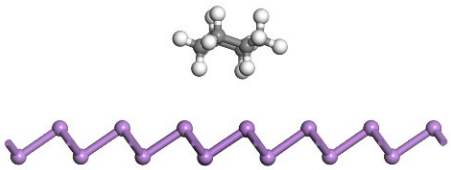
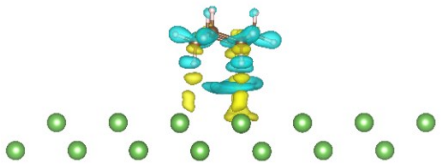
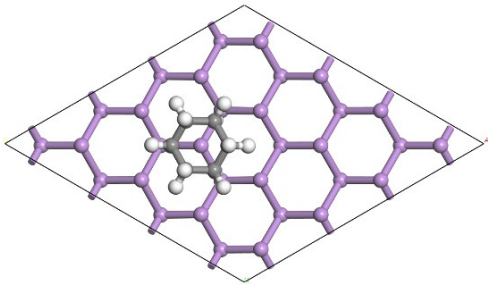
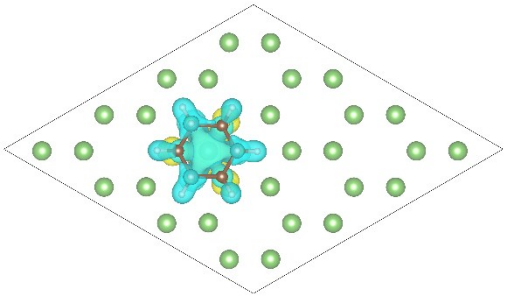
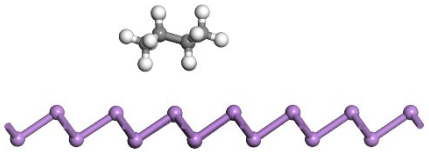
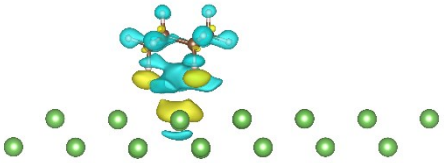
Cell viability (%) = (average of absorbance value of treatment group /average of A value of control)×100

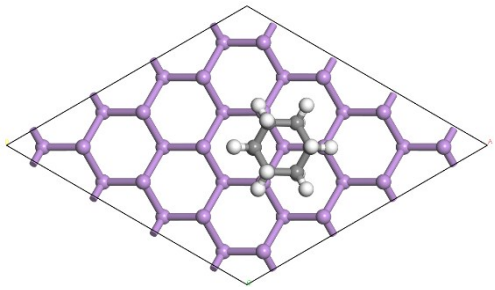
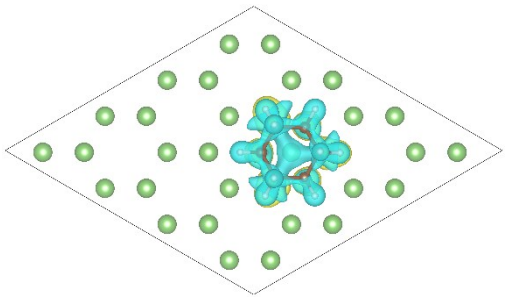
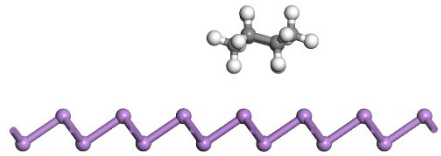
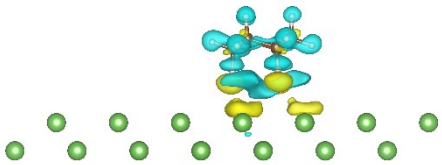
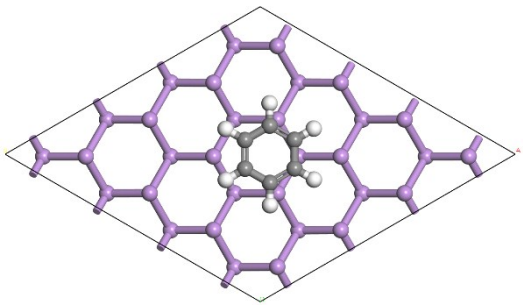
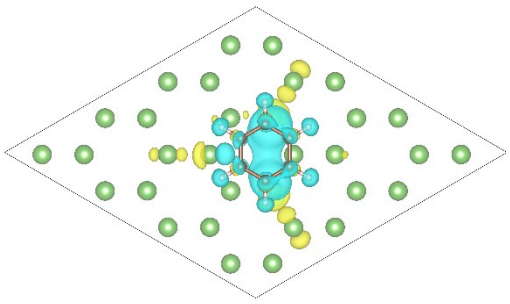
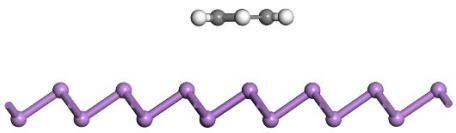
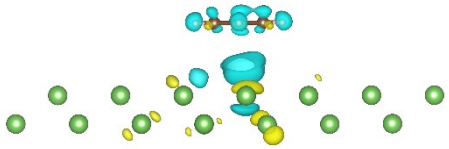
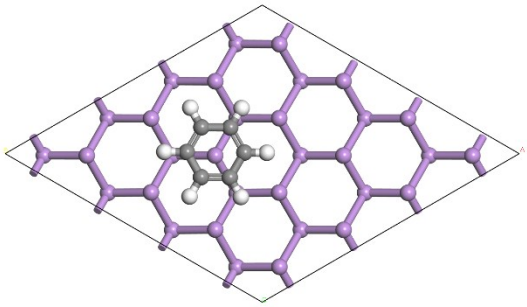
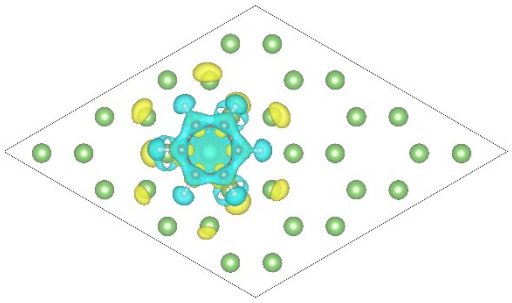
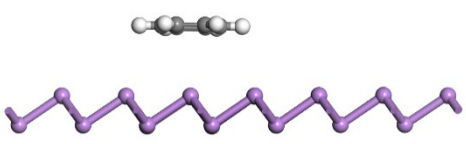
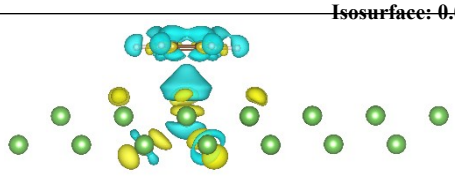
Table S1. The physical property (dielectric constant and p*K*a) and average computational results for all the solvents studied and experimental results for selected solvent.

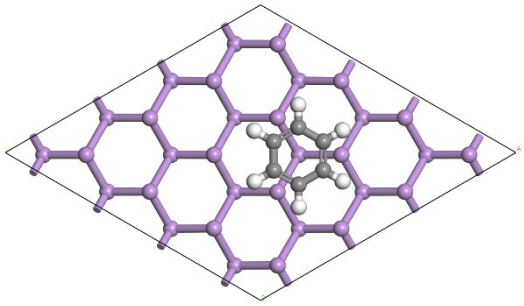
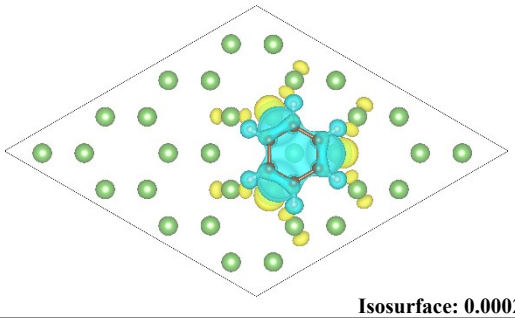
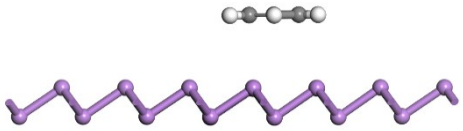
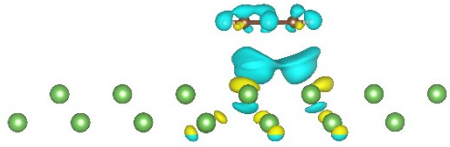
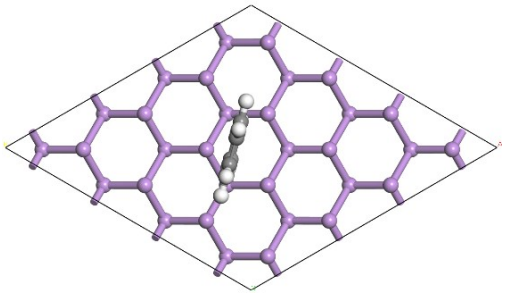
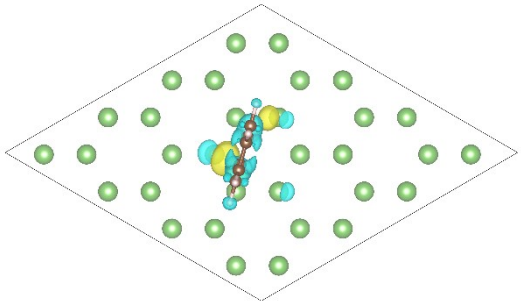
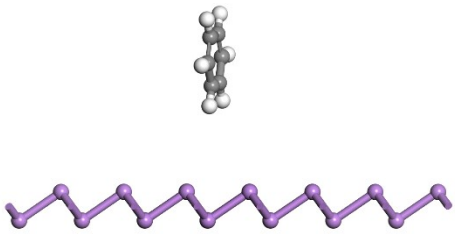
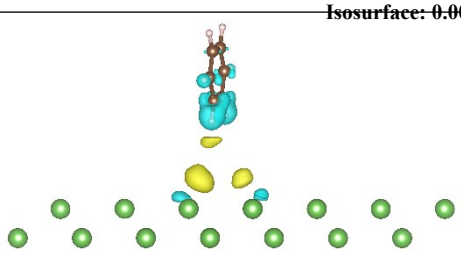
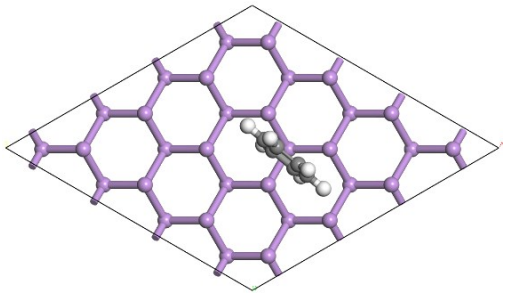
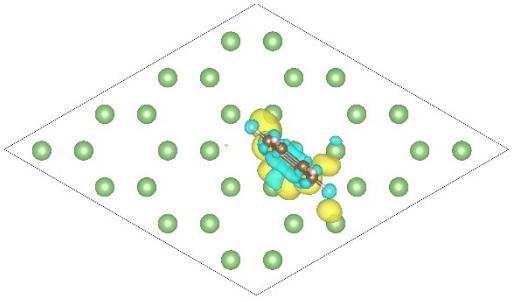
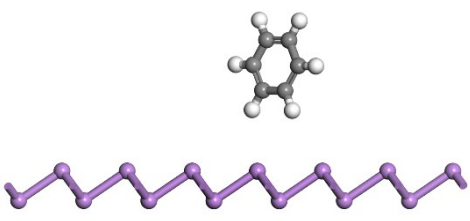
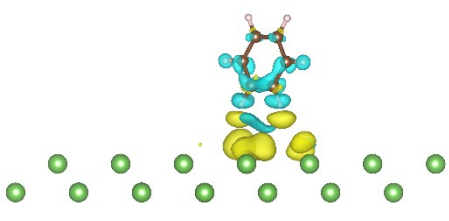
Solvent	**Physical Property**			**Average Computational Results**				**Experiment**
	Dielectric Constant	p*K*a	Surface Tension / mN/m	E_{ads} / eV	$E_{ads,per}$ / eV/nm^2	CT / e	CT_{per} / e/nm^2	Concentration/ mg/mL
Hexane	1.9	–	18	-0.51	-2.67	-0.0413	-0.216	–
Cyclohexane	2.0	–	24	-0.44	-2.20	-0.0348	-0.174	0.25
Benzene	2.3	–	28	-0.34	-2.40	-0.0106	-0.111	–
Chloroform	4.7	–	27	-0.38	-7.52	-0.0310	-0.642	1.41
Tetrahydrofuran	7.4	–	29	-0.45	-3.00	-0.0373	-0.249	0.66
Acetonitrile	35.7	–	29	-0.29	-3.60	-0.0218	-0.272	–
N,*N*-Dimethyl-formamide	37.2	–	40	-0.42	-2.98	-0.031	-0.220	–
Water	78.4	7.0	72	-0.13	-4.33	-0.0271	-0.904	–
Formic acid	51.1	3.8	37	-0.29	-3.58	-0.0472	-0.589	–
Methanol	32.6	15.5	22	-0.25	-4.11	-0.0380	-0.633	0.50
Ethanol	24.9	15.5	22	-0.25	-3.13	-0.0356	-0.445	–
2-Propanol	19.3	15.3	21	-0.32	-3.23	-0.0367	-0.367	–
Aniline	6.9	4.9	42	-0.26	-3.21	-0.0164	-0.205	–
Piperidine	4.3	11.1	29	-0.43	-2.15	-0.0203	-0.102	–

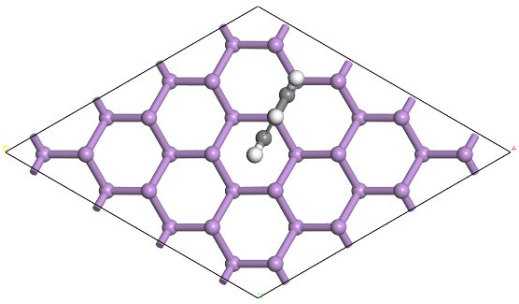
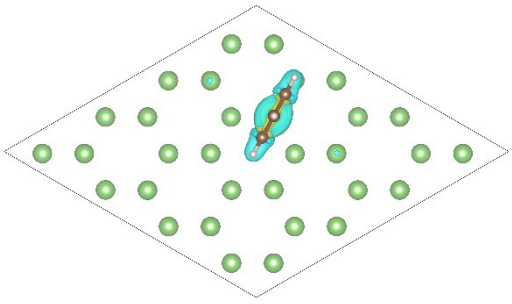
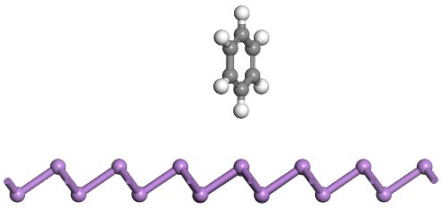
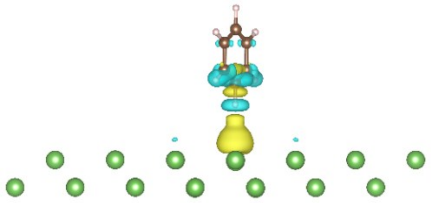
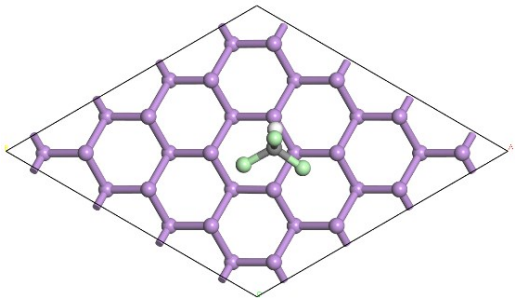
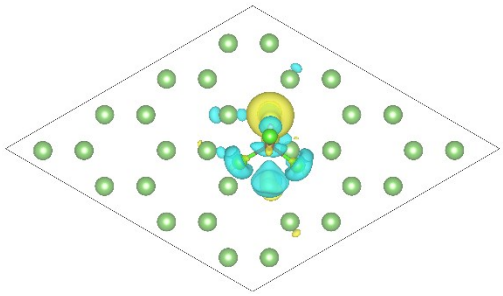
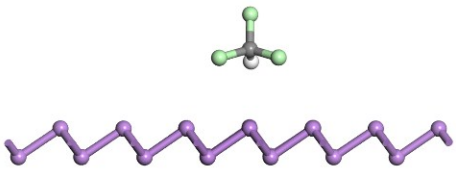
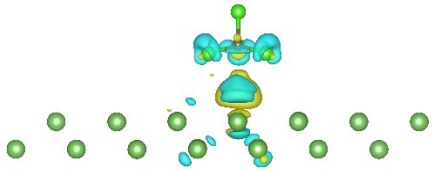
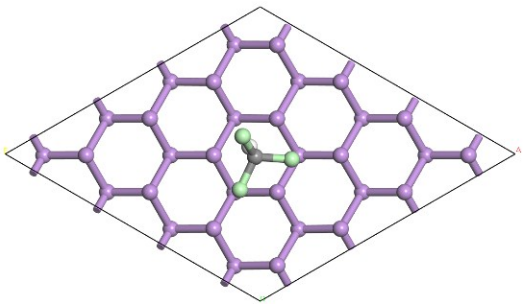
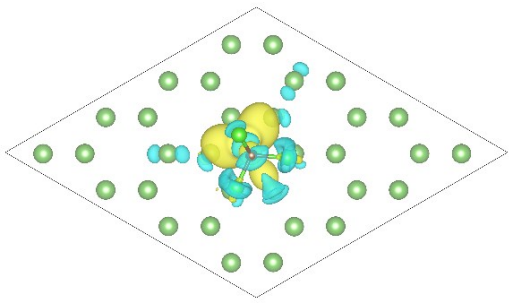
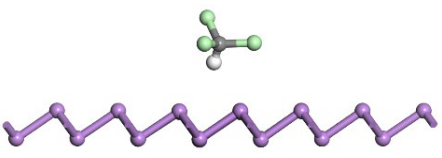
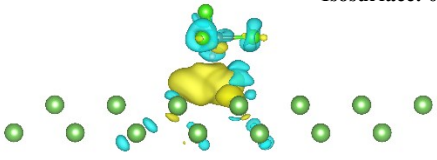
Scheme S1. Aprotic Solvents Adsorption on Arsenene.[a]

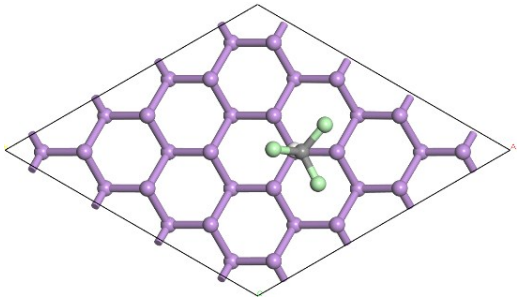
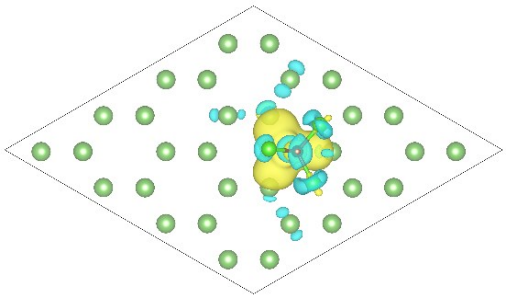
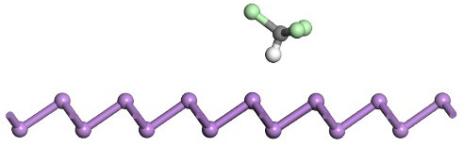
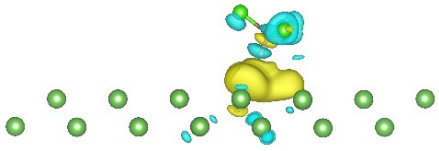
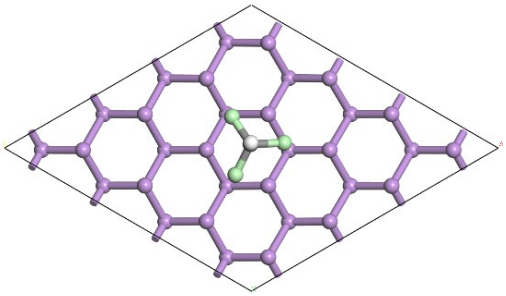
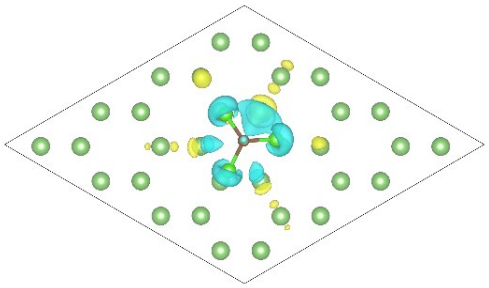
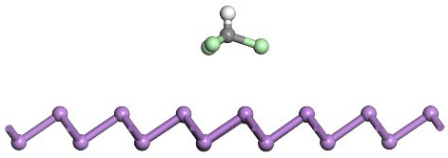
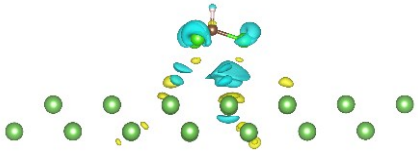
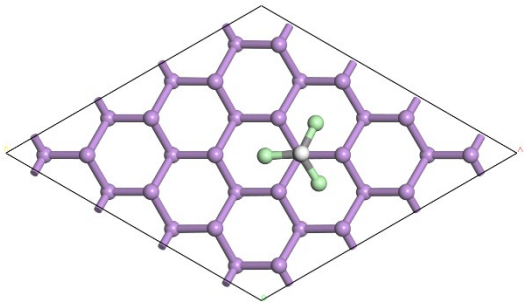
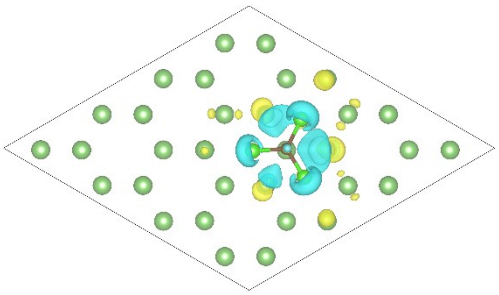
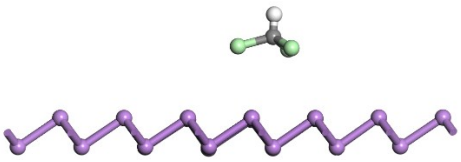
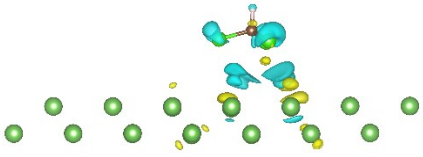
	Optimized geometries	*Charge transfer*
	Hexane	
(a1) *Top view*		 **Isosurface: 0.0001 e/Å³**
Side view		
	E_{ads} = –0.44 eV	**CT = –0.0310 e**
(a2) *Top view*		 **Isosurface: 0.0001 e/Å³**
Side view		
	E_{ads} = –0.48 eV	**CT = –0.0355 e**
(a3) *Top view*		 **Isosurface: 0.0001 e/Å³**
Side view		
	E_{ads} = –0.55 eV	**CT = –0.0483 e**

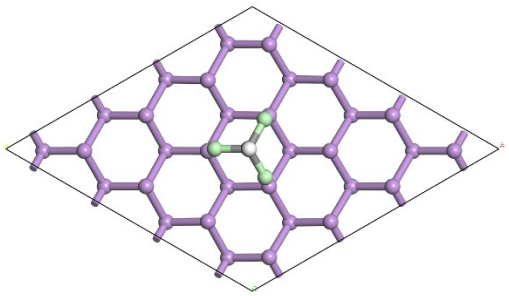
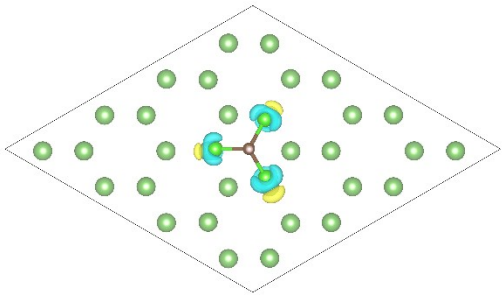
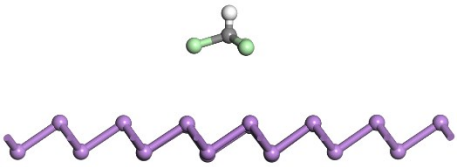
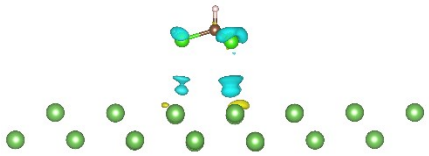
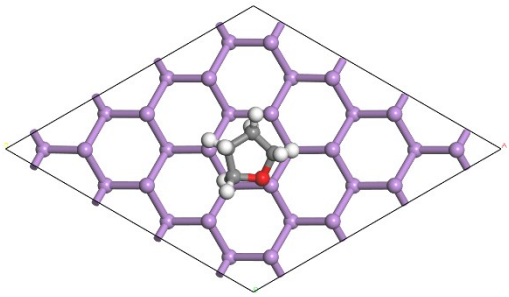
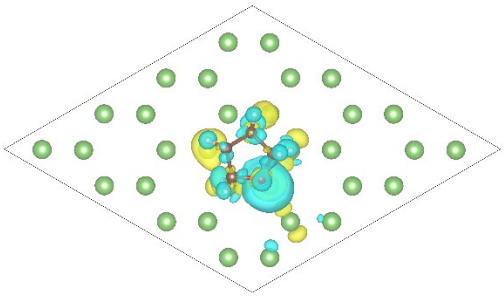
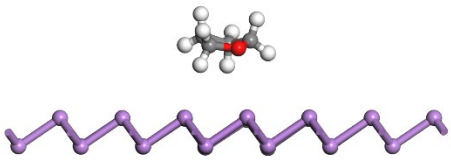
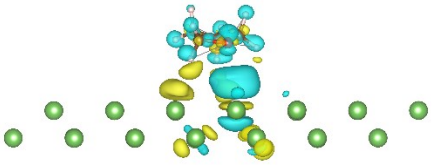
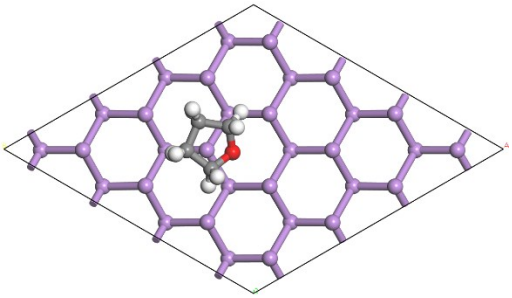
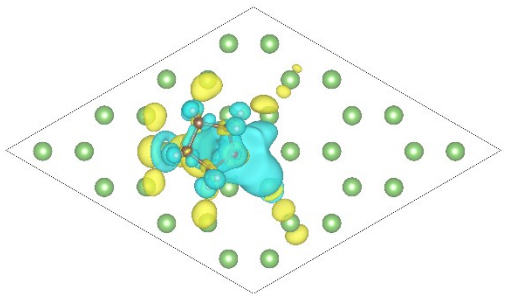
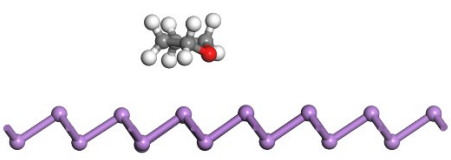
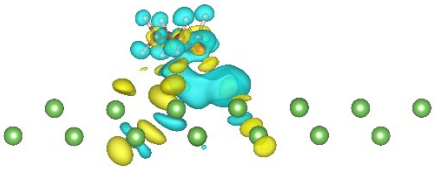
(a4)		
Top view		 Isosurface: 0.0001 e/Å^3
Side view		
	E_{ads} = –0.56 eV	CT = –0.0504 e
	Cyclohexane	
(b1)		
Top view		 Isosurface: 0.0001 e/Å^3
Side view		
	E_{ads} = –0.38 eV	CT = –0.0324 e
(b2)		
Top view		 Isosurface: 0.0001 e/Å^3
Side view		
	E_{ads} = –0.47 eV	CT = –0.0346 e

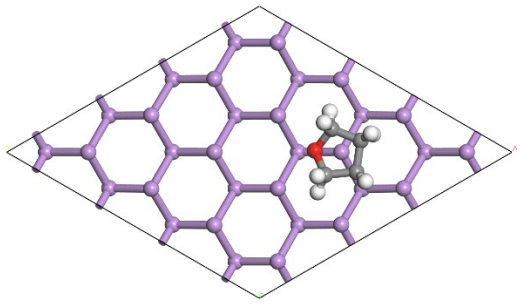
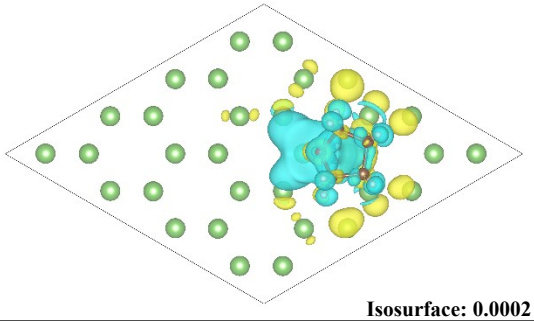
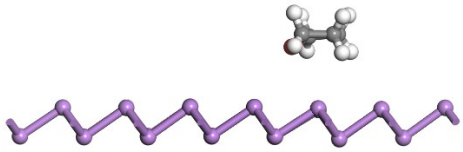
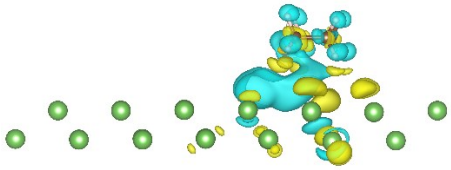
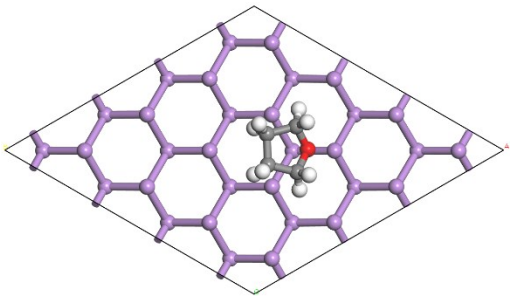
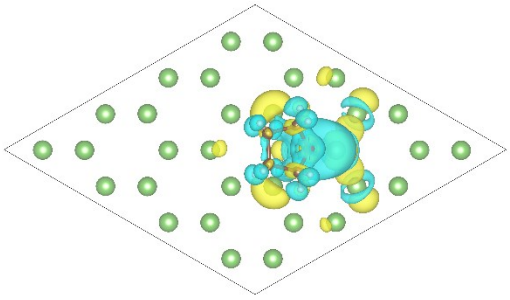
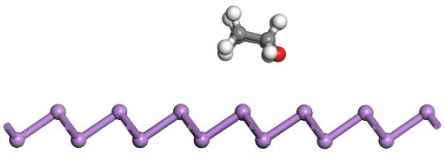
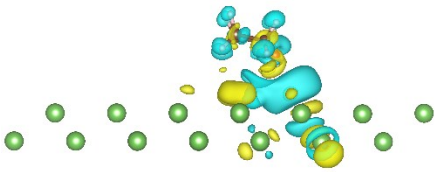
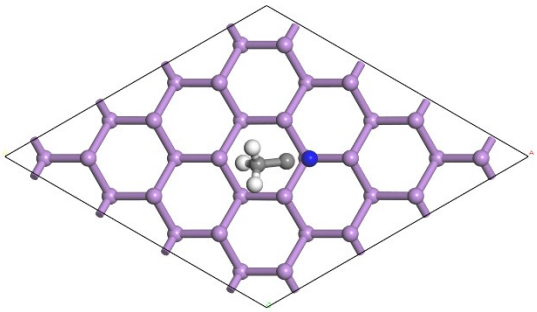
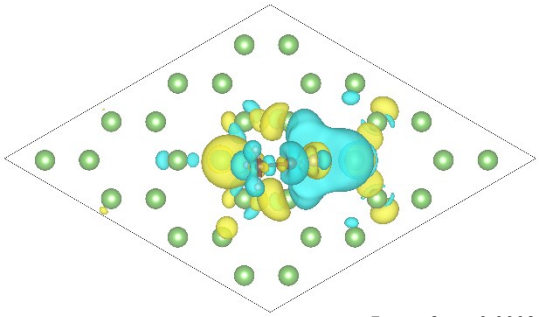
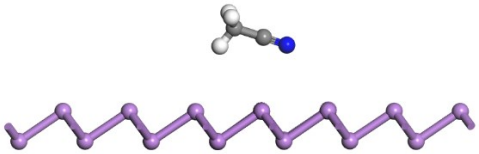
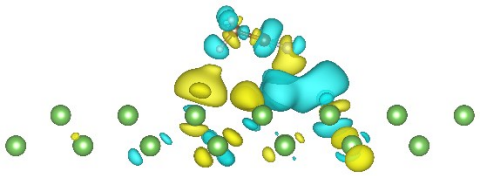
(b3)		
Top view		 **Isosurface: 0.0001 e/Å^3**
Side view		
	E_{ads} = –0.47 eV	**CT = –0.0373 e**
	Benzene	
(c1)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.46 eV	**CT = –0.0071 e**
(c2)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.53 eV	**CT = –0.0045 e**

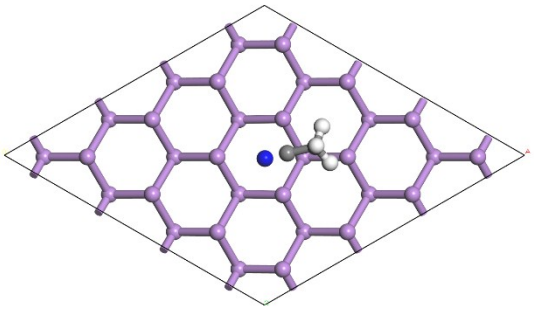
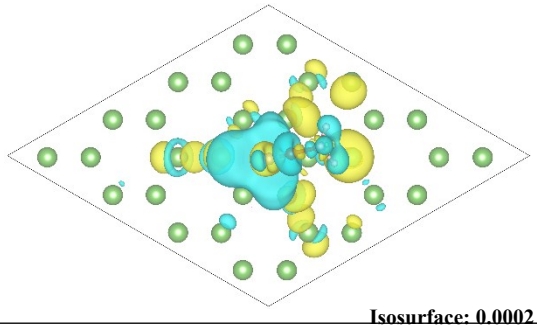
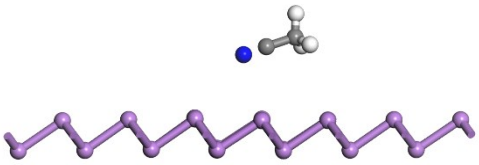
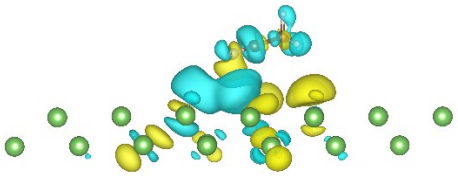
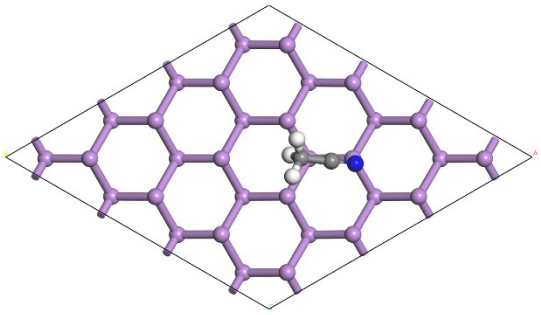
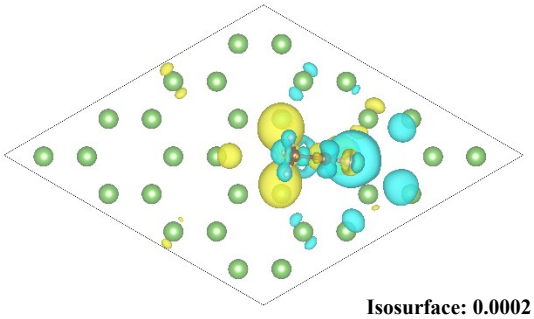
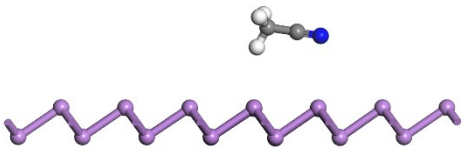
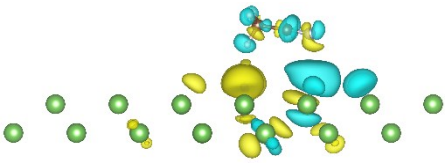
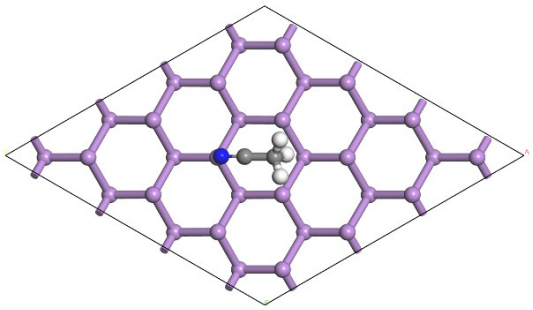
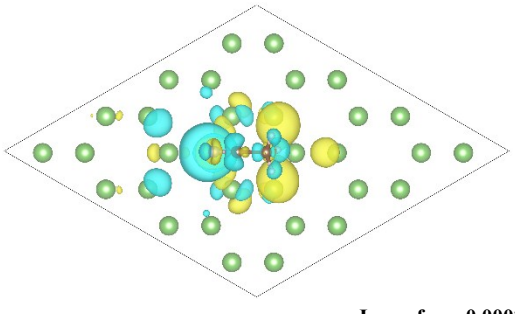
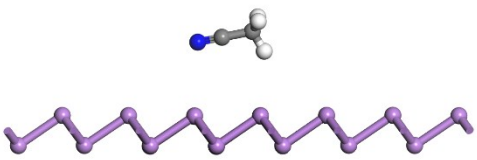
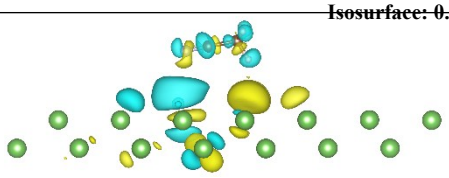
(c3)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.44 eV	**CT = –0.0057 e**
(c4)		
Top view		 **Isosurface: 0.00005 e/Å^3**
Side view		
	E_{ads} = –0.11 eV	**CT = –0.0053 e**
(c5)		
Top view		 **Isosurface: 0.0001 e/Å^3**
Side view		
	E_{ads} = –0.26 eV	**CT = –0.0213 e**

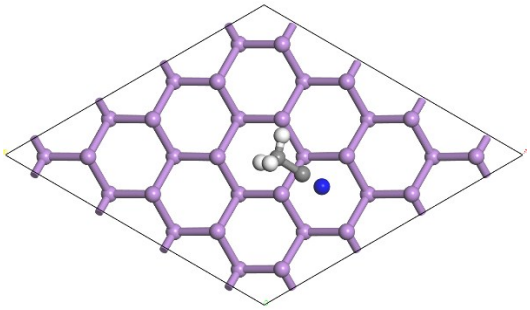
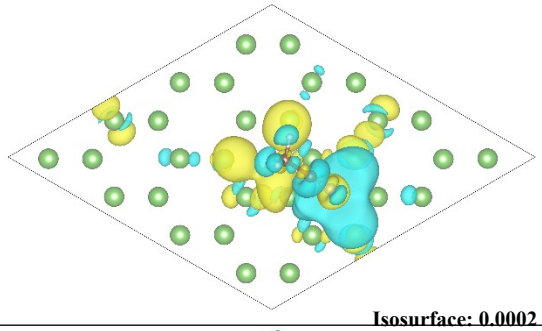
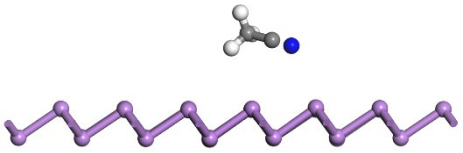
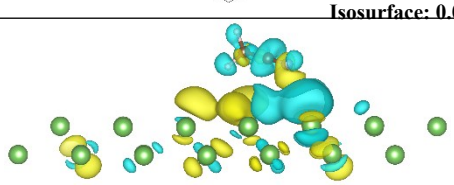
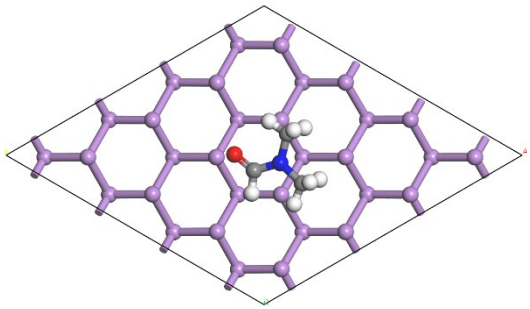
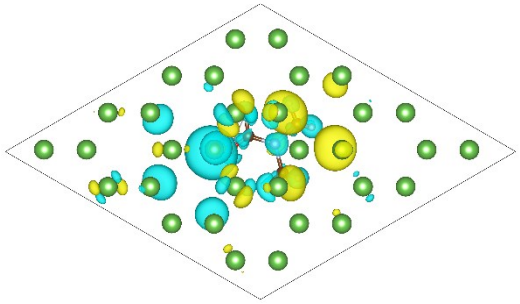
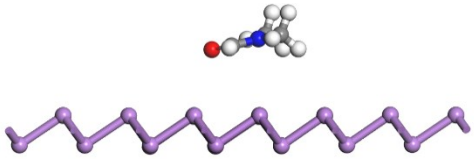
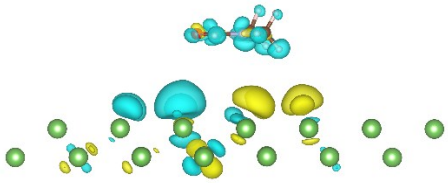
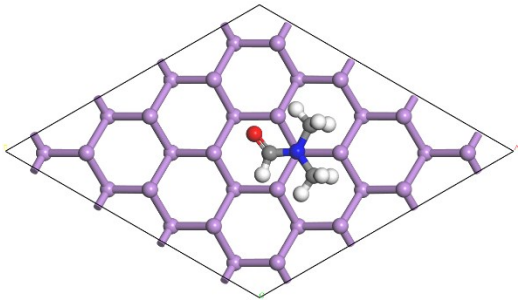
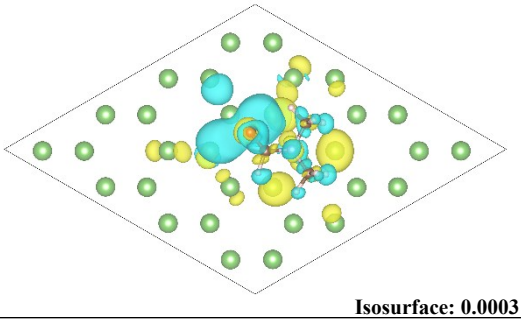
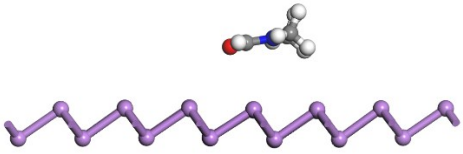
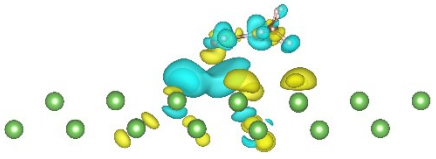
(c6)		
Top view		 Isosurface: 0.0001 e/Å^3
Side view		
	E_{ads} = –0.21 eV	CT = –0.0200 e
	Chloroform	
(d1)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.35 eV	CT = –0.0277 e
(d2)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.41 eV	CT = –0.0398 e

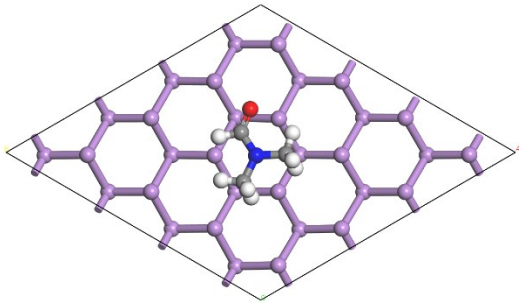
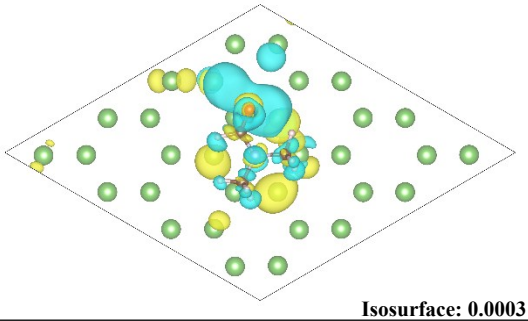
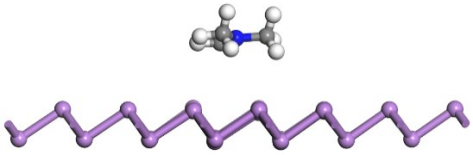
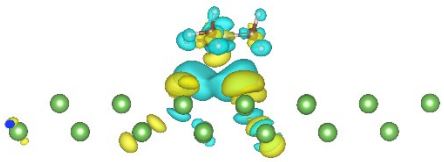
(d3)		
Top view		
		Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.41 eV	**CT = –0.0436 e**
(d4)		
Top view		
		Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.40 eV	**CT = –0.0284 e**
(d5)		
Top view		
		Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.39 eV	**CT = –0.0257 e**

(d6)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.32 eV	**CT = –0.0211 e**
	Tetrahydrofuran	
(e1)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.40 eV	**CT = –0.0350 e**
(e2)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.47 eV	**CT = –0.0388 e**

(e3)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.48 eV	**CT = –0.0400 e**
(e4)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.45 eV	**CT = –0.0355 e**
	Acetonitrile	
(f1)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.30 eV	**CT = –0.0216 e**

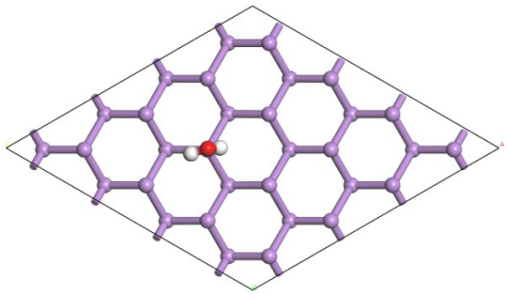
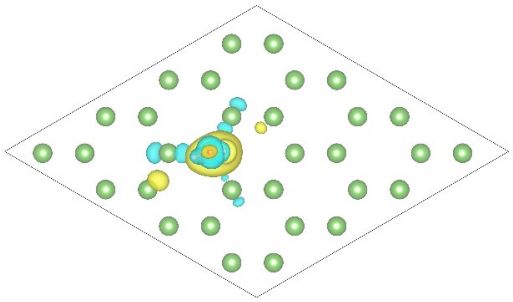
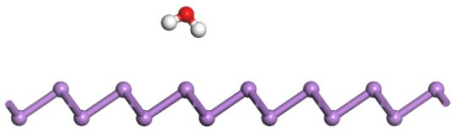
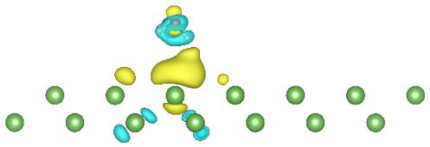
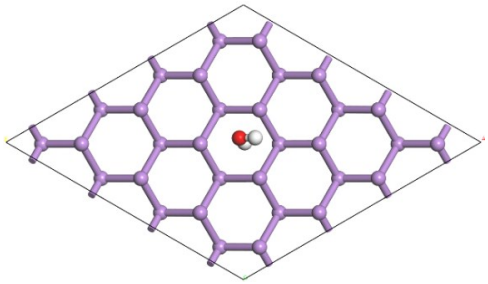
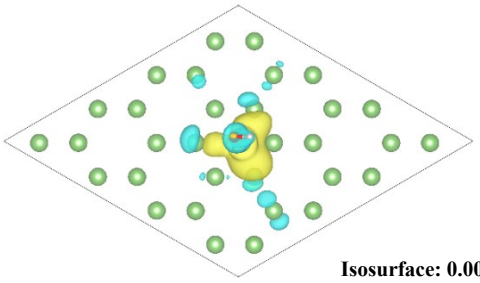
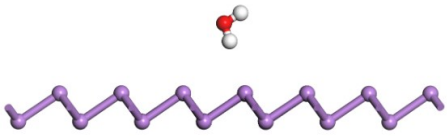
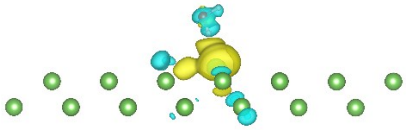
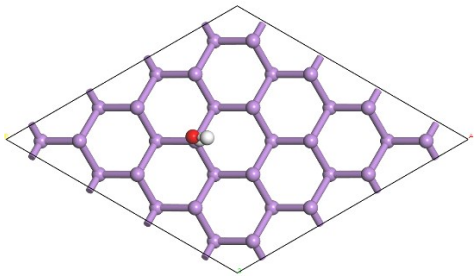
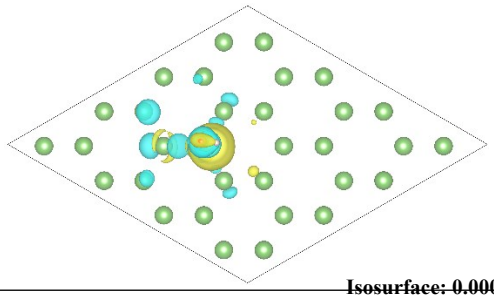
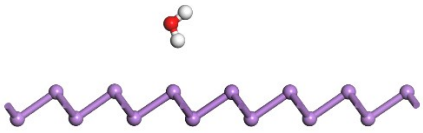
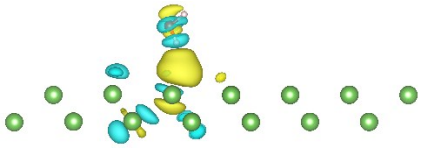
(f2)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.31 eV	**CT = –0.0190 e**
(f3)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.26 eV	**CT = –0.0226 e**
(f4)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.26 eV	**CT = –0.0216 e**

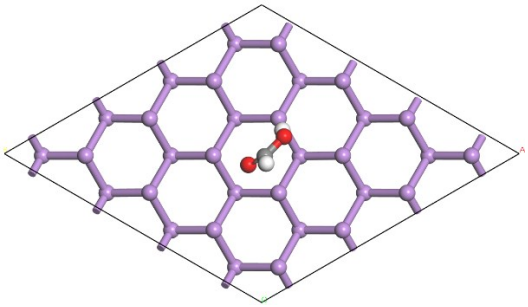
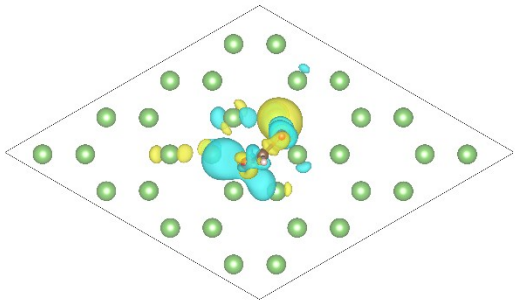
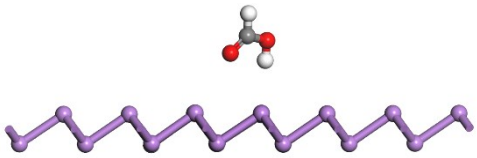
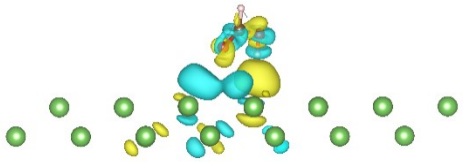
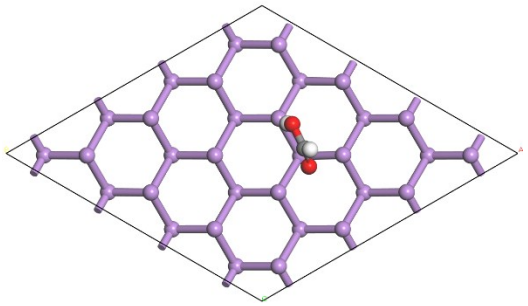
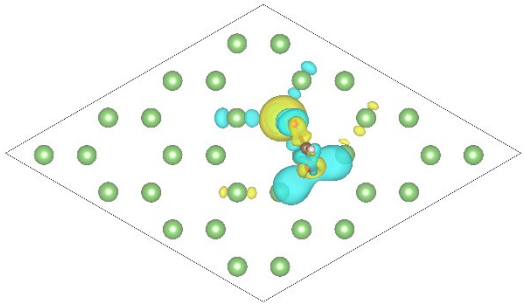
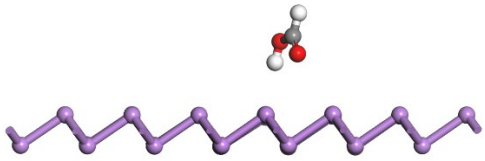
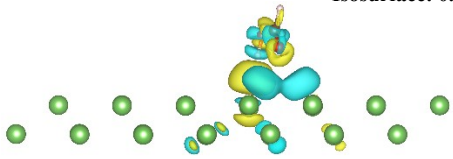
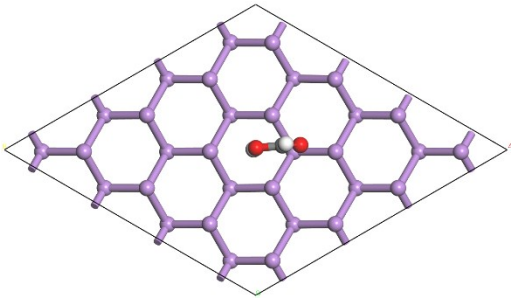
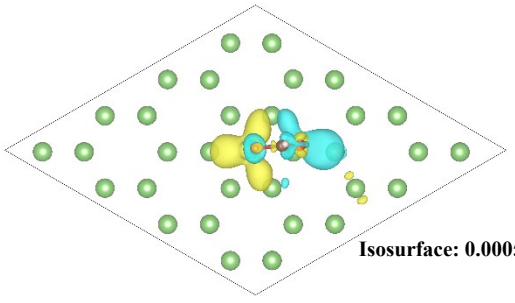
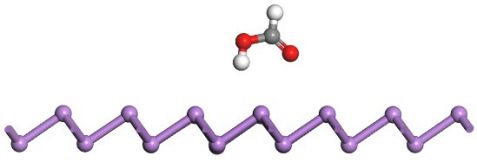
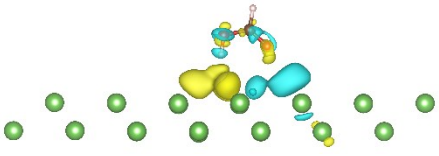
(f5)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.31 eV	CT = –0.0240 e
	***N*,*N*-Dimethylformamide**	
(g1)		
Top view		 Isosurface: 0.0001 e/Å^3
Side view		
	E_{ads} = –0.26 eV	CT = –0.0142 e
(g2)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.49 eV	CT = –0.0383 e

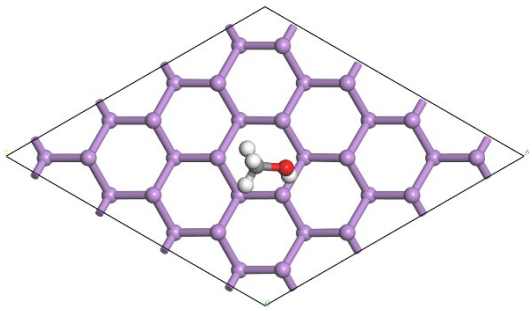
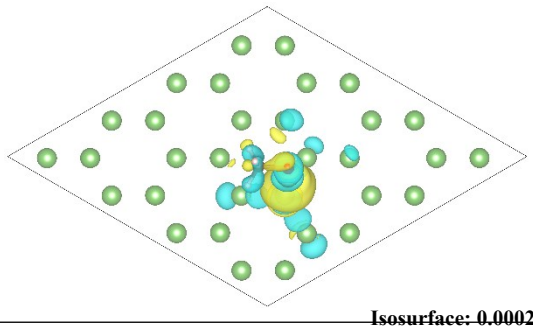
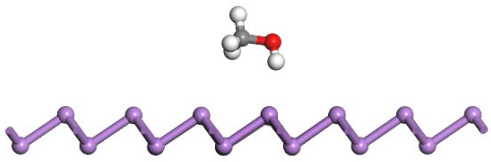
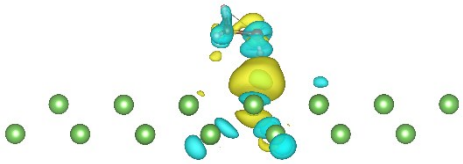
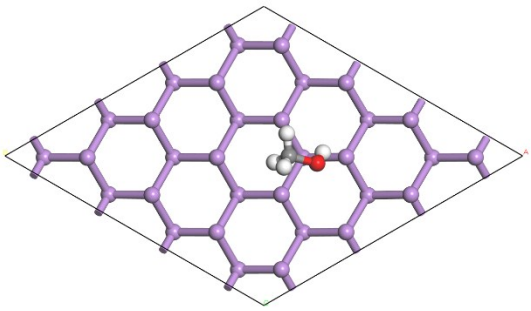
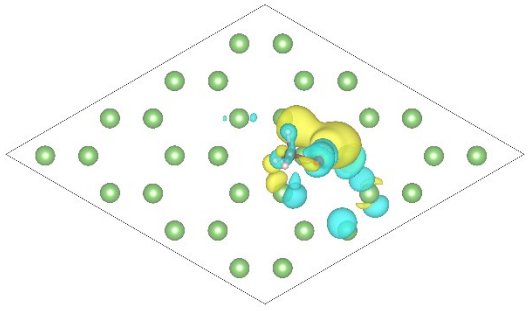
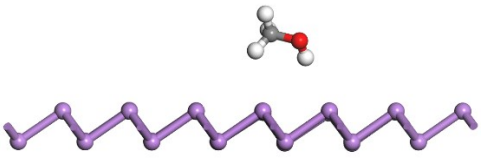
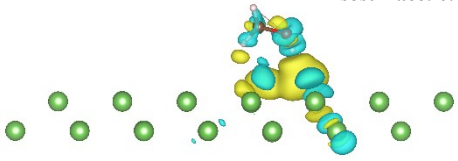
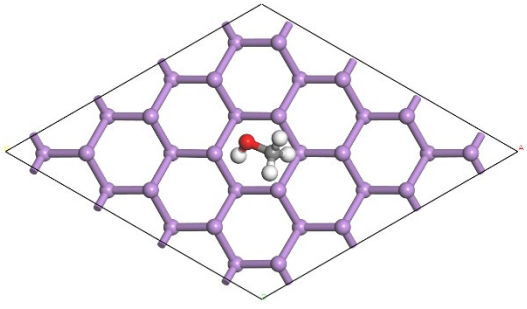
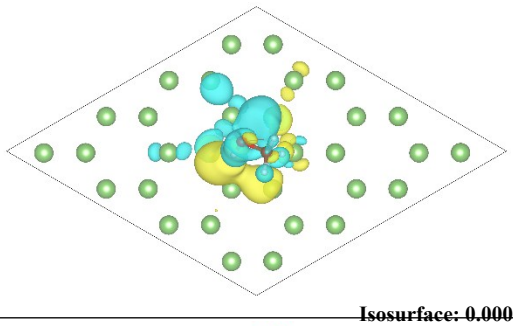
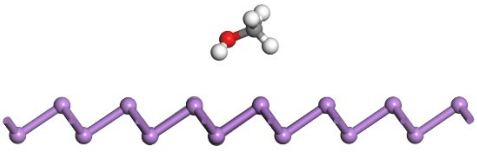
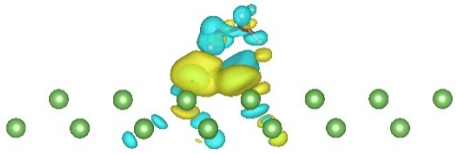
(g3)		
Top view		 **Isosurface: 0.0003 e/Å^3**
Side view		
	E_{ads} = –0.50 eV	**CT = –0.0400 e**

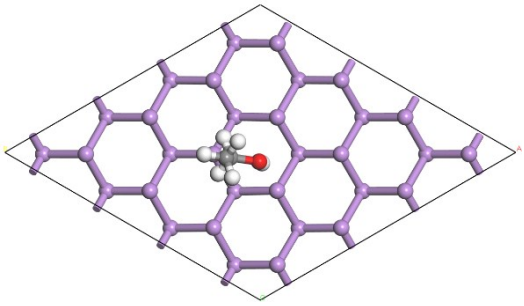
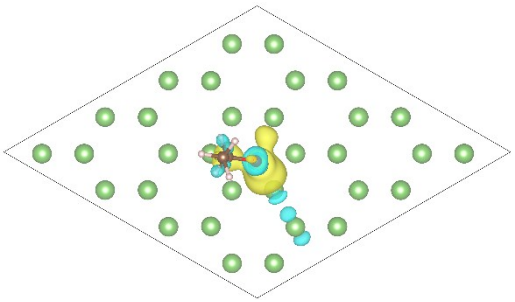
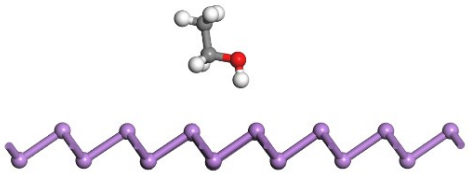
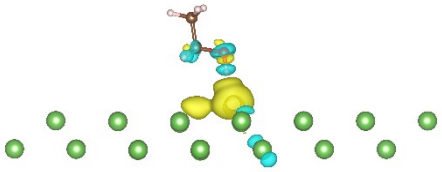
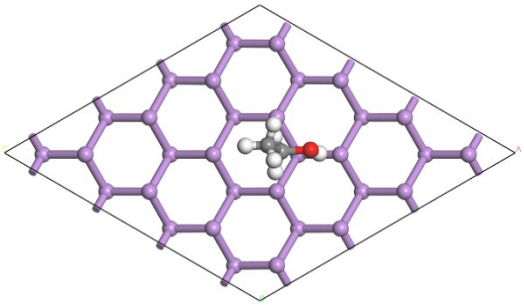
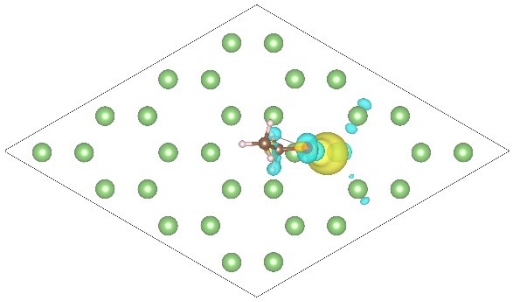
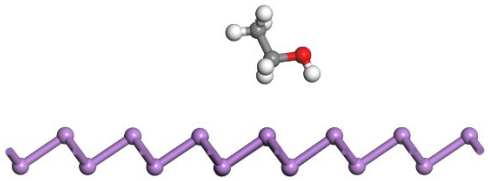
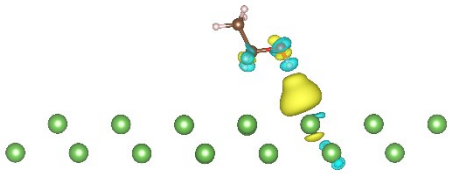
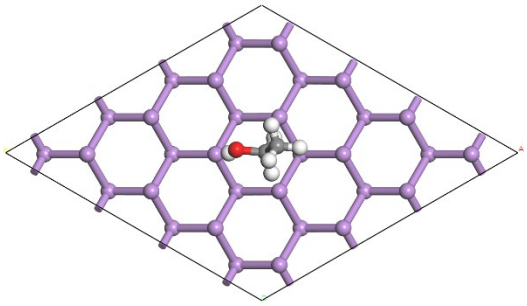
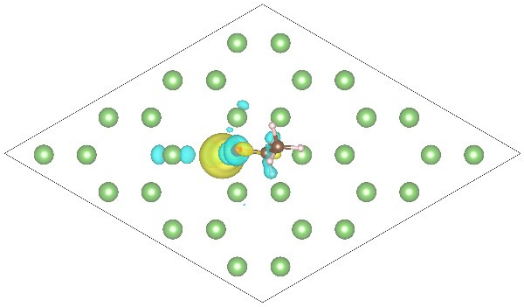
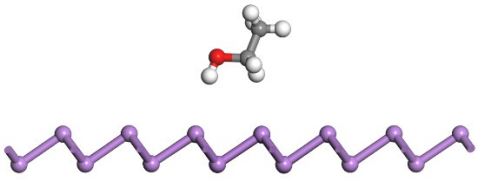
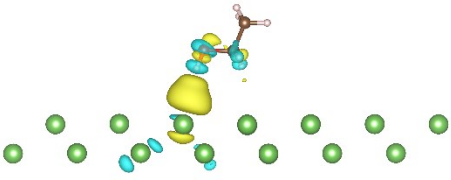
[a] The adsorption energy E_{ads} and the charge transfer value **CT** is labeled at the bottom of each picture. The isosurface level is labeled at the middle part of each charge-transfer picture. The blue region means losing electrons, while the yellow region means gaining electrons.

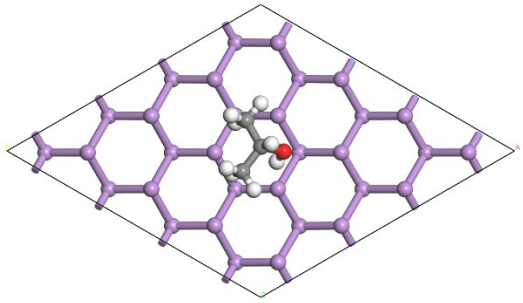
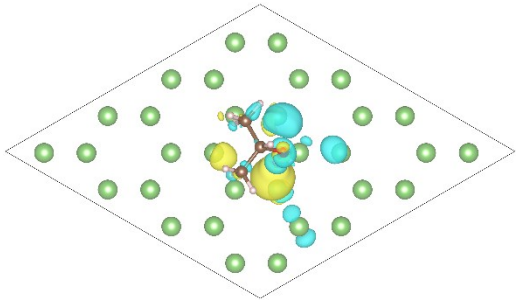
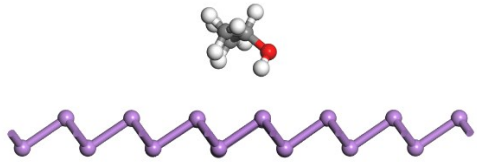
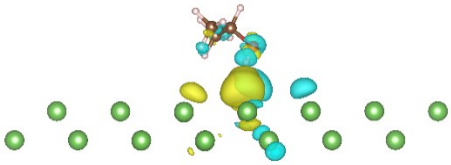
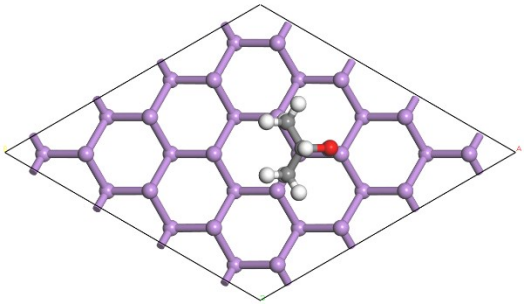
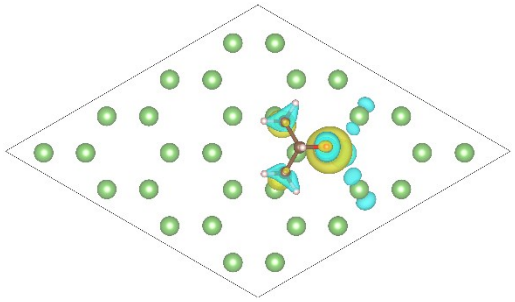
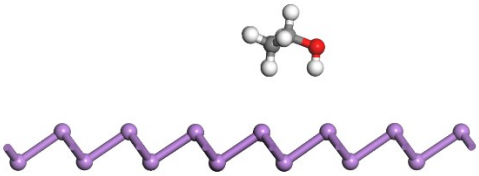
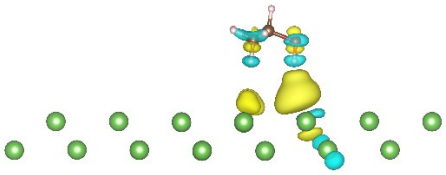
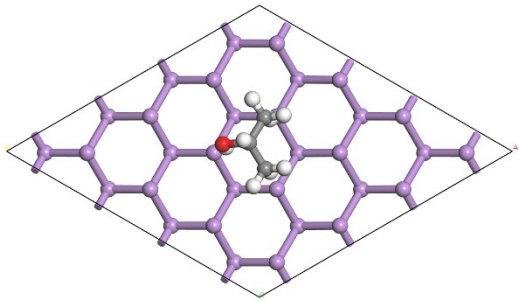
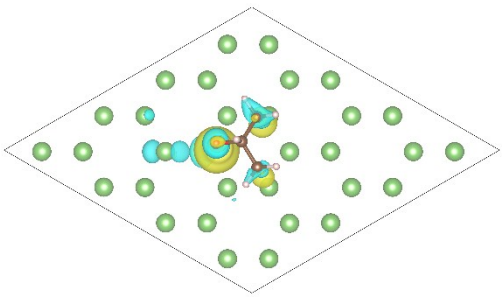
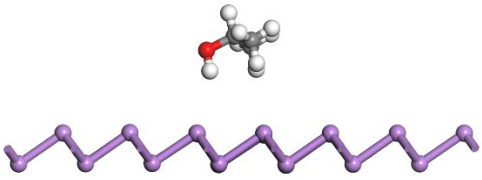
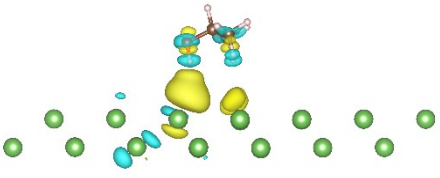
Scheme S2. Protic Solvents Adsorption on Arsenene.[a]

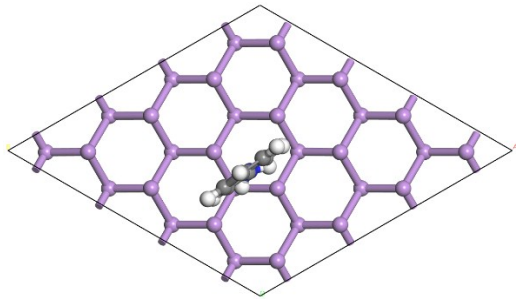
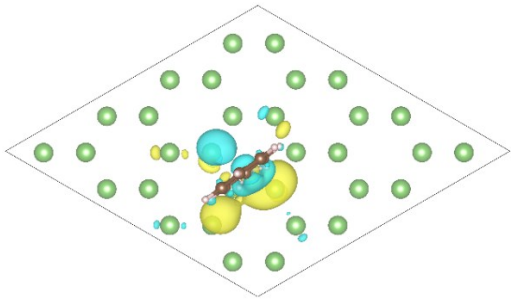
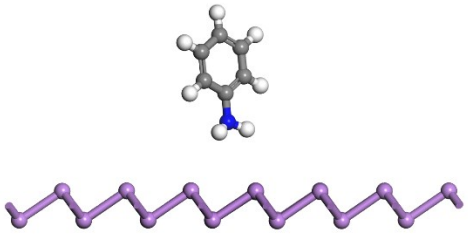
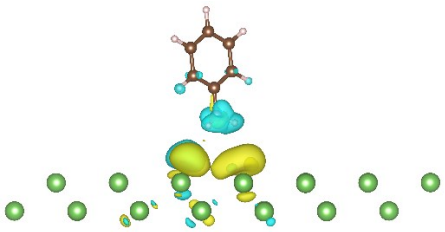
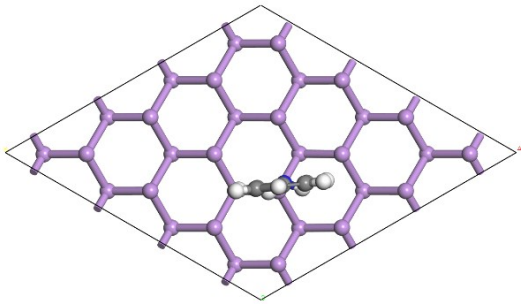
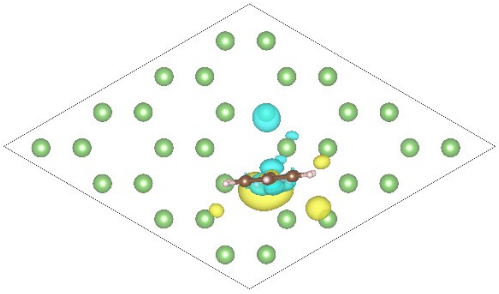
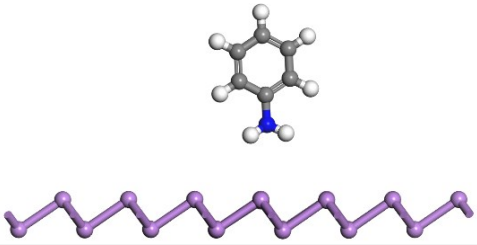
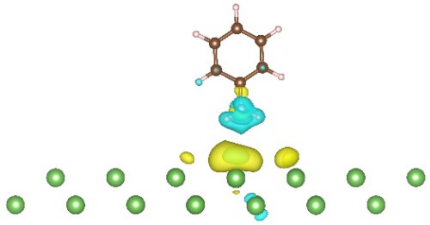
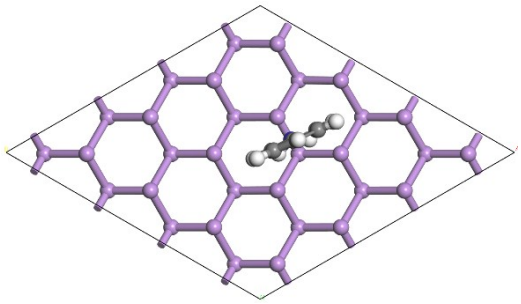
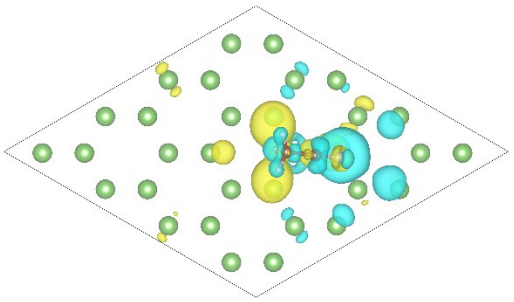
	Optimized geometries	*Charge transfer*
	Water	
(a1) *Top view*		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.12 eV	**CT = –0.0235 e**
(a2) *Top view*		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.13 eV	**CT = –0.0239 e**
(a3) *Top view*		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.14 eV	**CT = –0.0339 e**

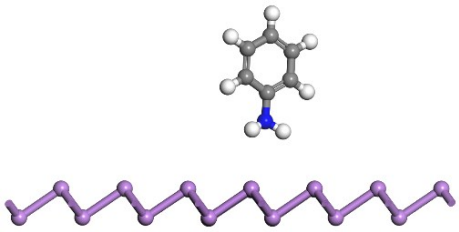
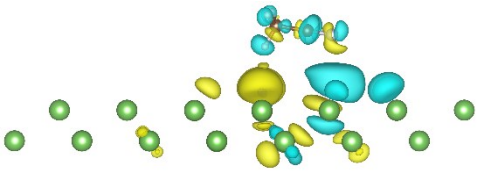
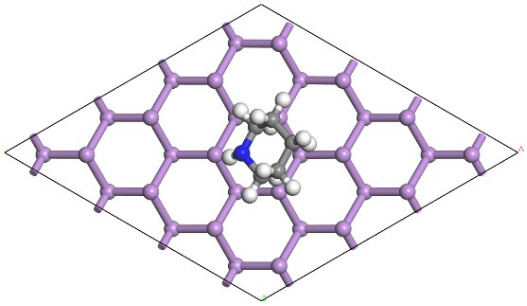
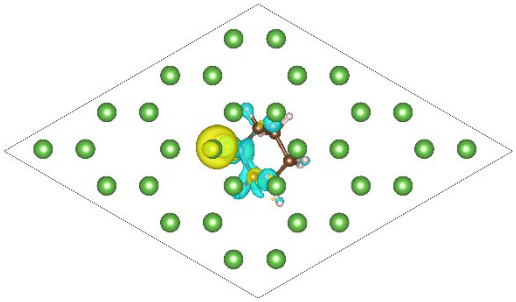
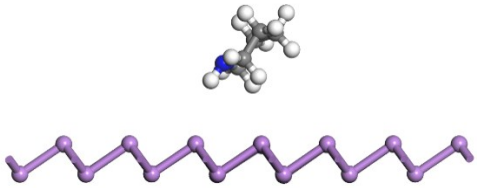
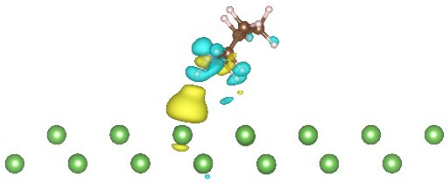
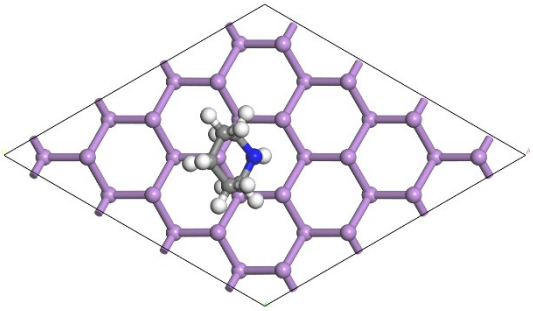
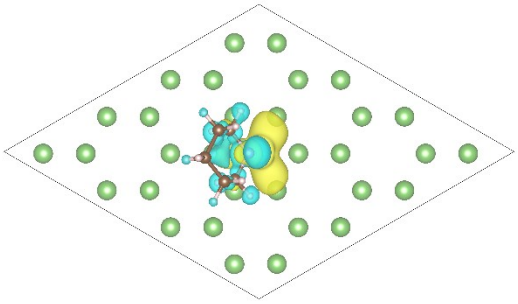
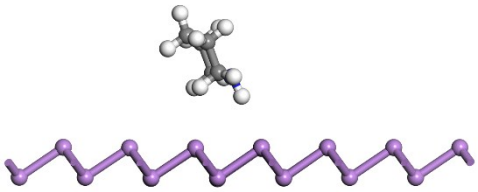
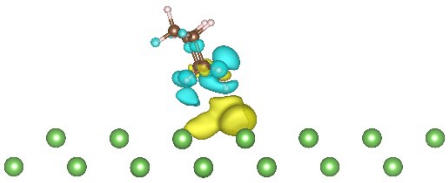
	Formic acid	
(b1)		
Top view		 Isosurface: 0.0005 e/Å^3
Side view		
	E_{ads} = –0.30 eV	**CT = –0.0501 e**
(b2)		
Top view		 Isosurface: 0.0005 e/Å^3
Side view		
	E_{ads} = –0.30 eV	**CT = –0.0551 e**
(b3)		
Top view		 Isosurface: 0.0005 e/Å^3
Side view		
	E_{ads} = –0.26 eV	**CT = –0.0362 e**

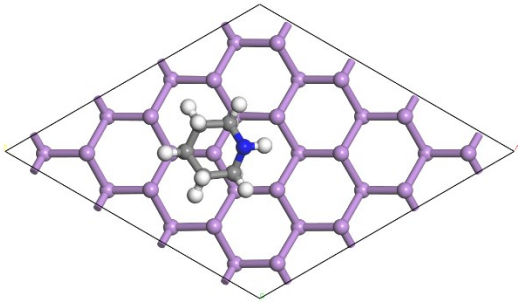
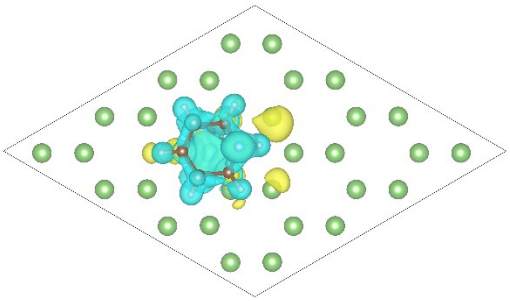
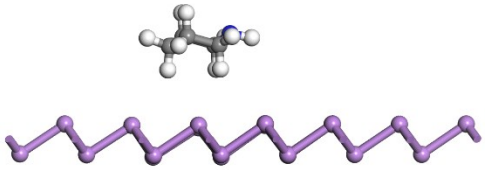
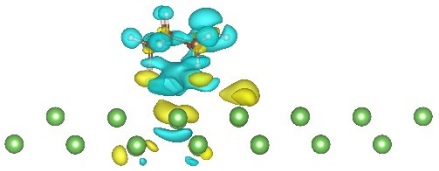
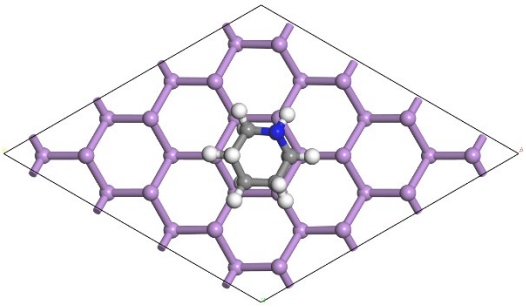
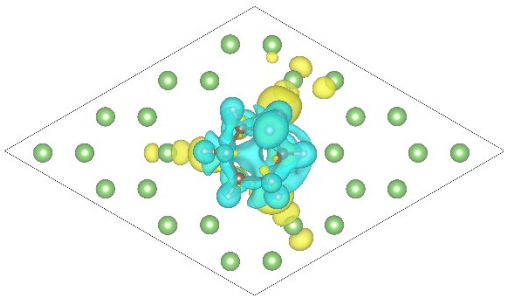
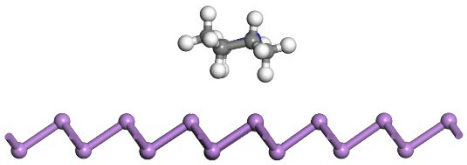
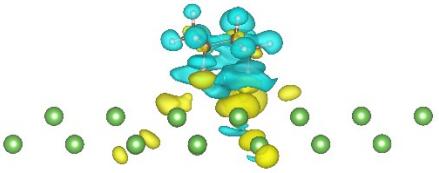
	Methanol	
(c1)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.25 eV	**CT = –0.0419 e**
(c2)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.24 eV	**CT = –0.0376 e**
(c3)		
Top view		 Isosurface: 0.0002 e/Å^3
Side view		
	E_{ads} = –0.25 eV	**CT = –0.0344 e**

	Ethanol	
(d1)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.24 eV	**CT = –0.0347 e**
(d2)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.25 eV	**CT = –0.0330 e**
(d3)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.26 eV	**CT = –0.0392 e**

	2-Propanol	
(e1)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.35 eV	**CT = –0.0389 e**
(e2)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.31 eV	**CT = –0.0347 e**
(e3)		
Top view		 Isosurface: 0.0003 e/Å^3
Side view		
	E_{ads} = –0.31 eV	**CT = –0.0366 e**

	Aniline	
(f1)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.27 eV	**CT = –0.0155 e**
(f2)		
Top view		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.24 eV	**CT = –0.0165 e**
(f3)		
Top view		 **Isosurface: 0.0002 e/Å^3**

Side view		
	E_{ads} = –0.26 eV	**CT = –0.0173 e**
	Piperidine	
(g1) *Top view*		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.37 eV	**CT = –0.0214 e**
(g2) *Top view*		 **Isosurface: 0.0002 e/Å^3**
Side view		
	E_{ads} = –0.42 eV	**CT = –0.0252 e**

(g3)		
Top view		 **Isosurface: 0.0001 e/Å^3**
Side view		
	E_{ads} = –0.46 eV	**CT = –0.0173 e**
(g4)		
Top view		 **Isosurface: 0.0001 e/Å^3**
Side view		
	E_{ads} = –0.47 eV	**CT = –0.0173 e**

[a] The adsorption energy E_{ads} and the charge transfer value **CT** is labeled at the bottom of each picture. The isosurface level is labeled at the middle part of each charge-transfer picture. The blue region means losing electrons, while the yellow region means gaining electrons.

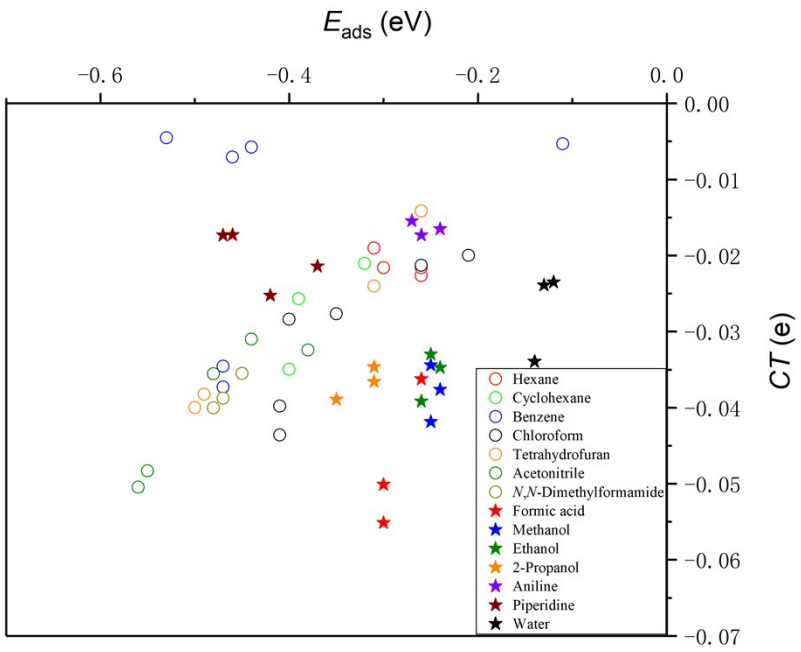
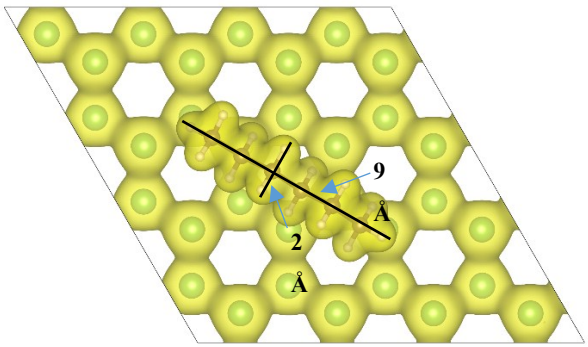
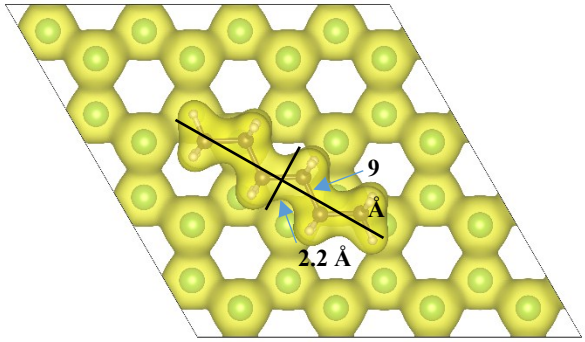
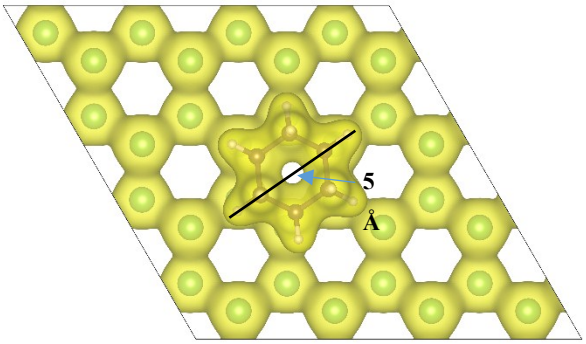
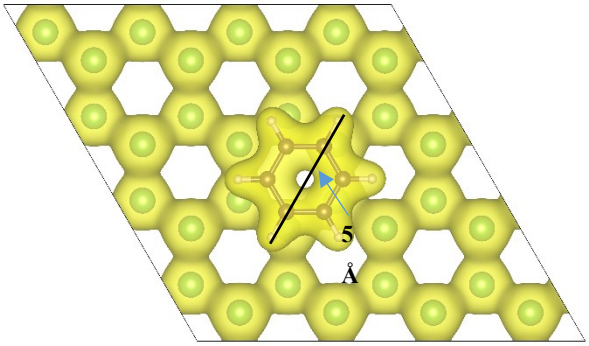
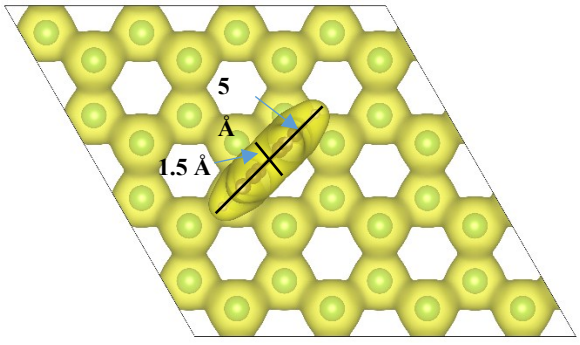
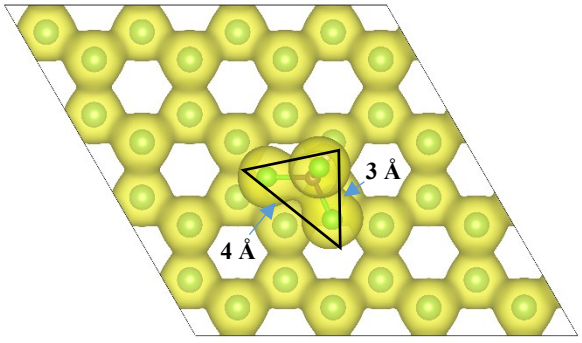
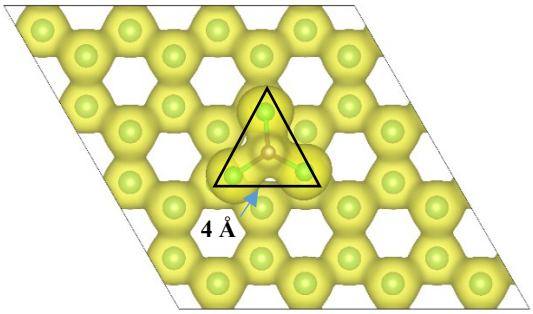
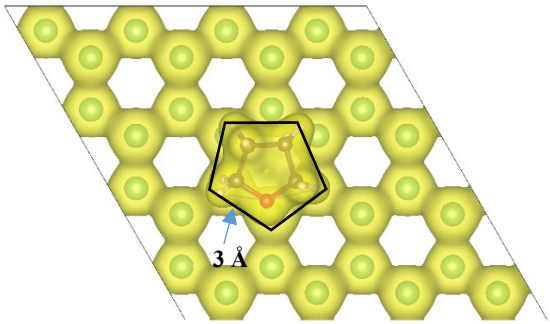
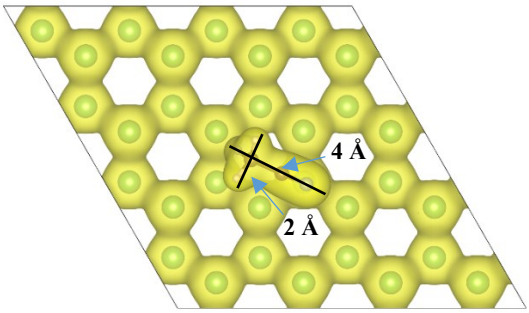
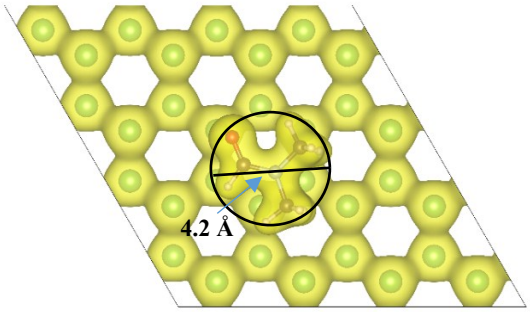
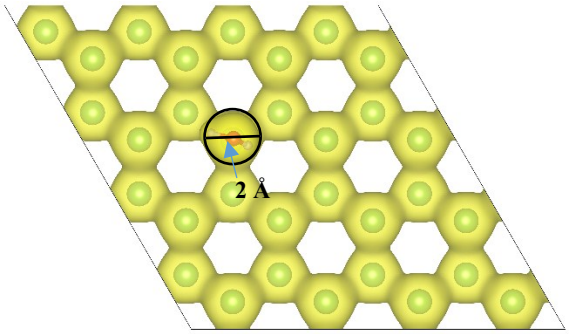
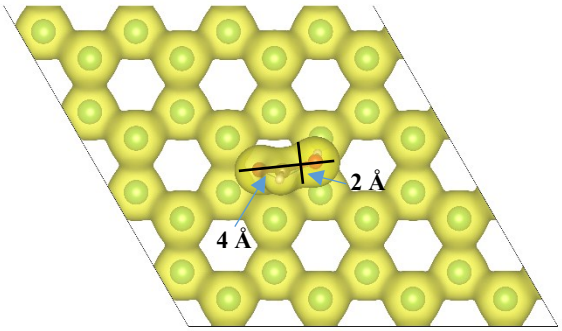
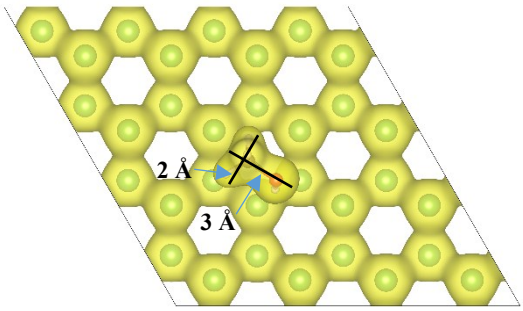
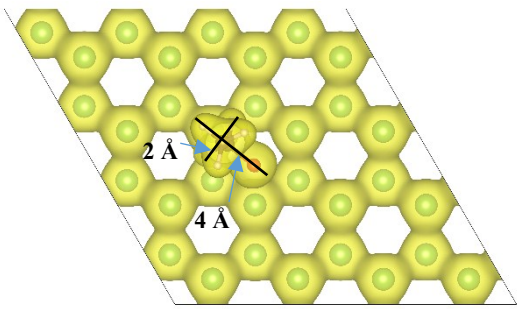
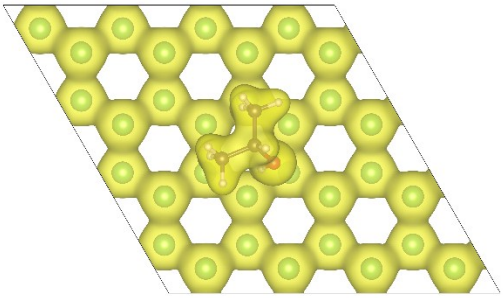
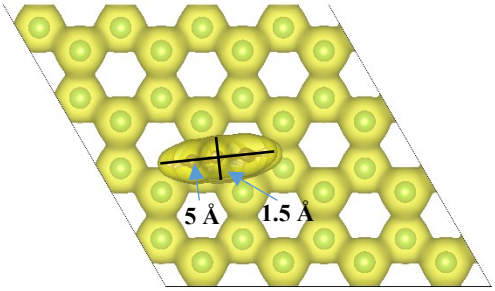
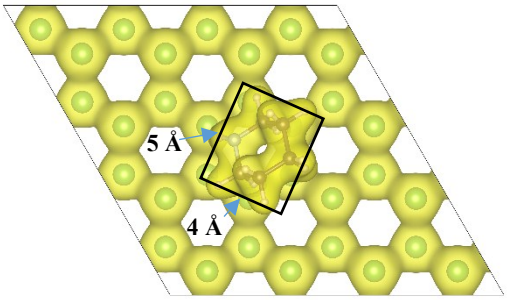
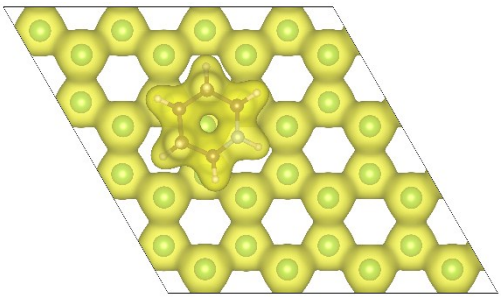


Figure S1. Plot of adsorption energy (***E*_{ads}**) versus charge transfer (***CT***) in different solvents. The circles are aprotic and the stars are protic solvents.

Scheme S3. Top View of Electron Contour for Solvents Adsorption on Arsenene.[a]

Hexane - a(1)	**Hexane** - a(3)
	
S = 0.18 nm^2	***S*** = 0.20 nm^2
Cyclohexane - b(1)	**Benzene** - c(1)
	
S = 0.20 nm^2	***S*** = 0.20 nm^2
Benzene - c(4)	**Chloroform** - d(1)
	
S = 0.08 nm^2	***S*** = 0.04 nm^2

Chloroform - d(4)	**Tetrahydrofuran** - e(1)
	
$\boldsymbol{S}$ = 0.07 nm^2	$\boldsymbol{S}$ = 0.15 nm^2
Acetonitrile - f(1)	***N*,*N*-Dimethylformamide** - g(1)
	
$\boldsymbol{S}$ = 0.08 nm^2	$\boldsymbol{S}$ = 0.14 nm^2
Water - a(1)	**Formic acid** - b(1)
	
$\boldsymbol{S}$ = 0.03 nm^2	$\boldsymbol{S}$ = 0.08 nm^2

Methanol - c(1)	**Ethanol** - d(1)
	
$\boldsymbol{S}$ = 0.06 nm^2	$\boldsymbol{S}$ = 0.08 nm^2
2-Propanol - e(1)	**Aniline** - f(1)
	
$\boldsymbol{S}$ = 0.10 nm^2	$\boldsymbol{S}$ = 0.08 nm^2
Piperidine - g(1)	**Piperidine** - g(3)
	
$\boldsymbol{S}$ = 0.20 nm^2	$\boldsymbol{S}$ = 0.20 nm^2

[a]Estimated projected area of each solvent is labeled at the bottom of each picture. All the isosurface level is set to 0.04 e/Å^3.

Table S2. Adsorption energies (per unit area) and charge transfer (per unit area) for solvents adsorbed on arsenene.

	E_{ads} / eV	CT / e	S / nm^2	$E_{ads,per}$ / eV/nm^2	CT_{per} / e/nm^2
Hexane					
a(1)	-0.44	-0.030982	0.18	-2.44	-0.172
a(2)	-0.48	-0.035548	0.18	-2.67	-0.197
a(3)	-0.55	-0.048309	0.20	-2.75	-0.242
a(4)	-0.56	-0.050447	0.20	-2.80	-0.252
Cyclohexane					
b(1)	-0.38	-0.032423	0.20	-1.90	-0.162
b(2)	-0.47	-0.034569	0.20	-2.35	-0.173
b(3)	-0.47	-0.037279	0.20	-2.35	-0.186
Benzene					
c(1)	-0.46	-0.007050	0.20	-2.30	-0.035
c(2)	-0.53	-0.004509	0.20	-2.65	-0.023
c(3)	-0.44	-0.005747	0.20	-2.20	-0.029
c(4)	-0.11	-0.005308	0.08	-1.38	-0.066
c(5)	-0.26	-0.021290	0.08	-3.25	-0.266
c(6)	-0.21	-0.019991	0.08	-2.63	-0.250
Chloroform					
d(1)	-0.35	-0.027662	0.04	-8.75	-0.692
d(2)	-0.41	-0.039810	0.04	-10.25	-0.995
d(3)	-0.41	-0.043608	0.04	-10.25	-1.090
d(4)	-0.40	-0.028372	0.07	-5.71	-0.405
d(5)	-0.39	-0.025697	0.07	-5.57	-0.367
d(6)	-0.32	-0.021052	0.07	-4.57	-0.301
Tetrahydrofuran					
e(1)	-0.40	-0.034975	0.15	-2.67	-0.233
e(2)	-0.47	-0.038758	0.15	-3.13	-0.258
e(3)	-0.48	-0.040038	0.15	-3.20	-0.267
e(4)	-0.45	-0.035519	0.15	-3.00	-0.237
Acetonitrile					
f(1)	-0.30	-0.021621	0.08	-3.75	-0.270
f(2)	-0.31	-0.019041	0.08	-3.88	-0.238
f(3)	-0.26	-0.022619	0.08	-3.25	-0.283
f(4)	-0.26	-0.021606	0.08	-3.25	-0.270
f(5)	-0.31	-0.024032	0.08	-3.88	-0.300
***N*,*N*-Dimethylformamide**					
g(1)	-0.26	-0.014173	0.14	-1.86	-0.101
g(2)	-0.49	-0.038266	0.14	-3.50	-0.273
g(3)	-0.50	-0.039993	0.14	-3.57	-0.286
Water					

a(1)	-0.12	-0.023500	0.03	-4.00	-0.783
a(2)	-0.13	-0.023891	0.03	-4.33	-0.796
a(3)	-0.14	-0.033931	0.03	-4.67	-1.131
Formic acid					
b(1)	-0.30	-0.050104	0.08	-3.75	-0.626
b(2)	-0.30	-0.055121	0.08	-3.75	-0.689
b(3)	-0.26	-0.036239	0.08	-3.25	-0.453
Methanol					
c(1)	-0.25	-0.041872	0.06	-4.17	-0.698
c(2)	-0.24	-0.037625	0.06	-4.00	-0.627
c(3)	-0.25	-0.034402	0.06	-4.17	-0.573
Ethanol					
d(1)	-0.24	-0.034739	0.08	-3.00	-0.434
d(2)	-0.25	-0.032978	0.08	-3.13	-0.412
d(3)	-0.26	-0.039163	0.08	-3.25	-0.490
2-Propanol					
e(1)	-0.35	-0.038916	0.10	-3.50	-0.389
e(2)	-0.31	-0.034658	0.10	-3.10	-0.347
e(3)	-0.31	-0.036578	0.10	-3.10	-0.366
Aniline					
f(1)	-0.27	-0.015456	0.08	-3.38	-0.193
f(2)	-0.24	-0.016505	0.08	-3.00	-0.206
f(3)	-0.26	-0.017314	0.08	-3.25	-0.216
Piperidine					
g(1)	-0.37	-0.021419	0.20	-1.85	-0.107
g(2)	-0.42	-0.025241	0.20	-2.10	-0.126
g(3)	-0.46	-0.017269	0.20	-2.30	-0.086
g(4)	-0.47	-0.017333	0.20	-2.35	-0.087

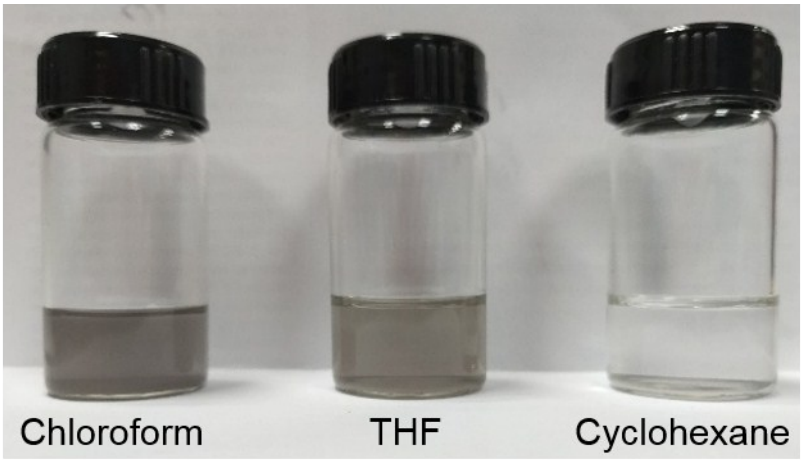


Figure S2. Photographs of the dispersions of arsenic nanosheets exfoliated in different solvents after 3000 r.p.m. (81*g*, $g = 9.8$ m/s^2) centrifugation for 5 min.

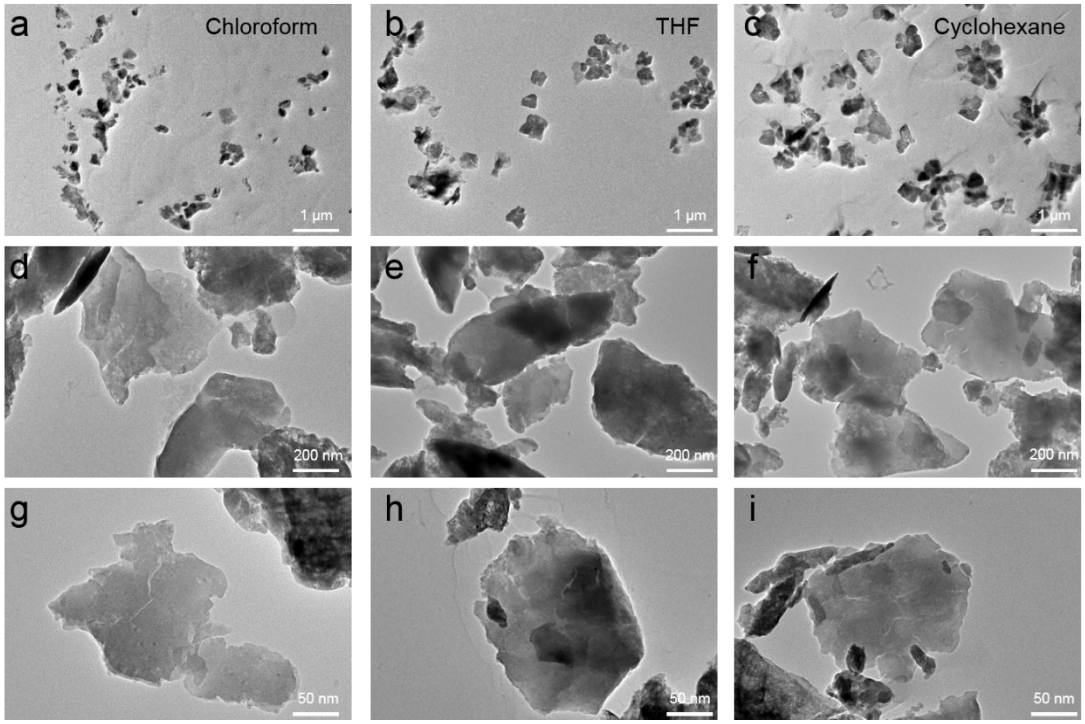


Figure S3. Differently magnified TEM images of exfoliated arsenic nanosheets.

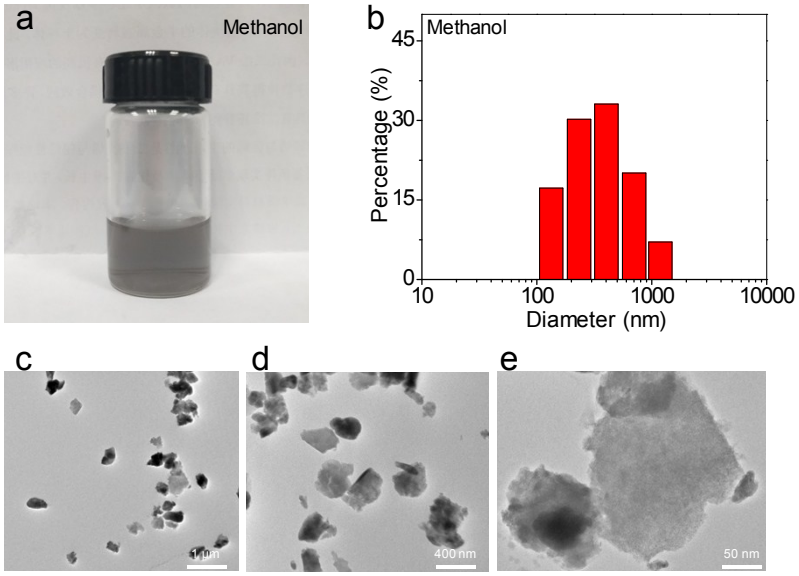


Figure S4. (a) Photographs of the dispersions of arsenic nanosheets exfoliated in methanol after 1000 r.p.m. (90*g*, g = 9.8 m/s^2) centrifugation for 5 min. The concentration of the exfoliated nanosheets is 0.5 mg/mL. (b) Sized distribution of the exfoliated nanosheets. (c)–(e) Differently magnified TEM images of the exfoliated nanosheets.

To obtain a more complete physical picture of how the exfoliation is affected by the variable, we selected methanol a representative of protic solvents. As shown in Figure S4, the concentration of the arsenic nanosheets exfoliated in methanol is 0.5 mg/mL. The adsorption energy per unit area $E_{ads,per}$ for methanol is -4.00 ~ -4.17 eV/nm^2 and the charge transfer per unit area CT_{per} is -0.573 ~ -0.698 e/nm^2, which implies the interaction intensity between methanol and arsenene is stronger than THF ($E_{ads,per}$ = -2.67 ~ -3.20 eV/nm^2, CT_{per} = -0.233 ~ -0.267 e/nm^2) and cyclohexane ($E_{ads,per}$ = -1.90 ~ -2.35 eV/nm^2, CT_{per} = -0.162 ~ -0.186 e/nm^2). However, the concentration of the arsenic nanosheets exfoliated is 0.66 mg/mL in THF and 0.25 mg/mL in cyclohexane. The reason is that in order to adsorb in the surface of arsenene, the protic solvent molecules need to overcome the intermolecular interactions (mainly hydrogen bond) between each other. The net energetic cost will be raised though the interaction intensity between methanol and arsenene is stronger. In contrast, for aprotic solvents, the intermolecular interactions is mainly van der Waals interaction which is much weaker than hydrogen bond. So the concentration of the arsenic nanosheets exfoliated in methanol is lower than in THF.

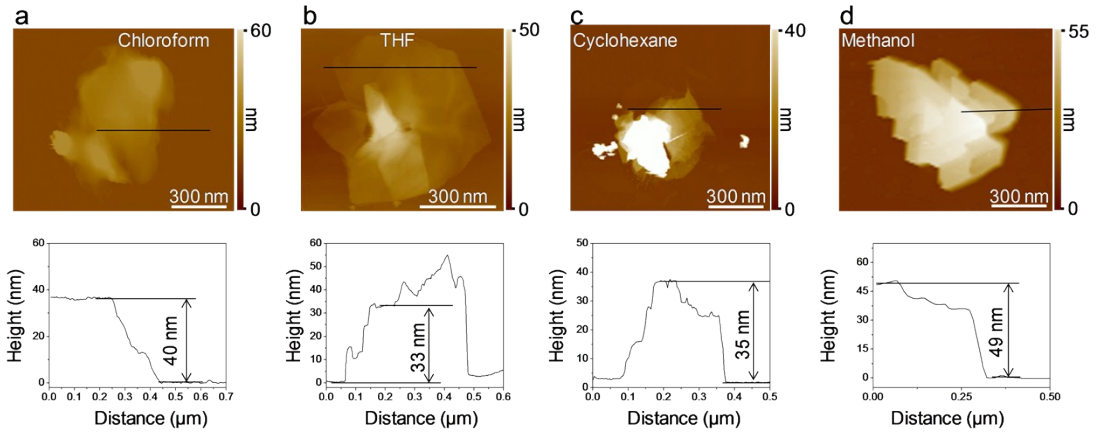


Figure S5. AFM images of arsenic nanosheets exfoliated in (a) chloroform, (b) THF, (c) cyclohexaneand and (d) methanol, respectively. Corresponding height profiles are given below each image.

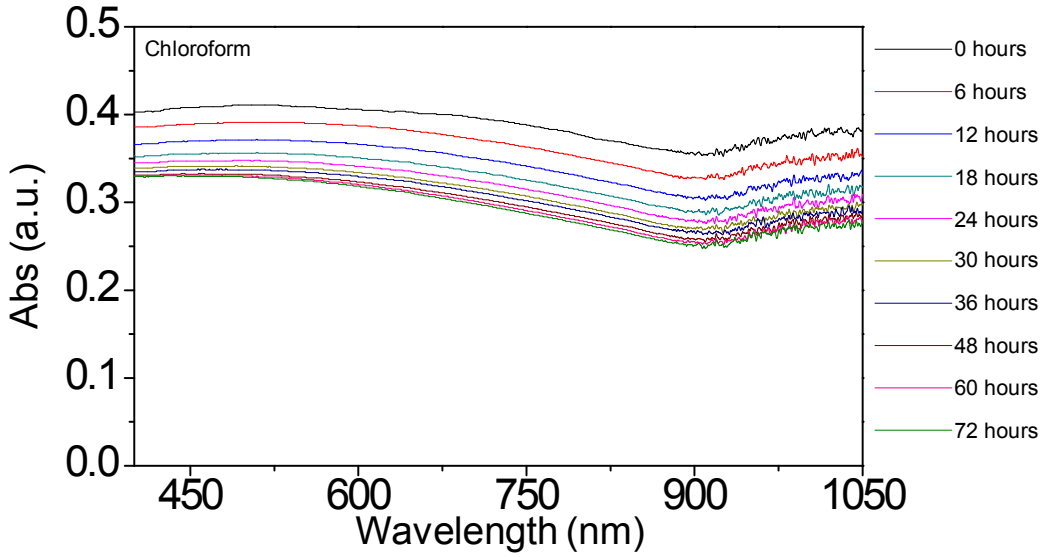


Figure S6. UV-Vis absorption spectrum of the arsenic nanosheets dispersed in chloroform as function of time.

To confirm the stability of the suspensions over time, we performed UV-Vis absorption spectrum of the arsenic nanosheets dispersed in chloroform as a representative sample. As shown in Figure S6, the value of absorbance reflects the concentration of the dispersed nanosheets. The absorbance rapidly decrease within 24 hours, which may attributed to the settle of relative large nanosheets. However, after 24 hours, the concentration of the dispersed nanosheets tend to be stable. The absorbance exhibit only about 17% decay after standing for 72 hours, indicating the good stability of prepared arsenene nanosheets suspensions.

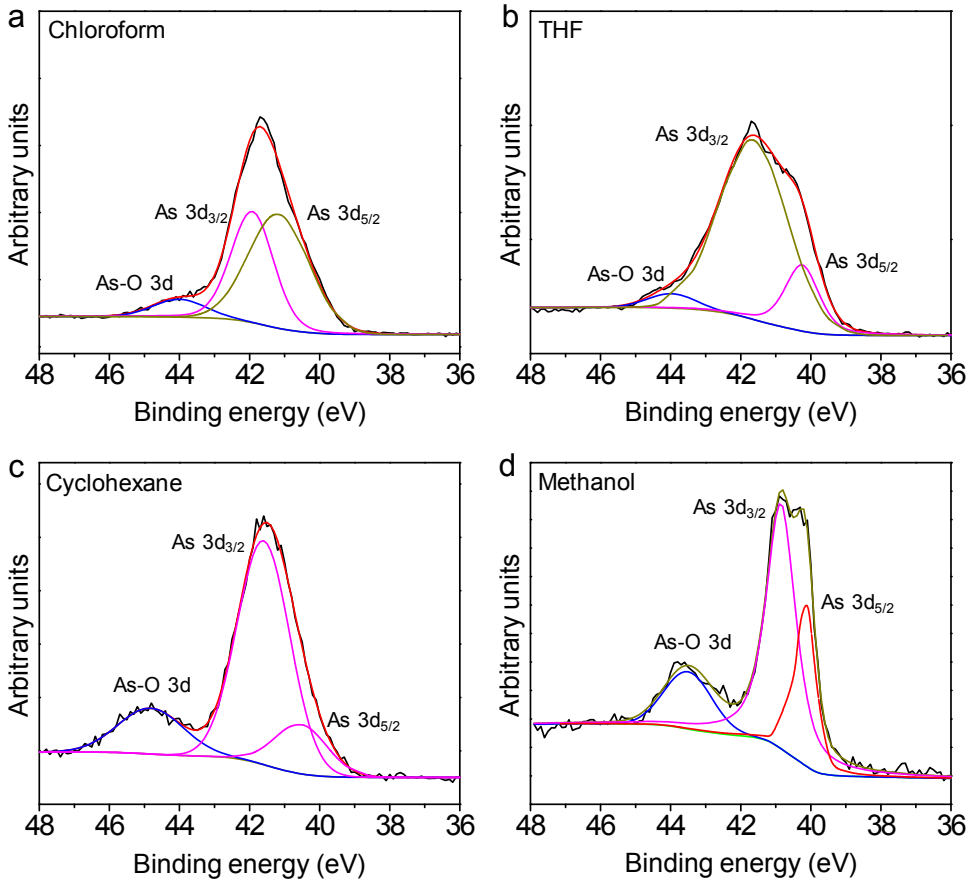


Figure S7. XPS spectrum of arsenic nanosheets exfoliated in (a) chloroform, (b) THF, (c) cyclohexane and (d) methanol.

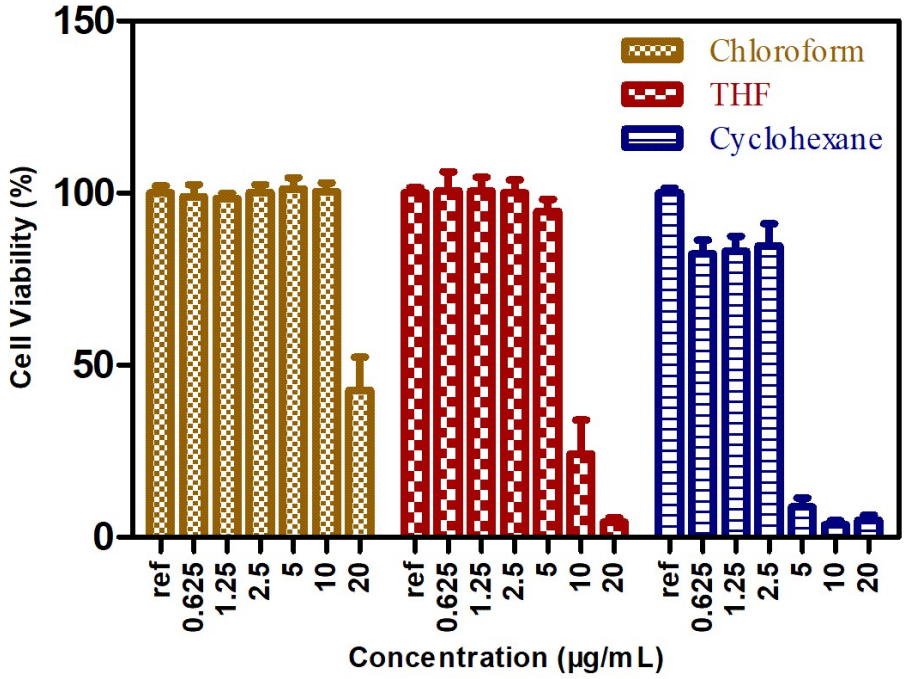


Figure S8. Percentage cell viability with different concentrations of arsenic nanosheets exfoliated in chloroform, THF and cyclohexane, respectively.

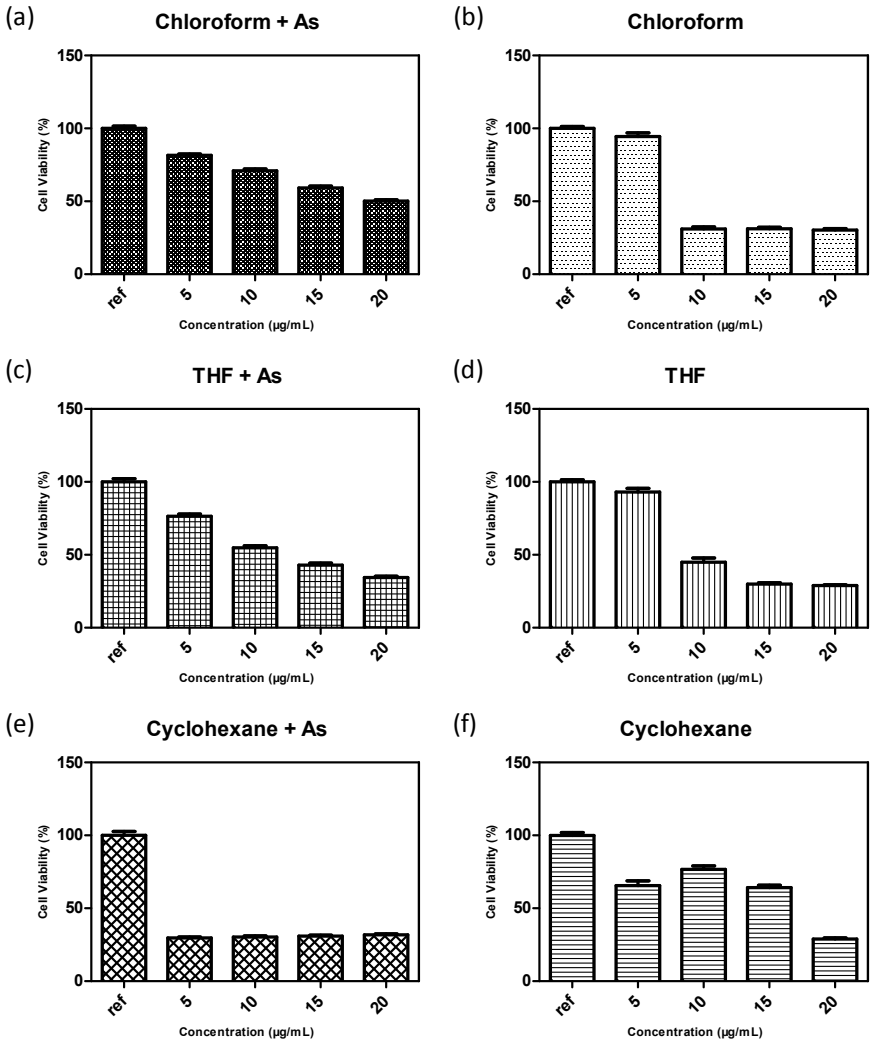


Figure S9. Percentage cell viability with different concentrations of mixture of arsenic nanosheets exfoliated in (a) chloroform, (c) THF and (e) cyclohexane and corresponding solvents, respectively. Percentage cell viability for (b) chloroform, (d) THF and (f) cyclohexane, respectively.

In order to see if it's the solvent that was responsible for the cytotoxicity, we have performed control experiments. As shown in Figure S9, the mixture of cyclohexane and arsenic nanosheets is indeed more cytotoxic than the mixture of chloroform and arsenic nanosheets. The different viability results for the arsenic nanosheets exfoliated in different solvents may be caused by the inevitable solvent vestigital.

References

1 G. Kresse and J. Furthmuller, Efficient Iterative Schemes for ab initio Total-Energy Calculations using a Plane-Wave Basis Set, *Phys. Rev. B: Condens. Matter.*, 1996, **54**, 11169–11186.

2 G. Kresse and J. Furthmüller, Efficiency of ab initio total energy calculations for metals and semiconductors using a planewave basis set, *Comput. Mater. Sci.*, 1996, **6**, 15–50.

3 J. Klimeš, D. R. Bowler and A. Michaelides, *J. Phys.: Cond. Matt.*, 2010, **22**, 022201.

4 W. Tang, E. Sanville and G. Henkelman, A grid-based Bader analysis algorithm without lattice bias, *J. Phys. Condens. Matter*, 2009, **21**, 084204.