**Electronic Supplementary Information**

# Strong Proton Shared Hydrogen Bonding in Methyl Imidazole-HCl Complex: Evidence from Matrix Isolation Infrared Spectroscopy and *Ab initio* Computations

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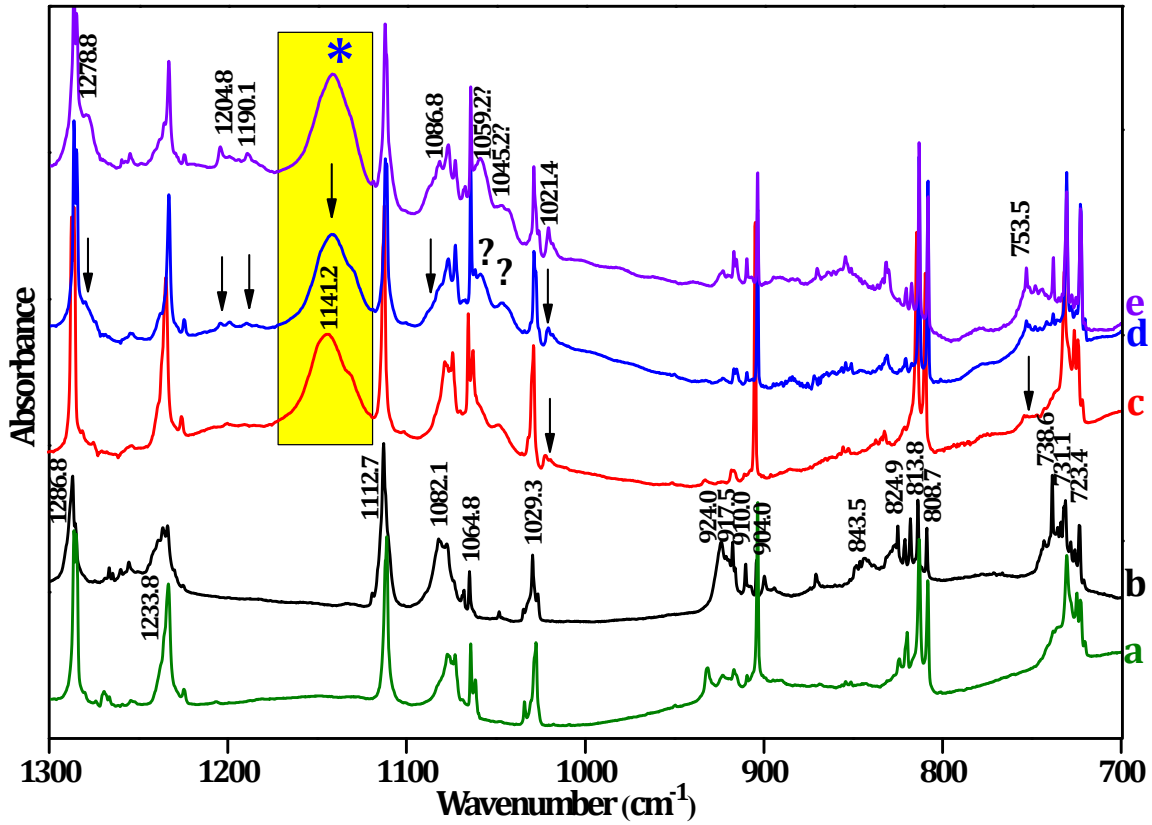


**Figure S1.** Matrix isolation infrared spectra of co-deposition experiments of M-Imid and HCl precursors in $N_2$ matrix. Trace 'a') M-Imid:$N_2$ (2:1000) as deposited at 12 K; Trace 'b') M-Imid:$N_2$ (2:1000) at 12 K after annealing at 30 K; Trace 'c', 'd' and 'e' are as a result of the codeposition experiments of HCl/M-Imid/$N_2$. Trace 'c'): 12 K; Trace 'd'): 25 K – 12 K; Trace 'e'): 32 K – 12 K. The feature marked with asterisk is due to H-Cl stretching of proton shared hydrogen bonded complex.

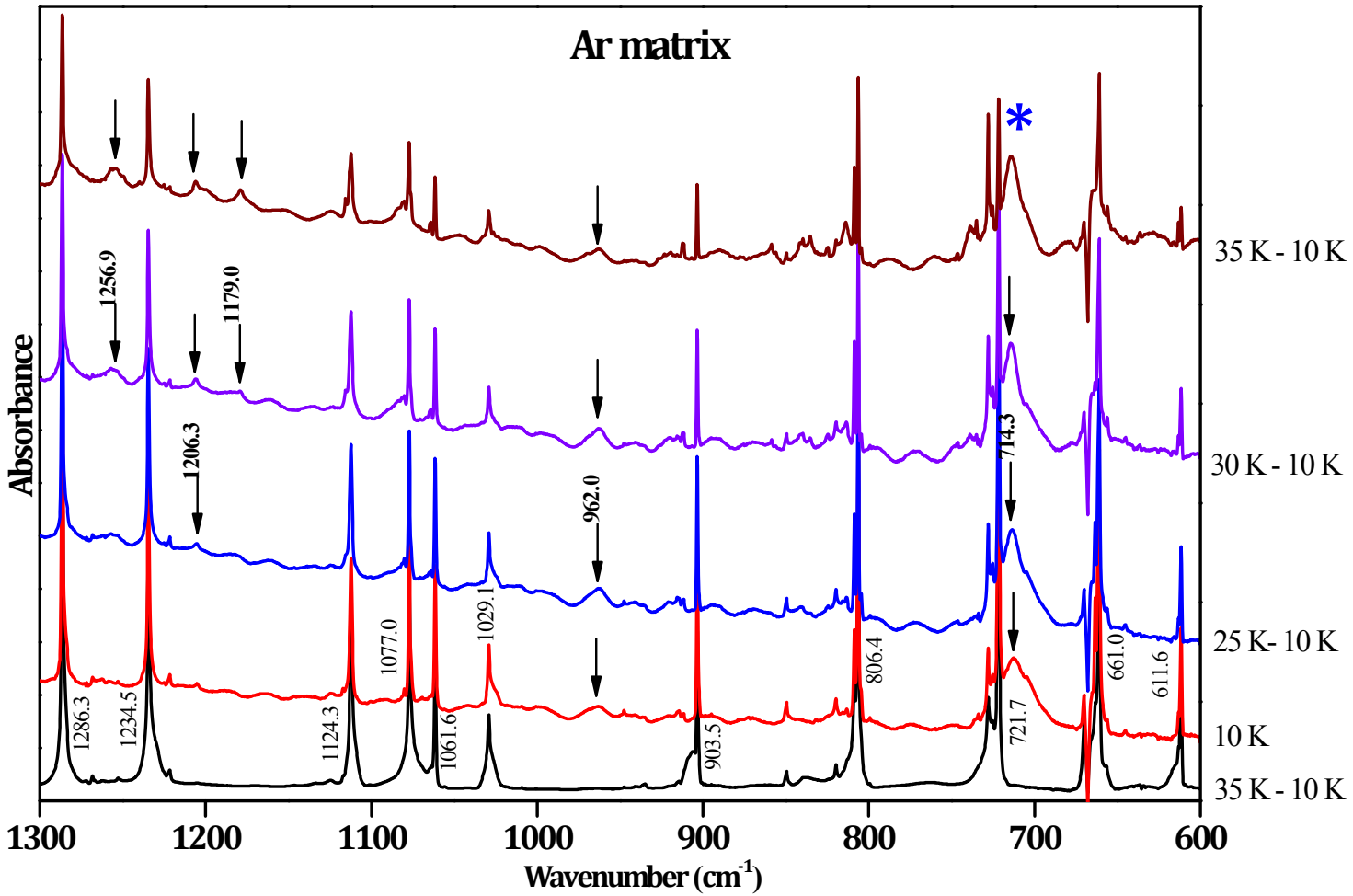


**Figure S2.** Matrix isolation infrared spectra of co-deposition experiments of M-Imid and HCl precursors in Ar matrix have been depicted. Trace 'a') M-Imid:$N_2$ (2:1000) as deposited at 12 K; Trace 'b') M-Imid:Ar (2:1000) at 12 K after annealing at 30 K; Trace 'c', 'd' and 'e' are as a result of the co-deposition experiments of HCl/M-Imid/$N_2$. Trace 'c'): 12 K; Trace 'd'): 25 K – 12 K; Trace 'e'): 32 K – 12 K. The feature marked with asterisk is due to H-Cl stretching of proton shared hydrogen bonded complex.

**Table S1.** Results of energy decomposition analysis performed on the complexes A, B and C at B3LYP-D3/TZ2P level of theory For comparison, the results of $NH_3$-HCl, Pyridine-HCl and $N(CH_3)_3$-HCl are also shown.

| **Complexes** | **Energy decomposition in kcal/mol** | | | | |
|---|---|---|---|---|---|
| | **Electrostatic** | **Charge-transfer** | **Dispersion** | **Pauli repulsion** | **Total binding energy** |
| complex A | -25.99 | -22.76 | -1.74 | +36.91 | -13.58 |
| complex B | -6.08 | -4.85 | -3.53 | +9.29 | -5.17 |
| complex C | -2.19 | -1.15 | -1.57 | +3.51 | -1.40 |
| $NH_3$-HCl | -20.17 | -16.25 | -1.15 | +26.99 | -10.58 |
| Pyridine-HCl | -27.31 | -25.12 | -2.00 | +41.13 | -13.3 |

**Table S2.** Results on binding energy and calculated N···H···Cl vibrational frequency ($cm^{-1}$) as a result of substitution of electron withdrawing and donating groups on to the C1 carbon (flanked by two nitrogen atoms in imidazole ring) and C4 carbon are provided.

| **Effect of substitution in M-Imid···HCl Complexes** | **Binding energy (kcal/mol)** | **Calculated N···H···Cl vibrational frequency ($cm^{-1}$)** | **Shift with respect to HCl monomer** |
|---|---|---|---|
| **Substitution at C1 carbon** | | | |
| -$NO_2$ | -8.45 | 2513.1 (1889) | -510.0 |
| -CN | -8.62 | 2408.6 (2338) | -614.5 |
| -H (complex A) | -12.66 | 1960.9 (3938) | -1062.2 |
| -$CH_3$ | -17.78 | 1261.2 (2340) | -1761.9 |
| -$NH_2$ | -62.71 | 2323.1 (2553)[a] | -- |
| -OH | -111.97 | 3285.9 (901) [a] | -- |
| **Substitution at C4 carbon** | | | |
| -$NO_2$ | -8.32 | 2530.3 (1740) | -492.7 |
| -CN | -8.51 | 2442.7 (2050) | -580.3 |
| -H (complex A) | -12.66 | 1960.9 (3938) | -1062.1 |
| -$CH_3$ | -14.32 | 1739.5 (3952) | -1283.5 |
| -$NH_2$ | -16.24 | 1322.3 (3002) | -1700.7 |
| -OH | -66.23 | 2519.3 (1578) [a] | -- |

[a]proton transferred hydrogen bonding

**Table S3.** Results on binding energy and calculated N···H···Cl vibrational frequency ($cm^{-1}$) as a result of substitution of electron withdrawing and donating groups on to the N8 nitrogen and C6 carbon are provided.

| **Effect of substitution in M-Imid···HCl Complexes** | **Calculated N···H···Cl vibrational frequency ($cm^{-1}$)** | **Shift with respect to HCl monomer** |
|---|---|---|
| **Substitution at N8 nitrogen** | | |
| $-NO_2$ | 2410.8 (2506) | -612.2 |
| -CN | 2445.1 (2380) | -577.9 |
| $-CH_3$ (complex A) | 1960.9 (3938) | -1062.1 |
| -H | 2071.9 (3447) | -951.1 |
| $-NH_2$ | 2052.2 (3695) | -970.8 |
| -OH | 2142.6 (3340) | -880.4 |
| **Substitution at C6 carbon** | | |
| $-NO_2$ | 2371.1 (2745) | -651.9 |
| -CN | 2321.3 (3012) | -701.7 |
| -H (complex A) | 1960.9 (3938) | -1062.1 |
| $-CH_3$ | 1825.9 (4462) | -1197.1 |
| $-NH_2$ | 1836.2 (4413) | -1186.8 |
| -OH | 1949.5 (3969) | -1073.5 |