Electronic supplementary information (ESI)

Matrix Isolation FTIR Study of Hydrogen-bonded Complexes of Methanol with Heterocyclic Organic Compounds

Xiaotong Jiang, Shijie Liu, Narcisse T. Tsona, Shanshan Tang, Lei Ding, Hailiang Zhao, Lin Du*

Environment Research Institute, Shandong University, Shanda South Road 27, 250100 Shandong, China

Corresponding author

*E-mail: lindu@sdu.edu.cn

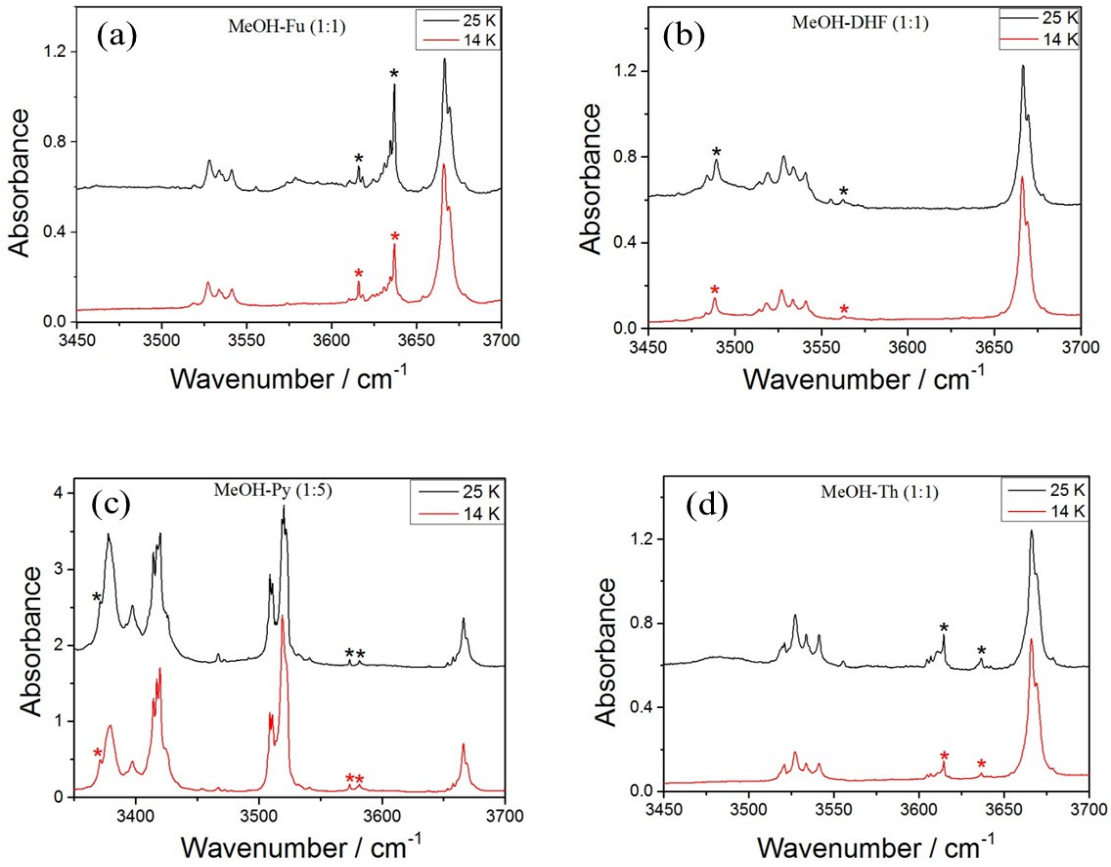

Fig. S1 Matrix isolation FTIR spectra of the MeOH complexes at different temperature. (a) MeOH/Fu/Ar = 1/1/700; (b) MeOH/DHF/Ar = 1/1/700; (c) MeOH/Py/Ar = 1/5/700; (d) MeOH/Th/Ar = 1/1/700. Bands marked with asterisk are new features from the complexes. The spectra were offset for clarity.

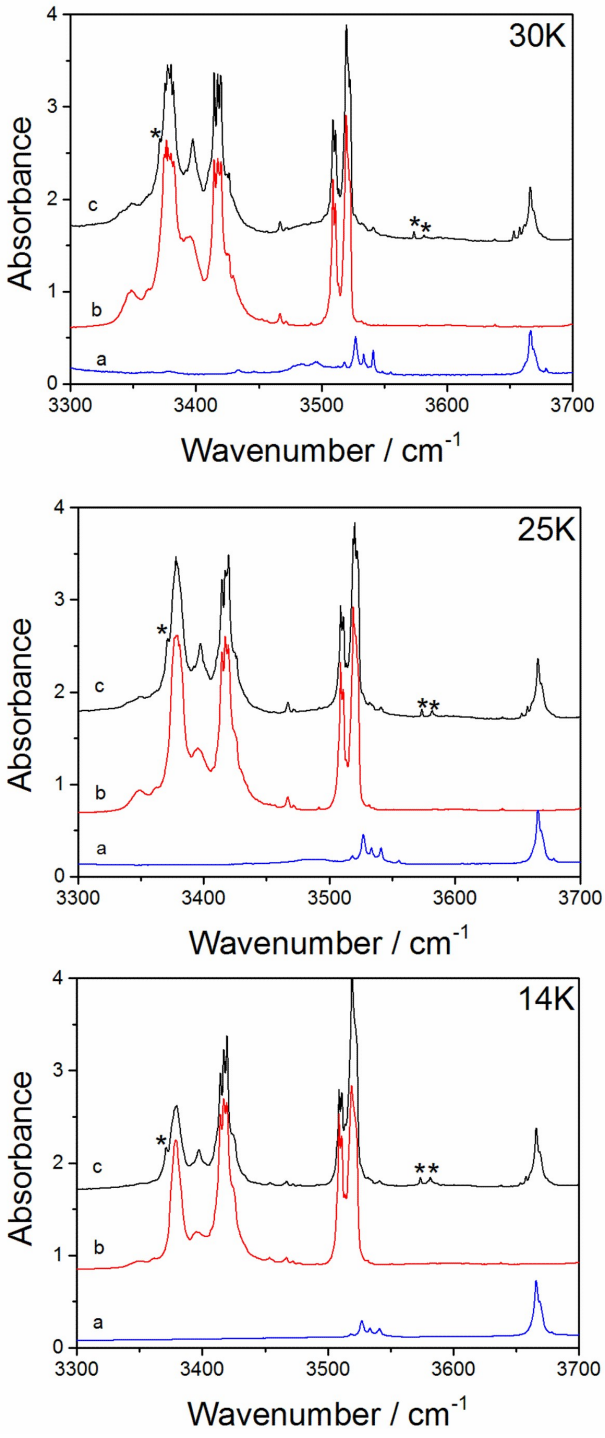

Fig. S2 Matrix isolation FTIR spectra of MeOH, pyrrole, and the co-deposition of them at 14 K, 25 K, 30 K. (a) MeOH/Ar = 1/140; (b) Py/Ar = 1/700; (c) MeOH/Py/Ar = 1/5/700. Bands marked with asterisk are new features from MeOH–Py complex. The spectra were offset for clarity.

Table S1 Selected optimized geometric parameters in the MeOH–Fu, MeOH–DHF, MeOH–Py and MeOH–Th complexes (angles in degrees and bond lengths in Å).

Conformer	Bond type	Method [a]	R(OH) [b]	Δr(OH) [c]	R(HB) [d]	θ(HB) [e]
MeOH–Fu (a)	O−H···π	M06-2X	0.9610	0.0025		
		ωB97XD	0.9590	0.0028		
		B3LYP-D3	0.9630	0.0022		
MeOH–Fu (b)	O−H···O	M06-2X	0.9609	0.0024	2.1595	134.1
		ωB97XD	0.9590	0.0029	2.1218	144.5
		B3LYP-D3	0.9627	0.0019	2.1590	140.3
MeOH–DHF (b)	O−H···O	M06-2X	0.9673	0.0088	1.8567	164.2
		ωB97XD	0.9668	0.0106	1.8445	172.3
		B3LYP-D3	0.9710	0.0102	1.8464	170.5
MeOH–Py (a) [g]	O−H···π	M06-2X	0.9662	0.0061		
		ωB97XD	0.9662	0.0087		
		B3LYP-D3	0.9704	0.0085		
Py–MeOH (b) [f]	N−H···O	M06-2X	1.0098	0.0512	1.9851	148.6
		ωB97XD	1.0101	0.0540	1.9291	166.1
		B3LYP-D3	1.0106	0.0498	1.9383	163.8
MeOH–Th (a) [g]	O−H···π	M06-2X	0.9717	0.0102		
		ωB97XD	0.9720	0.0136		
		B3LYP-D3	0.9764	0.0133		

[a] The MeOH–Th complexes are calculated with the aug-cc-pV(T+d)Z basis set, and all other complexes with the aug-cc-pVTZ basis set, respectively. [b] OH bond length in the complex. [c] Change in the OH/NH bond length upon complexation. [d] Intermolecular hydrogen bond distance. [e] Intermolecular hydrogen bond angle. [f] In the Py–MeOH (b) complex, MeOH acts as hydrogen bond acceptor. R(NH) for pyrrole. R(NH_b···O) and θ(NH_b···O) for the Py–MeOH complexes. [g] MeOH–DHF (a) and MeOH–Th (b) conformer couldn't be located with the M06-2X, ωB97XD and B3LYP-D3 functionals.

Table S2 Calculated binding energies (*BE*), zero point vibrational energy (ZPVE), enthalpies of formation (ΔH^{θ}), and Gibbs free energies of formation (ΔG^{θ}) for the MeOH–Fu, MeOH–DHF, MeOH–Py and MeOH–Th complexes with M06-2X, ωB97XD and B3LYP-D3 functionals.

Method [a]	Conformer	Bond type	*BE* [b]	ZPVE	ΔH^{θ}	ΔG^{θ}
M06-2X	MeOH–Fu (a)	O−H···π	-14.1	3.2	-14.4	25.2
	MeOH–Fu (b)	O−H···O	-11.1	5.7	-10.8	26.4
	MeOH–DHF (b) [d]	O−H···O	-19.6	5.8	-19.4	16.5
	MeOH–Py (a)	O−H···π	-18.3	4.9	-17.8	18.5
	Py–MeOH (b) [c]	N−H···O	-18.6	5.4	-13.9	17.1
	MeOH–Th (a) [d]	O−H···π	-15.1	3.7	-14.3	22.3
ωB97XD	MeOH–Fu (a)	O−H···π	-5.6	3.0	-6.4	38.3
	MeOH–Fu (b)	O−H···O	-10.9	4.3	-9.8	23.3
	MeOH–DHF (b)	O−H···O	-20.5	6.7	-19.7	15.2
	MeOH–Py (a)	O−H···π	-17.3	5.1	-16.7	18.7
	Py–MeOH (b) [c]	N−H···O	-19.3	5.2	-17.9	15.2
B3LYP-D3	MeOH–Fu (a)	O−H···π	-13.5	3.3	-11.8	19.6
	MeOH–Fu (b)	O−H···O	-12.9	4.1	-11.5	19.5
	MeOH–DHF (b)	O−H···O	-22.8	5.7	-22.1	10.8
	MeOH–Py (a)	O−H···π	-18.1	3.4	-16.4	13.3
	Py–MeOH (b) [c]	N−H···O	-21.9	3.8	-18.3	6.8
	MeOH–Th (a)	O−H···π	-15.0	3.2	-13.1	17.6

[a] The MeOH–Th complexes are calculated with the aug-cc-pV(T+d)Z basis set, and all other complexes with the aug-cc-pVTZ basis set, respectively. [b] *BE* corrected with ZPVE. All energies given in kJ mol^{-1}. [c] In the Py–MeOH (b) complex, MeOH acts as hydrogen bond acceptor. [d] MeOH–DHF (a) and MeOH–Th (b) conformer couldn't be located with the M06-2X, ωB97XD and B3LYP-D3 functionals.