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# Supplementary Information

## Combined experimental and theoretical studies on a conformationally diverse (thio)semicarbazone based semiconducting materials

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## Contents

**Device Fabrication and Characterization**:

To fabricate the Schottky device, at first, Indium Tin Oxide (ITO) coated glass substrate was cleaned by acetone, distilled water and isopropanol repeatedly and sequentially in ultra-sonication bath for 30 min. At the same time a well dispersed solution of the 1 and 2 in N N-dimethyl formamide (DMF) medium was prepared and spin coated onto the pre-cleaned ITO coated glass at 600 rpm for 1 min with the help of SCU 2700 spin coating unit. This spin coating step was repeated for 3 times. After drying in vacuum, the film thickness was measured as 1 μm by surface profiler. Aluminum (Al) electrodes were deposited onto the film by a Vacuum Coating Unit 12A4D of HINDHIVAC under a pressure of $10^{-6}$ Torr. The area of the Al electrodes was maintained as $7.065\times10^{-6}$ m$^2$ by the shadow mask. The current-voltage measurements of the fabricated device with 1 and 2 were carried out by a Keithley 2635B source meter interfaced with PC by two-probe technique under dark and illumination in the voltage range -1V to +1V at room temperature.

**Electrical Characterization:**

The Thermionic Emission (TE) theory is adopted to get more insights of the charge transport mechanism in the devices.[S1] The current of a diode can be expressed as the following equations according to TE theory.[S2]

$$\mathbf{I = I_0 exp\left(\frac{qV}{\eta kT}\right)\left[1 - exp\left(-\frac{qV}{\eta kT}\right)\right]} \quad \ldots\ldots(S1)$$

Where,

$$\mathbf{I_0 = AA^{*}T^2 exp\left(-\frac{q\phi_B}{kT}\right)} \quad \ldots\ldots(S2)$$

$$\mathbf{\phi_B = \frac{kT}{q} ln\left(\frac{AA^{*}T^2}{I_0}\right)} \quad \ldots\ldots\ldots(S3)$$

Where, $I_0$ indicates the saturation current, q represents the electronic charge, k is the Boltzmann constant, T is the temperature in Kelvin, V is the forward bias voltage, η is the ideality factor, $\phi_B$ is the effective barrier height at zero bias, A is the diode area ($7.065\times10^{-6}$ m$^2$), $A^*$ is the effective Richardson constant ($1.20\times10^6$ Am$^{-2}$K$^{-2}$). From Cheung, the forward bias I-V characteristics in term of series resistance can be expressed as.[S3]

$$\mathbf{I = I_0 exp\left[\frac{q(V - IR_S)}{\eta kT}\right]} \quad \ldots\ldots.(S4)$$

Where, the $IR_S$ term represents the voltage drop across series resistance of device. In this circumstance, the values of the series resistance can be determined from following functions using equation (S5 & S6).[S4]

According to Cheung's model:

$$\frac{dV}{d\ln(I)} = \left(\frac{\eta kT}{q}\right) + R_S I \qquad \text{............(S5)}$$

$$H(I) = R_S I + \eta\phi_B \qquad \text{...........(S6)}$$

and H(J) can be expressed as:

$$H(I) = V - \left(\frac{\eta kT}{q}\right)\ln\left(\frac{I}{AA^*T^2}\right) \qquad \text{............(S7)}$$

**Table S1:** Crystallographic bond distances in ligands **1** and **2**.

| Bonds | **1** | Bonds | **2** |
|---|---|---|---|
| O(1)-C(1) | 1.3645(11) | S(1)-C(8) | 1.6858(18) |
| O(3)-C(8) | 1.2428(12) | S(1A)-C(8A) | 1.6880(19) |
| N(1)-C(7) | 1.2898(12) | O(1A)-C(1A) | 1.3697(17) |
| N(1)-N(2) | 1.3739(11) | O(1)-C(1) | 1.3608(17) |
| N(2)-C(8) | 1.3651(12) | N(1)-C(7) | 1.2897(18) |
| N(3)-C(8) | 1.3376(13) | N(1)-N(2) | 1.3717(17) |
| C(1)-C(6) | 1.3967(12) | N(2)-C(8) | 1.3526(18) |
| | | N(2A)-C(8A) | 1.3481(17) |
| | | N(2A)-N(1A) | 1.3737(17) |
| | | N(1A)-C(7A) | 1.2784(17) |
| | | N(3)-C(8) | 1.3252(17) |
| | | N(3A)-C(8A) | 1.3256(19) |

**Table S2.** Hydrogen bonds for complex **1** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(9)-H(9A)...O(3)#1 | 0.98 | 2.54 | 3.5136(15) | 173.2 |
| N(3)-H(3B)...O(1)#2 | 0.898(16) | 2.125(16) | 3.0172(11) | 172.2(14) |
| O(1)-H(1)...N(1) | 0.874(19) | 1.872(18) | 2.6513(10) | 147.5(16) |
| N(2)-H(2)...O(3)#3 | 0.922(17) | 1.861(18) | 2.7805(11) | 175.4(15) |

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z-1 #2 x+1/2,-y+1/2,z+1/2 #3 -x+1,-y+1,-z+2

**Table S3.** Hydrogen bonds for complex **2** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(7)-H(7)...S(1)#1 | 0.95 | 2.95 | 3.797(3) | 148.8 |
| C(9A)-H(9AC)...O(1)#2 | 0.98 | 2.63 | 3.319(3) | 127.7 |
| O(1)-H(1)...N(1) | 0.82(2) | 1.91(2) | 2.629(2) | 147(2) |
| O(1A)-H(1A)...S(1)#3 | 0.78(2) | 2.74(2) | 3.298(3) | 130.2(19) |
| O(1A)-H(1A)...O(2A) | 0.78(2) | 2.09(2) | 2.614(2) | 124(2) |
| N(2A)-H(2A)...S(1A)#3 | 0.91(2) | 2.51(2) | 3.408(3) | 172.2(17) |
| N(2)-H(2)...S(1)#1 | 0.88(2) | 2.54(2) | 3.419(3) | 172.4(17) |
| N(3)-H(3B)...O(1A)#3 | 0.91(2) | 2.05(2) | 2.909(3) | 155.5(17) |
| N(3A)-H(3AB)...O(1) | 0.83(2) | 2.08(2) | 2.897(2) | 170.8(18) |
| N(3A)-H(3AB)...O(2) | 0.83(2) | 2.574(19) | 3.054(3) | 118.4(16) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z #2 -x+1,-y,-z+1 #3 -x,-y+1,-z+1

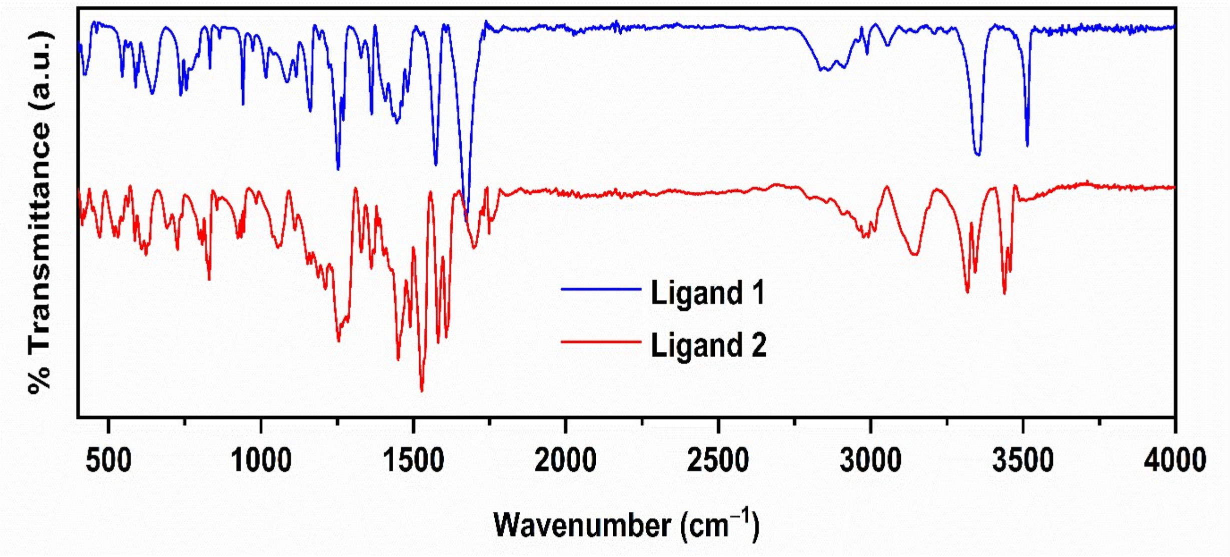


**Fig. S1.** IR spectra of Schiff base ligand 1 and 2.

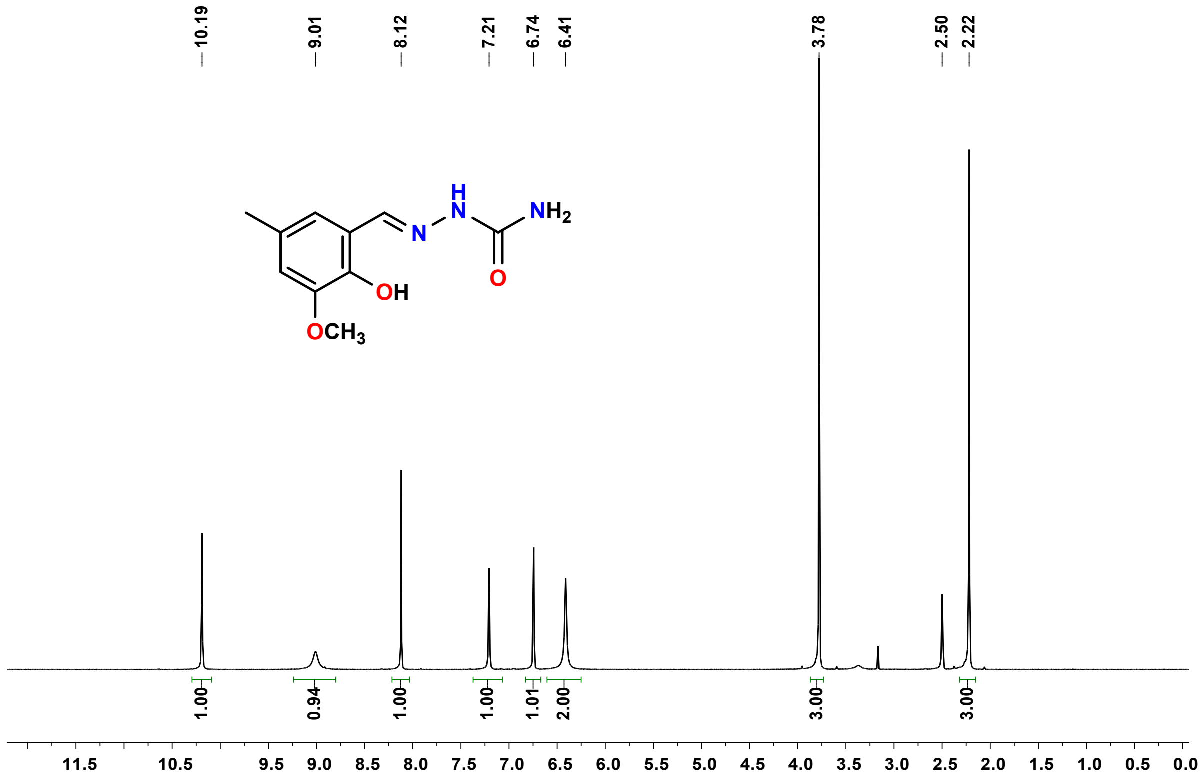


**Fig. S2:** $^{1}$H NMR of (*E*)-2-(2-hydroxy-3-methoxy-5-methylbenzylidene)hydrazine-1-carboxamide (**1**) in DMSO-$d_6$ at r.t.

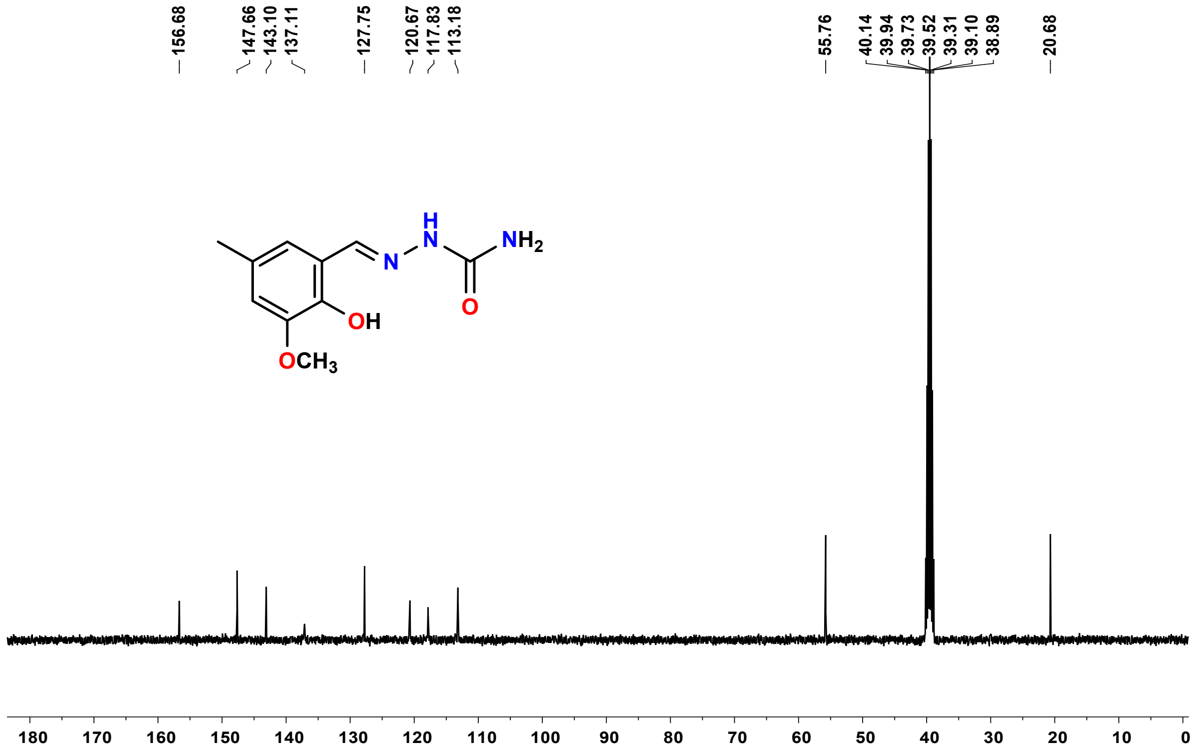


**Fig. S3:** $^{13}$C NMR of (*E*)-2-(2-hydroxy-3-methoxy-5-methylbenzylidene)hydrazine-1-carboxamide (**1**) in DMSO-$d_6$ at r.t.

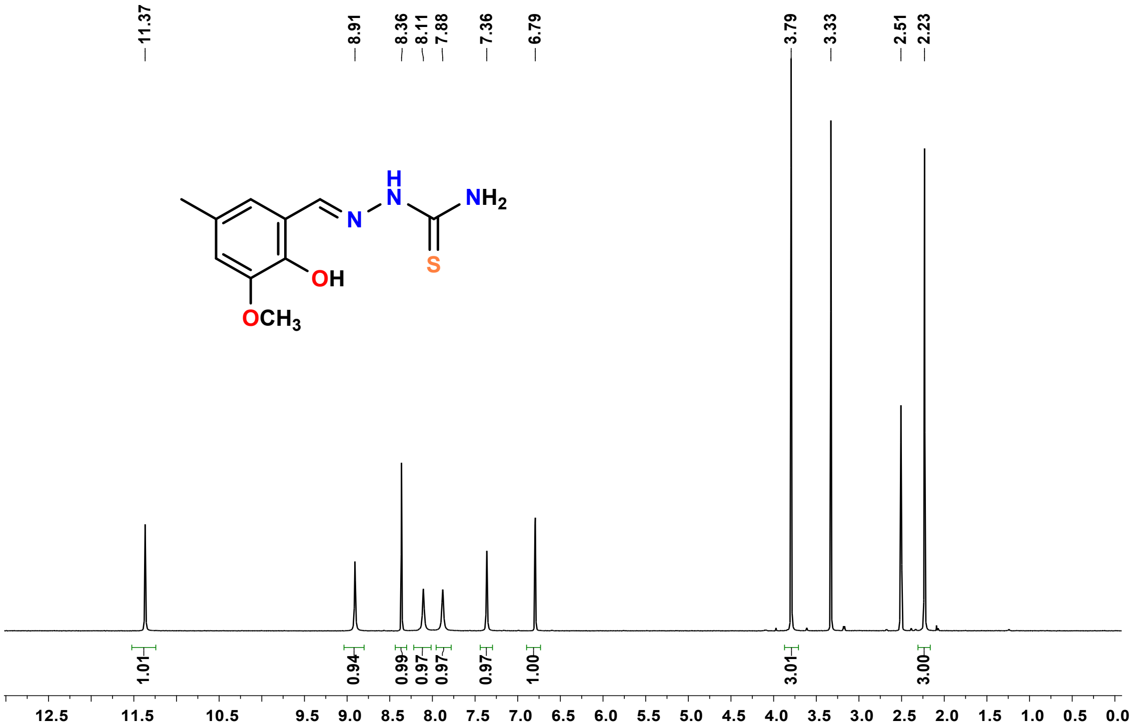


**Fig. S4:** $^1$H NMR of (E)-2-(2-hydroxy-3-methoxy-5-methylbenzylidene)hydrazine-1-carbothioamide (**2**) in DMSO-$d_6$ at r.t.

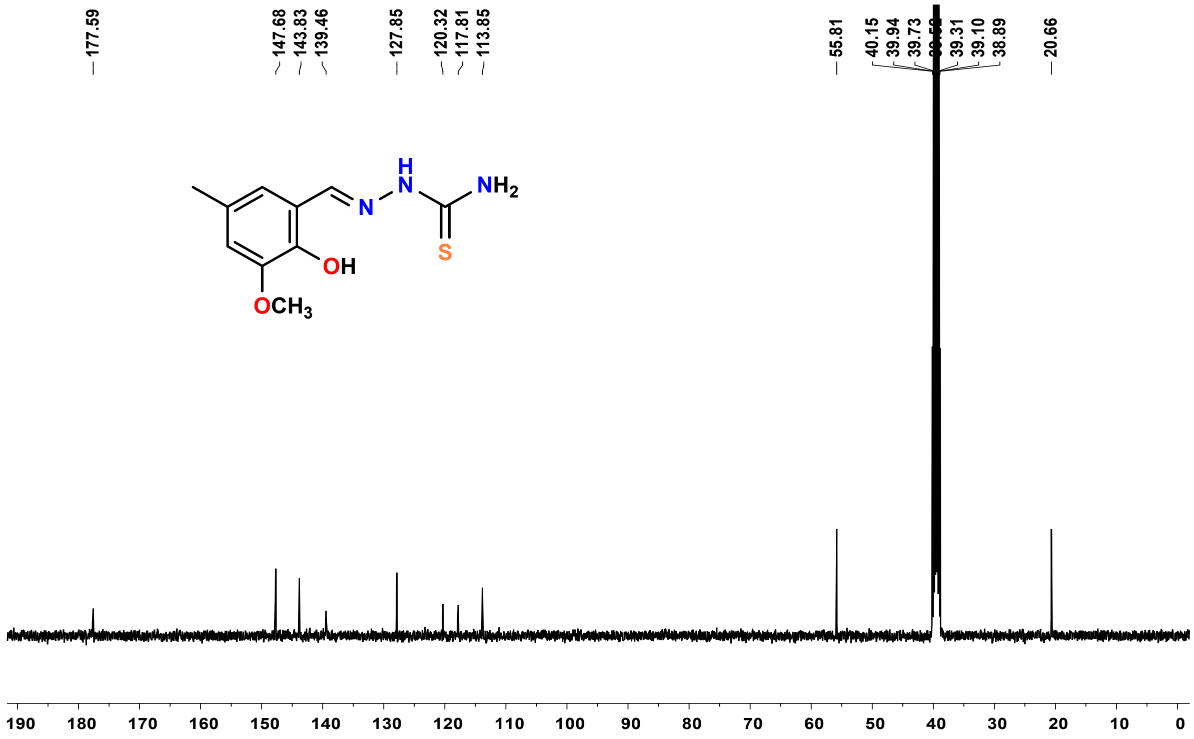


**Fig. S5:** 13C NMR of (E)-2-(2-hydroxy-3-methoxy-5-methylbenzylidene)hydrazine-1-carbothioamide (**2**) in DMSO-d6 at r.t

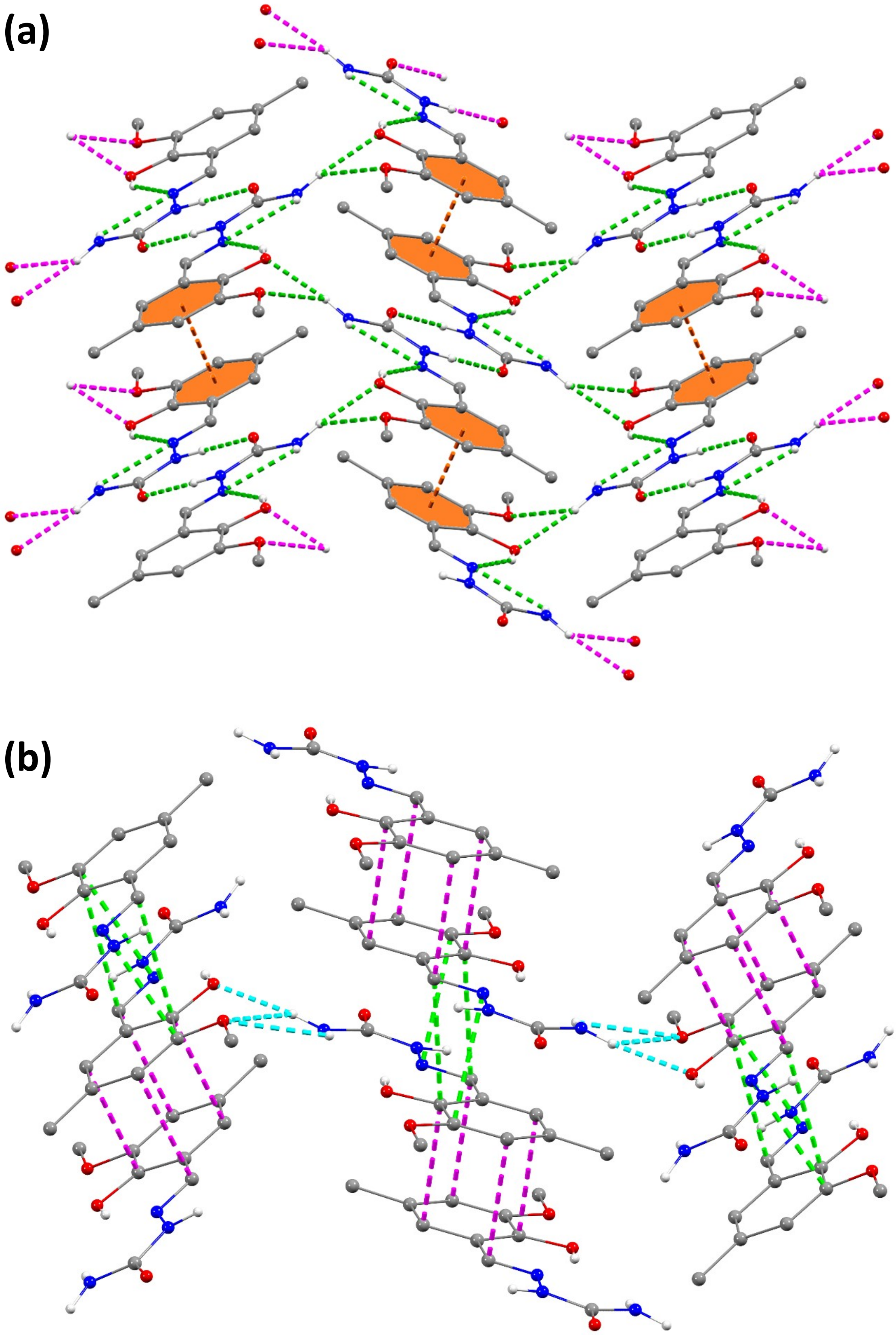


**Fig. S6**: Crystal packing of **1** focusing on various hydrogen bonding's and the π···π stacking interaction.

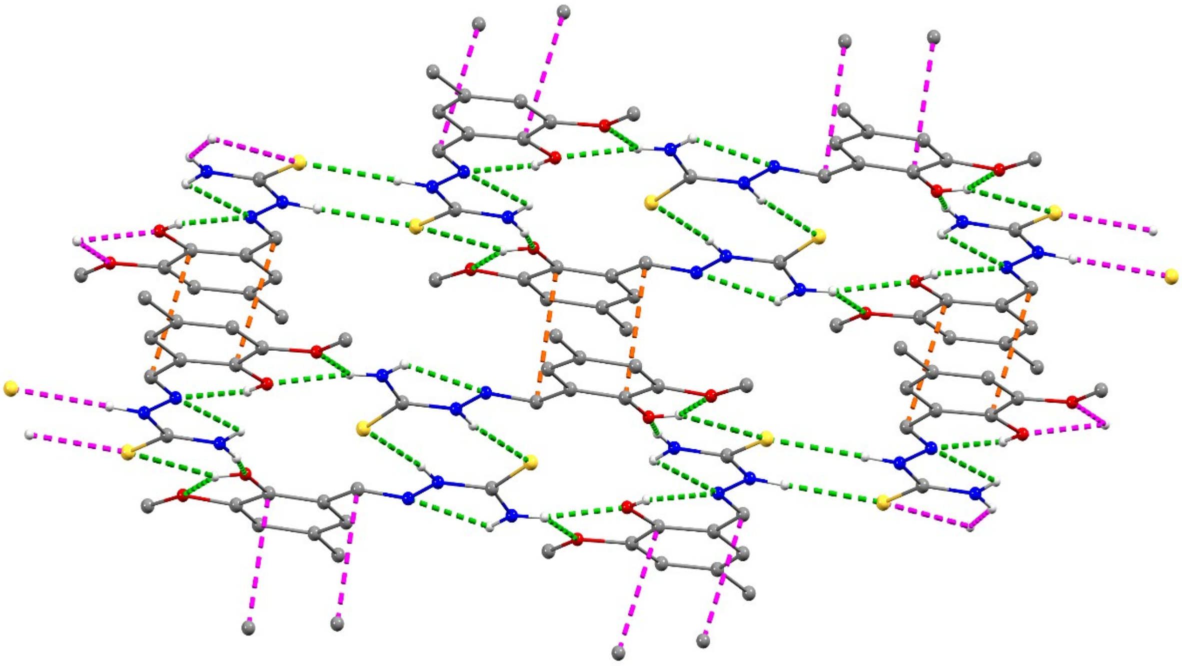


**Fig. S7**: Crystal packing of **2** focusing on various hydrogen bonding's and the π···π stacking interaction.

## Solid State Calculation:

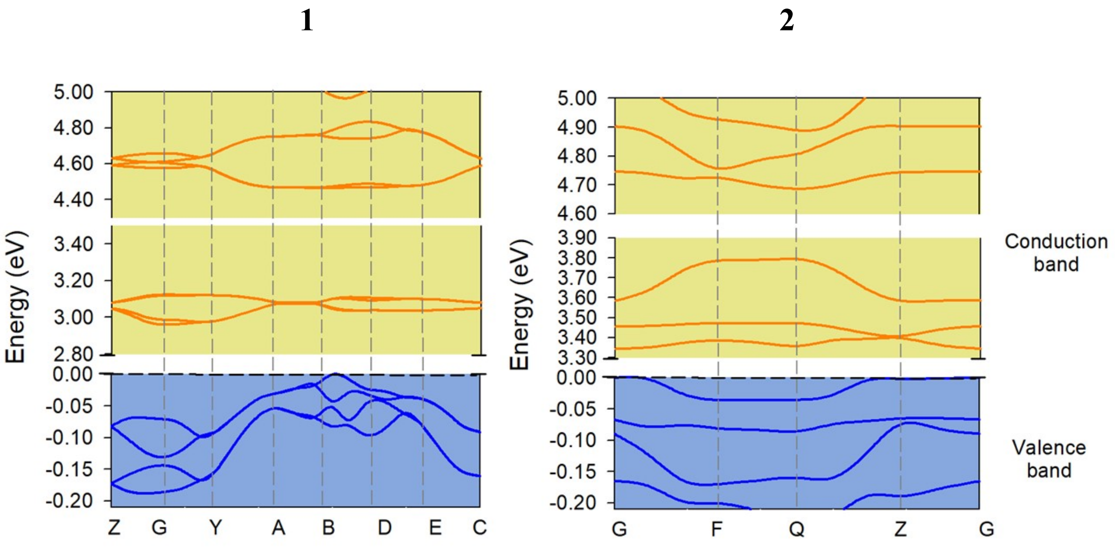


**Fig. S8.** Electronic band structures of the ground state for the crystals structure. Points of high symmetry in the first Brillouin zone are labeled as follows: Z = (0, 0, 0.5); G = (0, 0, 0); Y = (0, 0.5, 0); A = (-0.5, 0.5, 0); B = (-0.5, 0, 0); D = (-0,5, 0, 0.5); E = (-0.5, 0.5, 0.5); C = (0, 0.5, 0.5). F = (0, 0.5, 0); Q = (0, 0.5, 0.5); Z = (0, 0, 0.5). Scissor operator applied to compound **1** of 0.3 eV and compound **2** of 0.9 eV.

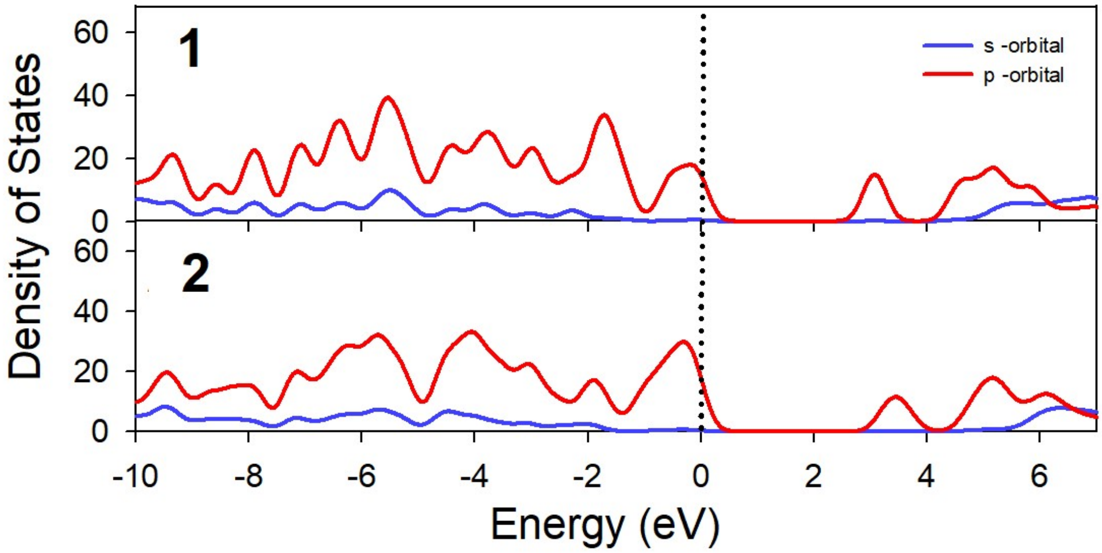


**Fig. S9**. Calculated total and partial density of states of the crystal cells. Panels show: 1) **1** crystal, B.) **2** crystal. The lines represent the s-orbital character (blue), p-orbital character (red) of the atoms into the crystal. Scissor operator applied to **1** of 0.3 eV and to **2** of 0.9 eV.

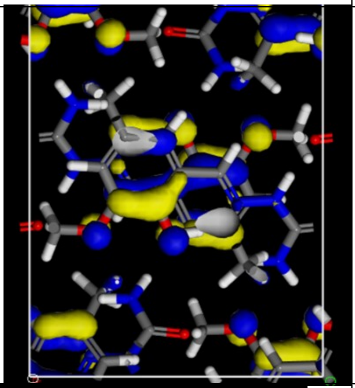
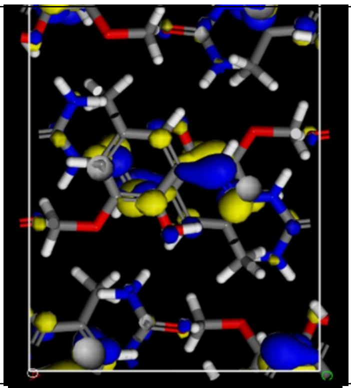
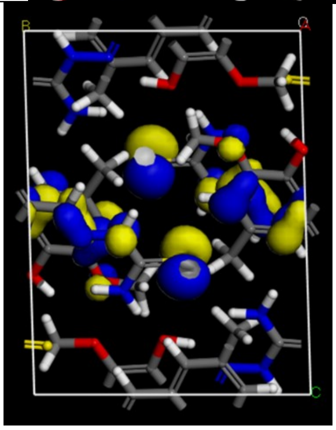
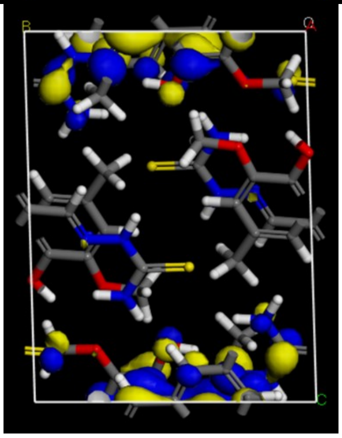
|  | HOMO<br>Π-bonding | LUMO<br>Π-antibonding |
|---|---|---|
| AML-1 |  |  |
| AML-2 |  |  |

**Fig. S10**. Representation of Homo-Lumo Orbitals of both crystals. The orbitals are represented using the 0.025 a.u. isovalue.

## References

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