Supporting Information for

Evolution of vibrational bands upon gradual protonation/deprotonation of arsinic acid $H_2As(O)OH$ in media of different polarity

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Table S1. Selected geometric and IR spectral parameters of complexes **4**–**44** with hydrogen bond AsO−H···B in a vacuum ($\varepsilon = 1$): interatomic distances ($r_{As=O}$, r_{As-O}, r_{O-H} and $r_{H...B}$), angle (∠OHB) and stretching vibrational frequencies (ν_{As-O}, $\nu_{As=O}$ and ν_{O-H}). Numbering of complexes in accordance with Scheme 2.

	$r_{As=O}$, Å	r_{As-O}, Å	r_{O-H}, Å	$r_{H...B}$, Å	∠OHB, °	$\nu_{As=O}$, cm^{-1}	ν_{As-O}, cm^{-1}	ν_{O-H}, cm^{-1}
4	1.631	1.743	0.993	2.471	155.1	988.4	749.3	3334.9
5	1.628	1.746	0.981	2.387	161.4	993.3	749.4	3542.1
6	1.630	1.743	0.981	2.344	175.5	990.5	754.2	3575.0
7	1.627	1.744	0.987	2.270	167.3	998.5	753.6	3426.0
8	1.632	1.738	1.002	2.186	156.5	984.7	757.5	3172.2
9	1.636	1.732	1.000	2.169	167.7	974.2	775.0	3261.4
10	1.627	1.746	0.976	2.063	159.3	998.8	749.1	3653.1
11	1.634	1.732	1.017	1.953	158.8	981.5	768.0	2929.1
12	1.647	1.730	0.981	1.885	139.7	938.5	777.1	3599.1
13	1.632	1.739	0.989	1.874	156.4	983.5	761.5	3426.3
14	1.639	1.732	0.989	1.826	165.1	977.3	766.6	3387.8
15	1.629	1.737	0.990	1.768	177.7	994.0	770.3	3389.4
16	1.632	1.734	0.999	1.771	167.8	987.5	772.0	3213.0
17	1.646	1.725	0.991	1.762	158.8	956.9	788.1	3392.0
18	1.635	1.735	0.993	1.765	156.3	977.3	770.9	3330.4
19	1.629	1.739	0.988	1.759	163.4	994.0	763.6	3439.7
20	1.640	1.724	0.992	1.724	167.9	968.4	792.7	3365.9
21	1.627	1.738	0.991	1.714	174.6	1000.0	767.4	3349.9
22	1.630	1.738	0.992	1.713	159.6	990.1	764.3	3363.4
23	1.630	1.733	1.007	1.723	178.6	990.7	776.8	3038.9
24	1.636	1.735	1.001	1.710	159.0	974.5	768.3	3170.9
25	1.632	1.732	1.013	1.715	164.9	984.1	776.4	2949.3
26	1.632	1.728	1.015	1.677	173.7	987.5	785.5	2901.9
27	1.630	1.730	1.016	1.673	179.6	990.5	783.7	2869.3
28	1.643	1.723	1.003	1.657	165.2	958.4	795.5	3146.8
29	1.640	1.721	1.020	1.660	171.2	969.0	797.7	2801.6
30	1.633	1.730	1.027	1.649	165.9	981.2	781.0	2687.5
31	1.632	1.729	1.023	1.644	161.2	986.7	773.9	2796.2
32	1.631	1.727	1.024	1.633	178.7	989.7	792.1	2714.1
33	1.636	1.724	1.025	1.628	167.9	976.0	792.0	2742.6
34	1.632	1.723	1.034	1.589	166.2	985.7	788.8	2603.0
35	1.636	1.636	1.036	1.584	170.9	978.1	798.0	2542.1
36	1.641	1.716	1.059	1.525	172.1	967.5	809.9	2157.8
37	1.666	1.666	1.477	1.092	176.6	894.8	854.2	2364.0
38	1.645	1.674	1.467	1.102	179.0	965.1	867.4	2111.1
39	1.646	1.670	1.546	1.079	179.0	966.5	871.9	2459.0
40	1.649	1.666	1.709	1.058	179.7	963.7	884.3	2894.1
41	1.659	1.661	1.844	1.036	168.8	955.7	889.3	3542.1
42	1.656	1.659	2.029	1.032	151.3	956.1	893.5	3337.1
43	1.650	1.665	2.327	1.020	116.9	957.7	884.9	3523.4
44	1.668	1.647	2.402	1.027	174.4	961.6	882.2	3418.6

Table S2. Selected geometric and IR spectral parameters of complexes **4**–**44** with hydrogen bond AsO−H···B in a media with $\varepsilon = 5$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$ and $r_{H...B}$), angle (∠OHB) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 2.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{H...B}$, Å	∠OHB, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	$\nu_{O–H}$, cm^{-1}
4	1.632	1.746	0.988	2.494	156.6	980.5	737.5	3414.0
5	1.634	1.749	0.980	2.421	158.9	973.6	733.5	3567.0
6	1.634	1.748	0.981	2.297	173.4	974.3	736.6	3555.9
7	1.632	1.746	0.987	2.256	170.6	979.7	741.0	3416.8
8	1.633	1.742	0.995	2.219	157.7	978.1	746.1	3288.1
9	1.643	1.737	0.995	2.204	166.6	956.1	757.3	3261.3
10	1.630	1.745	0.982	1.887	176.1	985.3	745.7	3523.8
11	1.634	1.737	1.005	1.993	160.3	974.7	753.9	3097.4
12	1.689	1.715	0.986	1.825	135.6	859.1	795.2	3506.9
13	1.634	1.741	0.995	1.784	170.0	978.4	752.1	3269.1
14	1.645	1.739	0.985	1.900	164.4	952.4	750.8	3466.7
15	1.634	1.741	0.990	1.754	175.9	975.7	754.6	3361.8
16	1.637	1.738	1.000	1.752	168.1	970.7	759.4	3160.2
17	1.656	1.728	0.990	1.766	164.7	856.4	775.7	3376.9
18	1.641	1.740	0.994	1.760	158.1	957.0	755.4	3301.7
19	1.635	1.741	0.991	1.722	170.6	976.1	752.3	3361.1
20	1.649	1.729	0.990	1.748	168.3	947.6	773.4	3390.1
21	1.633	1.740	0.995	1.682	173.5	979.1	756.6	3259.3
22	1.635	1.738	1.000	1.643	167.8	971.8	756.6	3179.0
23	1.636	1.735	1.010	1.701	176.5	971.9	765.3	2952.9
24	1.642	1.739	1.000	1.717	159.6	954.6	752.2	3176.5
25	1.638	1.732	1.026	1.641	170.2	966.9	770.7	2664.7
26	1.637	1.731	1.020	1.650	173.0	969.4	770.9	2779.9
27	1.636	1.732	1.020	1.654	176.9	971.8	771.2	2771.9
28	1.650	1.727	1.003	1.657	169.6	944.0	779.0	3113.8
29	1.645	1.728	1.016	1.674	170.6	953.2	776.9	2840.7
30	1.639	1.728	1.047	1.568	171.2	964.7	778.5	2287.2
31	1.637	1.729	1.035	1.589	169.5	972.0	772.1	2536.9
32	1.637	1.729	1.032	1.602	176.2	970.7	782.0	2550.1
33	1.640	1.727	1.035	1.584	171.8	963.1	776.3	2489.7
34	1.635	1.727	1.025	1.599	174.4	974.6	779.4	2685.3
35	1.641	1.722	1.058	1.518	175.1	959.4	783.2	2126.7
36	1.645	1.718	1.064	1.514	176.4	955.2	803.8	2017.1
37	1.667	1.667	1.595	1.059	175.8	879.8	870.6	2747.3
38	1.653	1.671	1.610	1.061	178.0	916.8	866.4	2702.8
39	1.654	1.669	1.690	1.049	178.6	921.2	871.6	2905.9
40	1.655	1.667	1.805	1.046	177.4	919.4	878.8	3068.4
41	1.656	1.673	1.920	1.030	156.4	910.3	863.9	3306.9
42	1.661	1.663	1.927	1.032	178.3	903.9	883.6	3266.7
43	1.664	1.659	2.128	1.025	177.0	904.6	888.4	3417.5
44	1.656	1.669	2.344	1.024	121.1	908.2	870.3	3467.4

Table S3. Selected of geometric and IR spectral parameters of complexes **4**–**44** with hydrogen bond AsO−H···B in a media with $\varepsilon = 10$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$ and $r_{H...B}$), angle (∠OHB) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 2.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{H...B}$, Å	∠OHB, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	$\nu_{O–H}$, cm^{-1}
4	1.632	1.746	0.987	2.492	157.6	978.0	735.7	3418.9
5	1.636	1.750	0.979	2.435	157.8	969.4	730.6	3576.6
6	1.635	1.748	0.981	2.274	173.7	971.1	733.2	3552.0
7	1.634	1.746	0.987	2.254	171.1	975.5	738.8	3414.1
8	1.633	1.743	0.994	2.215	159.4	975.6	742.9	3291.9
9	1.645	1.738	0.994	2.213	166.1	952.5	754.1	3277.5
10	1.632	1.744	0.983	1.878	177.4	979.9	744.6	3512.0
11	1.634	1.737	1.005	1.985	163.4	973.5	753.6	3085.0
12	1.691	1.715	0.987	1.806	138.5	852.2	794.6	3473.6
13	1.635	1.742	0.994	1.794	166.7	974.2	747.5	3291.0
14	1.646	1.740	0.983	1.925	163.9	948.5	746.7	3491.5
15	1.635	1.741	0.990	1.752	175.7	971.9	751.5	3357.8
16	1.638	1.739	1.001	1.748	168.2	964.0	757.6	3150.6
17	1.659	1.728	0.991	1.763	165.9	838.0	774.1	3367.3
18	1.643	1.740	0.993	1.761	158.3	953.1	752.5	3300.6
19	1.636	1.742	0.991	1.717	172.4	969.2	750.3	3348.1
20	1.651	1.730	0.990	1.746	169.3	882.5	771.2	3384.1
21	1.634	1.740	0.996	1.678	173.0	974.5	754.8	3244.7
22	1.637	1.739	1.001	1.636	168.7	967.7	754.9	3151.2
23	1.637	1.735	1.010	1.700	175.8	967.7	762.5	2945.6
24	1.644	1.740	0.999	1.721	159.6	950.9	749.0	3184.0
25	1.639	1.731	1.029	1.626	171.7	964.1	770.8	2597.0
26	1.638	1.732	1.021	1.644	173.1	967.3	770.0	2777.4
27	1.637	1.732	1.020	1.650	176.6	967.9	768.8	2752.5
28	1.651	1.728	1.003	1.659	170.3	893.6	775.5	3115.4
29	1.646	1.729	1.015	1.679	170.3	949.8	772.3	2856.1
30	1.638	1.727	1.043	1.580	175.2	967.6	782.3	2326.1
31	1.638	1.730	1.033	1.593	170.5	966.6	769.4	2556.0
32	1.638	1.729	1.034	1.595	176.2	965.3	763.9	2513.1
33	1.640	1.728	1.037	1.579	172.0	959.4	772.1	2534.5
34	1.636	1.729	1.020	1.618	175.0	970.8	774.4	2764.9
35	1.642	1.722	1.065	1.500	176.1	957.3	782.3	2004.0
36	1.646	1.718	1.070	1.502	176.7	952.4	790.7	1928.5
37	1.668	1.668	1.618	1.054	175.7	877.1	869.5	2814.0
38	1.655	1.672	1.632	1.056	177.7	910.8	864.5	2766.2
39	1.656	1.670	1.712	1.046	178.9	911.3	868.6	2960.3
40	1.657	1.668	1.817	1.045	176.3	907.1	874.8	3080.0
41	1.658	1.674	1.962	1.030	156.8	898.5	859.9	3307.7
42	1.661	1.665	1.925	1.032	179.8	898.3	880.1	3265.7
43	1.664	1.661	2.115	1.025	177.8	899.4	885.6	3410.3
44	1.657	1.671	2.620	1.023	112.2	904.7	867.1	3472.0

Table S4. Selected of geometric and IR spectral parameters of complexes **4**–**44** with hydrogen bond AsO−H···B in a media with $\varepsilon = 20$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$ and $r_{H...B}$), angle (∠OHB) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 2.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{H...B}$, Å	∠OHB, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	$\nu_{O–H}$, cm^{-1}
4	1.632	1.747	0.987	2.488	159.0	976.6	734.6	3416.7
5	1.636	1.750	0.979	2.445	157.1	967.0	729.0	3582.7
6	1.635	1.749	0.981	2.254	174.3	969.8	731.4	3549.2
7	1.635	1.747	0.987	2.252	171.3	972.8	737.6	3412.3
8	1.633	1.743	0.994	2.210	161.3	974.5	741.8	3286.1
9	1.646	1.738	0.993	2.219	165.8	950.3	752.3	3287.9
10	1.633	1.744	0.983	1.874	178.0	976.6	743.8	3505.2
11	1.634	1.738	1.005	1.985	164.6	972.6	752.4	3088.4
12	1.693	1.714	0.988	1.794	140.2	848.0	794.2	3452.6
13	1.635	1.743	0.994	1.791	166.8	974.2	747.5	3291.0
14	1.647	1.741	0.983	1.942	163.6	946.5	743.7	3507.6
15	1.636	1.742	0.990	1.752	175.7	968.1	747.8	3357.5
16	1.638	1.739	1.001	1.747	168.2	962.9	756.8	3145.4
17	1.695	1.714	0.988	1.796	139.7	842.4	795.7	3451.6
18	1.643	1.741	0.993	1.763	158.3	950.8	750.9	3301.8
19	1.636	1.742	0.991	1.715	173.4	967.7	749.3	3341.4
20	1.652	1.730	0.990	1.746	169.7	879.3	769.6	3381.1
21	1.635	1.740	0.996	1.675	172.7	971.6	753.7	3235.5
22	1.637	1.739	1.001	1.633	169.2	965.7	754.0	3137.4
23	1.638	1.736	1.010	1.699	175.4	965.3	760.8	2941.7
24	1.645	1.740	0.999	1.724	159.6	948.9	747.2	3189.6
25	1.637	1.730	1.023	1.648	179.1	968.1	774.4	2690.2
26	1.639	1.732	1.021	1.641	173.3	964.0	766.5	2739.3
27	1.638	1.733	1.021	1.648	176.4	965.6	767.4	2742.3
28	1.652	1.729	1.003	1.661	170.7	892.1	773.5	3117.5
29	1.647	1.730	1.015	1.683	170.0	947.9	769.8	2867.6
30	1.638	1.727	1.042	1.584	179.0	965.5	782.0	2329.1
31	1.639	1.730	1.032	1.596	171.2	963.6	768.0	2565.6
32	1.639	1.729	1.035	1.591	176.4	963.5	780.5	2492.1
33	1.641	1.729	1.037	1.576	172.3	958.2	771.1	2459.8
34	1.637	1.730	1.018	1.630	176.6	968.7	772.7	2808.9
35	1.643	1.722	1.070	1.489	176.7	956.6	781.7	1917.6
36	1.647	1.718	1.074	1.492	176.9	950.8	802.2	1859.3
37	1.668	1.668	1.630	1.051	175.5	875.8	868.5	2849.1
38	1.659	1.670	1.750	1.042	178.3	898.6	869.1	3035.5
39	1.657	1.670	1.722	1.045	178.6	906.3	866.9	2986.6
40	1.658	1.668	1.824	1.045	174.6	904.2	871.4	3079.1
41	1.659	1.674	1.942	1.029	155.6	897.7	859.3	3308.7
42	1.661	1.665	1.925	1.032	179.1	895.1	878.1	3265.1
43	1.664	1.662	2.109	1.025	177.9	896.1	883.6	3406.3
44	1.658	1.670	2.621	1.023	113.1	900.4	868.0	3472.0

Table S5. Selected of geometric and IR spectral parameters of complexes **4**–**44** with hydrogen bond AsO−H···B in a media with $\varepsilon = 40$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$ and $r_{H...B}$), angle (∠OHB) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 2.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{H...B}$, Å	∠OHB, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	$\nu_{O–H}$, cm^{-1}
4	1.632	1.747	0.987	2.485	159.9	975.9	733.9	3414.8
5	1.637	1.750	0.979	2.451	156.7	965.7	728.2	3586.2
6	1.635	1.749	0.981	2.243	174.7	969.2	730.6	3547.8
7	1.635	1.747	0.987	2.252	171.3	971.5	736.9	3411.6
8	1.633	1.743	0.994	2.206	162.5	973.9	741.6	3281.0
9	1.646	1.739	0.993	2.223	165.6	949.2	751.4	3293.8
10	1.634	1.744	0.983	1.873	178.3	974.8	743.2	3501.7
11	1.634	1.738	1.005	1.983	165.6	971.9	751.9	3086.7
12	1.694	1.714	0.989	1.785	141.4	845.7	794.2	3436.6
13	1.636	1.743	0.994	1.790	166.8	970.1	745.0	3283.0
14	1.647	1.741	0.982	1.953	163.3	945.4	742.7	3517.1
15	1.636	1.742	0.990	1.751	175.7	968.6	748.3	3357.1
16	1.639	1.739	1.001	1.746	168.1	962.1	756.5	3143.6
17	1.695	1.714	0.989	1.790	140.6	841.0	795.9	3442.8
18	1.644	1.741	0.993	1.765	158.2	949.8	750.3	3303.6
19	1.637	1.742	0.991	1.714	173.9	966.7	748.8	3338.0
20	1.653	1.730	0.990	1.746	170.0	940.8	768.8	3379.7
21	1.636	1.740	0.996	1.674	172.5	969.9	753.1	3230.8
22	1.638	1.739	1.002	1.631	169.4	964.7	753.5	3129.5
23	1.638	1.736	1.010	1.698	175.3	964.0	760.0	2938.3
24	1.645	1.741	0.999	1.726	159.6	947.8	746.2	3193.0
25	1.638	1.730	1.024	1.644	179.1	966.5	774.4	2669.0
26	1.639	1.732	1.022	1.640	173.2	962.9	766.0	2739.8
27	1.639	1.733	1.021	1.646	176.3	964.3	766.8	2736.1
28	1.653	1.729	1.002	1.662	170.9	940.7	772.4	3118.9
29	1.647	1.731	1.014	1.685	169.9	947.1	768.5	2873.2
30	1.639	1.727	1.043	1.579	176.9	963.9	781.5	2319.4
31	1.639	1.731	1.032	1.597	171.7	962.0	767.3	2571.9
32	1.639	1.729	1.010	1.589	176.4	962.3	762.9	2482.3
33	1.641	1.729	1.038	1.574	172.5	957.4	770.5	2449.5
34	1.637	1.731	1.016	1.636	176.6	967.3	770.5	2834.2
35	1.643	1.721	1.073	1.481	177.0	951.1	781.4	1864.7
36	1.648	1.718	1.076	1.486	177.0	949.9	801.9	1814.1
37	1.668	1.668	1.637	1.050	175.5	875.0	867.9	2867.0
38	1.659	1.670	1.747	1.042	178.4	897.3	867.8	3032.9
39	1.657	1.670	1.727	1.044	178.3	904.0	866.0	2998.8
40	1.658	1.669	1.828	1.045	174.5	901.7	870.4	3082.7
41	1.674	1.659	2.243	1.025	161.0	858.5	895.1	3438.6
42	1.662	1.666	1.924	1.032	178.6	893.6	877.0	3264.6
43	1.664	1.663	2.106	1.025	177.9	894.3	882.6	3404.1
44	1.670	1.659	2.584	1.023	159.4	868.3	898.1	3471.4

Table S6. Selected of geometric and IR spectral parameters of complexes **4**–**44** with hydrogen bond AsO−H···B in a media with $\varepsilon = 80$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$ and $r_{H...B}$), angle (∠OHB) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 2.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{H...B}$, Å	∠OHB, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	$\nu_{O–H}$, cm^{-1}
4	1.633	1.747	0.987	2.483	160.4	975.6	733.4	3413.8
5	1.637	1.750	0.979	2.454	156.4	965.0	727.7	3588.1
6	1.635	1.749	0.981	2.236	175.1	968.9	730.1	3547.0
7	1.635	1.747	0.987	2.251	171.3	970.8	736.4	3411.5
8	1.633	1.743	0.994	2.205	163.0	973.6	741.3	3279.8
9	1.646	1.739	0.993	2.225	165.4	948.6	750.9	3297.0
10	1.634	1.744	0.983	1.872	178.5	973.9	743.0	3500.0
11	1.634	1.738	1.005	1.982	166.2	971.6	751.8	3085.1
12	1.694	1.714	0.990	1.778	142.2	844.4	794.2	3426.5
13	1.636	1.743	0.994	1.790	166.7	969.3	744.4	3282.0
14	1.648	1.742	0.982	1.960	163.2	944.8	741.8	3521.1
15	1.636	1.742	0.990	1.752	175.7	968.1	747.8	3357.5
16	1.639	1.740	1.001	1.746	168.0	961.6	756.2	3143.6
17	1.696	1.714	0.989	1.788	141.0	840.3	796.1	3438.4
18	1.644	1.741	0.993	1.766	158.1	949.3	750.2	3305.0
19	1.637	1.742	0.992	1.713	174.2	966.2	748.5	3336.4
20	1.653	1.731	0.990	1.746	170.1	876.5	768.2	3379.0
21	1.627	1.738	0.991	1.714	174.6	1000.0	767.4	3349.9
22	1.638	1.739	1.002	1.630	169.5	964.2	753.2	3125.6
23	1.639	1.736	1.010	1.698	175.2	963.3	759.6	2936.0
24	1.645	1.741	0.998	1.727	159.6	947.3	745.7	3194.9
25	1.638	1.730	1.025	1.641	179.0	965.7	774.6	2657.1
26	1.639	1.732	1.022	1.639	173.3	962.4	765.1	2730.4
27	1.639	1.733	1.021	1.645	176.2	963.5	766.3	2733.1
28	1.653	1.729	1.002	1.663	171.0	890.6	771.8	3119.7
29	1.647	1.731	1.014	1.685	169.8	946.7	767.9	2876.2
30	1.639	1.727	1.044	1.576	176.9	963.0	781.4	2306.9
31	1.640	1.731	1.031	1.598	171.9	961.1	766.9	2575.5
32	1.639	1.729	1.035	1.588	176.4	961.8	762.5	2480.6
33	1.641	1.729	1.038	1.573	172.6	957.0	770.2	2443.4
34	1.637	1.732	1.016	1.639	176.5	966.3	769.3	2847.0
35	1.644	1.721	1.075	1.477	177.2	950.9	797.9	1835.5
36	1.648	1.718	1.078	1.483	177.1	941.7	787.6	1787.8
37	1.668	1.668	1.640	1.050	175.5	874.6	867.5	2876.1
38	1.656	1.673	1.652	1.053	177.9	904.8	861.3	2817.8
39	1.657	1.670	1.730	1.043	178.2	902.9	865.5	3004.5
40	1.659	1.669	1.830	1.045	174.0	900.4	869.8	3084.1
41	1.659	1.674	1.950	1.030	157.5	893.6	858.2	3311.1
42	1.662	1.666	1.924	1.032	178.2	892.8	876.4	3264.6
43	1.664	1.663	2.105	1.025	177.8	893.4	881.9	3402.9
44	1.660	1.670	2.620	1.023	114.0	896.8	868.3	3471.0

Table S7. Selected of geometric and IR spectral parameters of complexes **45**–**82** with hydrogen bond As=O···HA in a vacuum (ε = 1): interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$, $r_{As=O\ldots H}$ and $r_{H–A}$), angle (∠OHA) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 3.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{As=O\ldots H}$, Å	$r_{H–A}$, Å	∠OHA, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	ν_{OH}, cm^{-1}
45	1.626	1.749	0.972	2.203	1.086	129.7	1001.3	743.4	3211.8
46	1.630	1.743	0.981	2.121	1.016	149.4	990.5	754.2	3575.0
47	1.627	1.745	0.976	2.159	1.091	155.7	997.6	752.2	3105.8
48	1.626	1.749	0.972	2.151	1.087	133.9	999.7	744.1	3190.1
49	1.626	1.748	0.973	2.150	1.087	145.0	1000.7	747.1	3220.8
50	1.625	1.750	0.971	2.151	1.090	145.8	1003.0	743.2	3176.5
51	1.636	1.735	1.001	1.865	0.984	148.6	974.5	768.3	3493.2
52	1.630	1.751	0.970	1.824	0.979	158.6	988.0	744.1	3550.1
53	1.639	1.732	0.989	1.798	0.994	145.0	977.3	766.6	3387.8
54	1.634	1.743	0.979	1.776	0.989	154.6	978.0	748.5	3604.7
55	1.628	1.746	0.981	2.112	1.349	149.1	993.3	749.4	2644.9
56	1.637	1.738	0.983	1.712	0.992	158.9	969.4	763.6	3292.7
57	1.636	1.738	0.975	1.679	0.996	161.9	972.5	763.3	3251.5
58	1.636	1.732	1.000	1.674	0.997	171.1	974.2	775.0	3146.3
59	1.631	1.744	0.971	1.653	0.998	170.6	987.7	752.0	3210.1
60	1.639	1.735	0.982	1.588	0.966	159.4	965.7	769.9	3583.4
61	1.635	1.739	0.973	1.582	1.011	172.2	978.9	762.5	3001.7
62	1.634	1.738	0.973	1.572	1.011	176.3	1000.8	792.9	3069.7
63	1.643	1.723	1.003	1.569	1.020	167.4	958.4	795.5	2846.3
64	1.639	1.735	0.979	1.547	1.024	177.2	965.5	769.4	2774.2
65	1.639	1.734	0.970	1.571	1.058	169.2	985.0	770.1	3785.3
66	1.640	1.724	0.992	1.516	1.030	177.1	968.4	792.7	2674.8
67	1.640	1.724	0.993	1.515	1.030	176.7	968.4	793.1	2662.6
68	1.641	1.724	0.990	1.489	1.036	177.6	967.9	792.4	2571.5
69	1.646	1.725	0.991	1.488	1.041	168.1	956.9	788.1	2505.9
70	1.641	1.731	0.970	1.520	1.073	166.3	979.2	774.6	3783.1
71	1.643	1.733	0.976	1.469	1.046	176.1	955.1	773.2	2441.9
72	1.642	1.730	0.970	1.455	1.095	170.5	981.1	778.0	2295.1
73	1.647	1.730	0.981	1.420	1.062	176.9	938.5	777.1	2173.1
74	1.686	1.714	0.979	1.035	1.491	174.9	808.4	875.7	2580.9
75	1.683	1.709	0.972	1.018	1.545	176.2	879.8	806.3	2875.0
76	1.682	1.712	0.973	1.041	1.568	172.1	879.7	803.8	3750.2
77	1.696	1.696	1.002	1.002	1.592	167.1	859.9	829.6	3223.2
78	1.700	1.700	1.002	1.002	1.685	166.9	852.4	820.7	3202.2
79	1.681	1.713	0.973	1.060	1.883	177.1	875.1	800.4	3751.9
80	1.700	1.703	0.976	0.982	1.868	169.8	845.4	813.7	3705.6
81	1.700	1.703	0.975	0.980	1.902	168.8	844.7	813.9	3708.6
82	1.689	1.708	0.973	1.012	2.082	177.4	861.2	808.4	2968.0

Table S8. Selected of geometric and IR spectral parameters of complexes **45**–**82** with hydrogen bond As=O···HA in a media with $\varepsilon = 40$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$, $r_{As=O…H}$ and $r_{H–A}$), angle (∠OHA) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 3.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{As=O…H}$, Å	$r_{H–A}$, Å	∠OHA, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	ν_{OH}, cm^{-1}
45	1.64	1.75	0.97	2.12	1.09	152.0	970.3	724.9	3184.2
46	1.64	1.75	0.98	2.51	1.01	174.7	969.2	730.6	3547.8
47	1.63	1.75	0.98	2.34	1.09	148.8	973.1	731.0	3129.9
48	1.64	1.75	0.97	2.06	1.09	157.5	968.7	725.3	3150.6
49	1.63	1.75	0.97	2.14	1.09	154.6	971.2	724.4	3208.1
50	1.63	1.75	0.97	2.07	1.09	170.8	971.5	722.9	3138.0
51	1.65	1.74	1.00	1.83	0.99	152.2	947.8	746.2	3441.5
52	1.64	1.75	0.97	1.72	0.99	175.9	961.5	732.0	3401.1
53	1.65	1.74	0.98	1.70	1.01	151.3	945.4	742.7	3156.1
54	1.64	1.75	0.97	1.65	1.00	177.1	954.6	733.6	3766.6
55	1.64	1.75	0.98	2.16	1.35	152.4	965.7	728.2	2652.5
56	1.65	1.74	0.98	1.70	0.99	159.7	944.5	739.8	3244.9
57	1.65	1.74	0.98	1.61	1.00	171.1	949.5	749.0	3077.7
58	1.65	1.74	0.99	1.62	1.00	176.0	949.2	751.4	3052.3
59	1.64	1.75	0.97	1.61	1.01	167.7	955.2	736.9	3041.1
60	1.65	1.74	0.98	1.49	0.98	167.8	939.9	747.3	3658.9
61	1.65	1.74	0.97	1.49	1.03	177.0	949.3	744.5	2606.3
62	1.65	1.74	0.97	1.48	1.04	176.5	943.9	746.0	2514.3
63	1.65	1.73	1.00	1.53	1.03	170.8	891.1	772.4	2662.6
64	1.65	1.73	1.00	1.55	1.02	172.3	948.6	773.8	2755.4
65	1.64	1.74	0.97	1.58	1.06	174.4	954.5	740.9	3761.8
66	1.65	1.73	0.99	1.44	1.05	174.3	940.8	768.8	2228.0
67	1.65	1.73	0.99	1.46	1.05	173.4	939.8	769.2	2305.9
68	1.66	1.73	0.99	1.38	1.08	175.3	858.3	767.7	1914.3
69	1.70	1.71	0.99	1.03	1.52	175.6	841.0	795.9	2574.0
70	1.64	1.74	0.97	1.59	1.06	168.7	956.0	740.3	3761.1
71	1.65	1.73	0.99	1.44	1.05	174.5	940.0	768.0	2239.2
72	1.64	1.74	0.97	1.57	1.07	174.6	954.5	741.9	3765.8
73	1.69	1.71	0.99	1.03	1.50	178.8	845.7	794.2	2574.8
74	1.70	1.71	0.98	1.01	1.60	177.2	835.0	799.0	2987.2
75	1.69	1.72	0.97	1.02	1.55	177.9	850.9	789.0	3743.7
76	1.69	1.72	0.97	1.04	1.56	177.2	856.7	782.7	3746.1
77	1.71	1.71	0.99	0.99	1.71	166.9	823.7	807.6	3436.2
78	1.71	1.71	0.99	0.99	1.75	169.4	823.1	807.1	3323.9
79	1.70	1.71	0.97	1.02	2.02	176.3	834.1	791.2	3748.5
80	1.70	1.71	0.97	1.01	1.60	177.9	842.6	792.9	3731.8
81	1.71	0.98	0.98	0.98	1.86	168.0	812.6	802.0	3684.6
82	1.70	1.71	0.97	1.00	2.17	177.4	826.0	795.6	3738.2

Table S9. Selected of geometric and IR spectral parameters of complexes **45**–**82** with hydrogen bond As=O···HA in a media with $\varepsilon = 80$: interatomic distances ($r_{As=O}$, $r_{As–O}$, $r_{O–H}$, $r_{As=O…H}$ and $r_{H–A}$), angle (∠OHA) and stretching vibrational frequencies ($\nu_{As–O}$, $\nu_{As=O}$ and $\nu_{O–H}$). Numbering of complexes in accordance with Scheme 3.

	$r_{As=O}$, Å	$r_{As–O}$, Å	$r_{O–H}$, Å	$r_{As=O…H}$, Å	$r_{H–A}$, Å	∠OHA, °	$\nu_{As=O}$, cm^{-1}	$\nu_{As–O}$, cm^{-1}	ν_{OH}, cm^{-1}
45	1.64	1.75	0.97	2.12	1.09	152.2	969.5	724.6	3183.7
46	1.64	1.75	0.98	2.53	1.01	110.2	968.8	730.1	3547.0
47	1.63	1.75	0.98	2.35	1.09	148.9	972.4	730.5	3657.5
48	1.64	1.75	0.97	2.06	1.09	158.1	967.9	724.8	3149.4
49	1.63	1.75	0.97	2.14	1.09	156.2	970.3	724.2	3206.3
50	1.63	1.75	0.97	2.07	1.09	171.4	970.4	722.6	3771.8
51	1.65	1.74	1.00	1.82	0.99	152.3	947.3	745.7	3194.9
52	1.64	1.75	0.97	1.72	0.99	176.0	960.8	731.8	3396.8
53	1.65	1.74	0.98	1.69	1.01	151.6	944.8	741.8	3145.0
54	1.64	1.75	0.98	1.67	1.00	166.6	949.4	733.7	3185.7
55	1.64	1.75	0.98	2.16	1.35	152.6	965.0	727.7	2652.0
56	1.65	1.74	0.98	1.70	0.99	169.7	944.0	739.2	3243.6
57	1.65	1.74	0.98	1.61	1.00	171.3	949.1	748.5	3072.8
58	1.65	1.74	0.99	1.61	1.01	176.1	948.6	750.9	3048.1
59	1.64	1.75	0.97	1.61	1.01	167.6	954.5	736.7	3038.1
60	1.65	1.74	0.98	1.48	0.98	168.0	939.3	746.8	2817.5
61	1.65	1.74	0.97	1.49	1.03	176.9	948.7	744.3	2588.0
62	1.65	1.74	0.97	1.47	1.04	176.4	936.1	744.7	2473.5
63	1.65	1.73	1.00	1.53	1.03	170.8	940.4	771.8	2657.4
64	1.65	1.73	1.00	1.55	1.02	172.2	948.1	773.2	2750.4
65	1.64	1.74	0.97	1.60	1.06	168.8	953.2	760.1	3757.8
66	1.65	1.73	0.99	1.44	1.05	174.2	876.5	768.2	2214.3
67	1.65	1.74	0.98	1.61	1.00	171.2	935.9	769.0	2301.1
68	1.66	1.73	0.99	1.38	1.08	175.2	856.1	767.3	1899.9
69	1.70	1.71	0.99	1.03	1.52	175.6	840.3	796.1	2582.9
70	1.64	1.74	0.97	1.59	1.06	174.3	953.5	740.7	3768.7
71	1.65	1.73	0.99	1.44	1.05	174.5	939.5	767.5	2223.9
72	1.64	1.74	0.97	1.58	1.07	174.8	953.7	741.2	3765.8
73	1.69	1.71	0.99	1.03	1.50	178.7	844.4	794.2	2588.8
74	1.70	1.71	0.98	1.01	1.60	177.2	833.7	798.8	2998.3
75	1.69	1.72	0.97	1.02	1.55	178.0	835.1	799.1	3014.3
76	1.69	1.72	0.97	1.04	1.56	177.3	850.3	788.5	3742.8
77	1.71	1.71	0.99	0.99	1.72	166.8	856.2	782.9	3744.7
78	1.71	1.71		0.99	1.75	169.4	822.7	807.0	3441.6
79	1.70	1.71	0.97	1.02	2.02	176.1	822.2	806.6	3329.4
80	1.70	1.72	0.97	1.01	1.60	177.9	833.6	790.8	3748.2
81	1.71	1.71	0.98	0.98	1.86	167.9	841.7	792.1	3732.1
82	1.70	1.71	0.97	1.00	2.17	177.6	811.9	801.7	3678.9

Table S10. Selected geometric parameters of $H_2As(O)OH$ monomer **1** in a dielectric continuum with various ε: interatomic distances ($r_{As–O}$, $r_{As=O}$, r_{OH} and r_{AsH}), angles (OAsO and HAsH) and dihedral angle OAsOH.

ε	$r_{As–O}$, Å	$r_{As=O}$, Å	r_{OH}, Å	r_{AsH}, Å	∠OAsO, °	∠HAsH, °	∠OAsOH, °
1	1.758	1.621	0.970	1.501	114	105	0
5	1.755	1.628	0.970	1.498	115	107	37
10	1.755	1.630	0.970	1.496	115	108	54
20	1.755	1.630	0.970	1.497	115	107	47
40	1.755	1.631	0.970	1.496	115	107	51
80	1.755	1.631	0.970	1.491	115	108	53

Table S11. Selected geometric parameters of $H_2AsO_2^-$ anion **2** in a dielectric continuum with various ε: interatomic distances ($r_{As–O}$ and r_{AsH}) and angles (OAsO and HAsH).

ε	$r_{As–O}$, Å	r_{AsH}, Å	∠OAsO, °	∠HAsH, °
1	1.654	1.539	123	99
5	1.658	1.524	120	101
10	1.660	1.521	119	101
20	1.660	1.519	119	101
40	1.661	1.519	119	102
80	1.661	1.518	119	102

Table S12. Selected geometric parameters of $H_2As(OH)_2^+$ cation **3** in a dielectric continuum with various ε: interatomic distances ($r_{As–O}$, r_{OH} and r_{AsH}), angles (OAsO and HAsH) and dihedral angle (OAsOH).

ε	$r_{As–O}$, Å	r_{OH}, Å	r_{AsH}, Å	∠OAsO, °	∠HAsH, °	∠OAsOH, °
1	1.702	0.974	1.484	113	115	65
5	1.706	0.974	1.479	112	116	69
10	1.707	0.974	1.479	112	116	70
20	1.708	0.974	1.478	112	116	70
40	1.708	0.974	1.478	112	116	70

80	1.709	0.974	1.478	112	116	70

Figure S1. The dependencies of the difference between the band positions $\Delta\nu = \nu_{As=O} - \nu_{As-O}$ and coordinate q_1 for complexes $H_2As(O)OH\cdots B$ in $\varepsilon = 1$, 5, 10, 20, 40 and 80, which are approximated by linear functions.

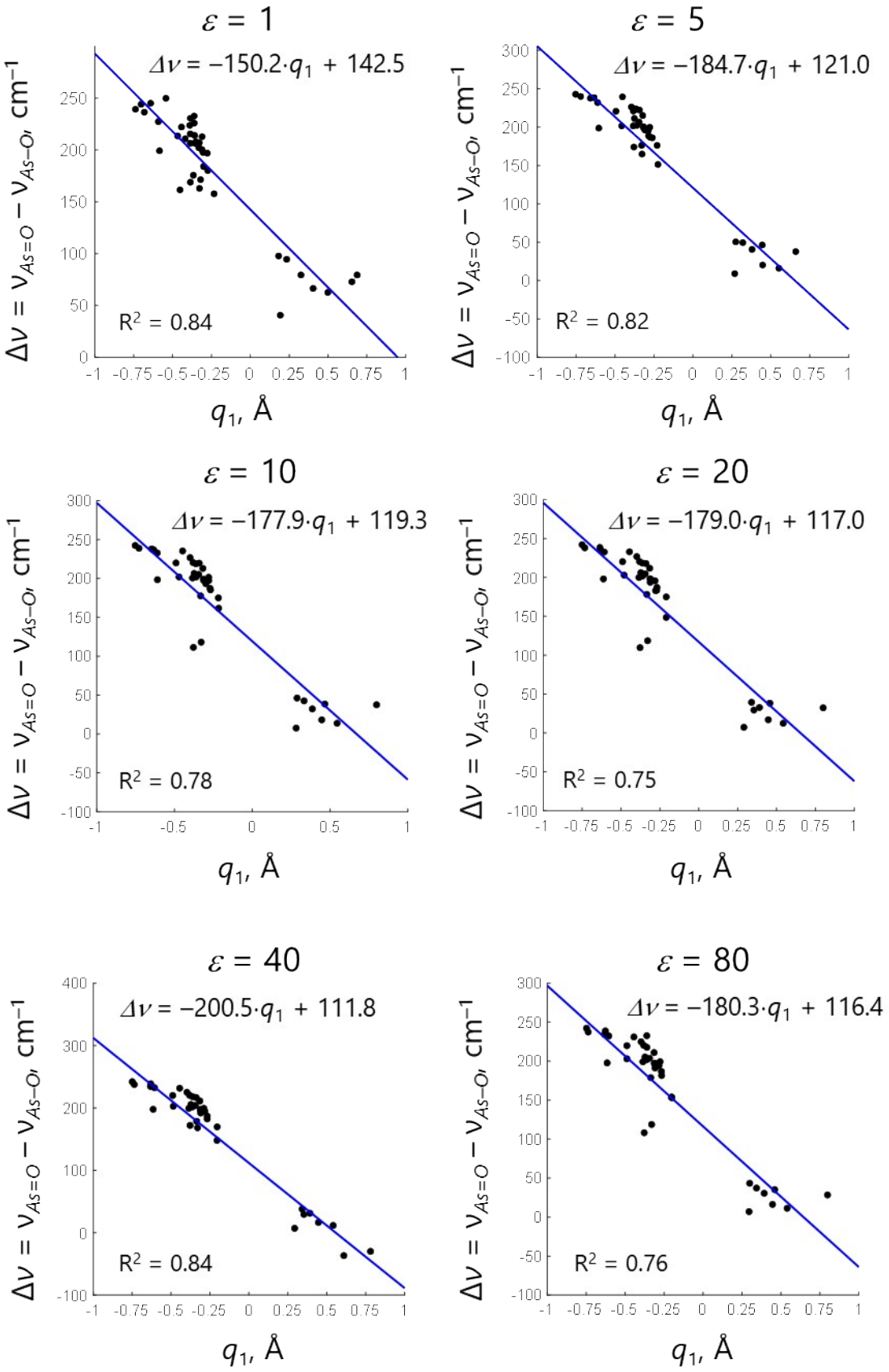

Figure S2. The dependencies of the difference between the band positions $\Delta\nu = \nu_{As=O} - \nu_{As-O}$ and coordinate q_1 for complexes $H_2As(OH)O\cdots HA$ in $\varepsilon = 1$, 40 and 80, which are approximated by linear functions.