

SUPPORTING INFORMATION

**New Coordination Polymers of Copper(I) and Silver(I) with
Pyrazine and Piperazine: A Step Toward “Green”
Chemistry and Optoelectronic Applications**

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S1. Additional Crystallographic Data:**Table S1.** Significant Bond Distances and Bond Angles for the Coordination Geometry of Complexes **1-6**.

COMPLEX	BOND	Bond Length, Å	ANGLE	Bond Angle, °
1	Cu(1)-N(1) Cu(1)-N(6) Cu(1)-N(7) N(1)-C(1) N(1)-N(2)	1.935(3) 1.957(3) 2.067(3) 1.343(5) 1.368(4)	N(1)-Cu(1)-N(6) N(1)-Cu(1)-N(7) N(6)-Cu(1)-N(7) C(1)-N(1)-N(2) C(1)-N(1)-Cu(1)	131.04(11) 119.72(11) 109.01(11) 107.3(3) 132.7(2)
2	Cu(1)-N(1) Cu(1)-N(8) Cu(1)-N(3) Cu(1)-N(5) N(1)-C(1)	2.0006(19) 2.0216(19) 2.028(2) 2.1618(19) 1.343(3)	N(1)-Cu(1)-N(8) N(1)-Cu(1)-N(3) N(8)-Cu(1)-N(3) N(1)-Cu(1)-N(5) N(8)-Cu(1)-N(5)	116.34(8) 118.64(8) 110.36(8) 103.56(7) 103.00(7)
3	Cu(1)-N(3) Cu(1)-N(1) Cu(1)-N(7) Cu(2)-N(2) Cu(2)-N(6)	1.930(3) 1.942(3) 2.069(3) 1.926(3) 1.933(3)	N(3)-Cu(1)-N(1) N(3)-Cu(1)-N(7) N(1)-Cu(1)-N(7) N(2)-Cu(2)-N(6) N(6)-Cu(2)-N(8)#1	135.25(11) 113.90(11) 110.78(10) 137.04(11) 114.10(11)
4	Ag(1)-N(6) Ag(1)-N(1) Ag(2)-N(2) Ag(2)-N(3) Ag(2)-N(7)	2.077(7) 2.087(7) 2.137(6) 2.138(6) 2.562(7)	N(6)-Ag(1)-N(1) N(2)-Ag(2)-N(3) N(2)-Ag(2)-N(7) N(3)-Ag(2)-N(7) N(4)-Ag(3)-N(5)	176.6(3) 169.0(3) 95.8(2) 95.2(2) 168.4(3)
5	Ag(1)-N(1) Ag(1)-N(5) Ag(1)-N(3) Ag(1)- Ag(1)#1 Ag(2)- N(4)#1	2.1643(18) 2.2490(18) 2.3266(18) 3.3064(5) 2.1420(18)	N(1)-Ag(1)-N(5) N(1)-Ag(1)-N(3) N(5)-Ag(1)-N(3) N(1)-Ag(1)- Ag(1)#1 N(5)-Ag(1)- Ag(1)#1	142.11(7) 119.05(6) 97.00(6) 91.85(5) 80.78(5)
6	Cu(1)-N(1A) Cu(1)-N(2A) Cu(1)-N(1) Cu(1)- N(2)#1 N(1)-C(1)	1.9446(18) 1.9516(18) 2.0774(15) 2.1041(15) 1.333(2)	N(1A)-Cu(1)- N(2A) N(1A)-Cu(1)-N(1) N(2A)-Cu(1)-N(1) N(1A)-Cu(1)- N(2)#1 N(2A)-Cu(1)- N(2)#1	129.72(7) 108.74(7) 105.16(6) 104.83(7) 102.21(6)

Symmetry transformations used to generate equivalent atoms:

For complex 3: #1 -x+2,-y+2,-z+2

For complex 5: #1 -x+1,y,-z+1/2

For complex 6: #1 -x,y-1/2,-z+3/2

S2. Absorption Spectra:

Figure S1 shows absorption spectra of complex **1** in the UV and visible region using different concentrations. Due to ligand-centered $\pi\text{-}\pi^*$ transitions, the absorption bands in the UV region appear at similar wavelengths to those for free pyrazine at a lower concentration, 10^{-5} M, whereas the absorption bands at longer wavelengths in the near-UV into the onset of the visible region at higher concentrations, 10^{-3} and 10^{-2} M, are assignable to metal-to-ligand charge transfer (MLCT) transitions.

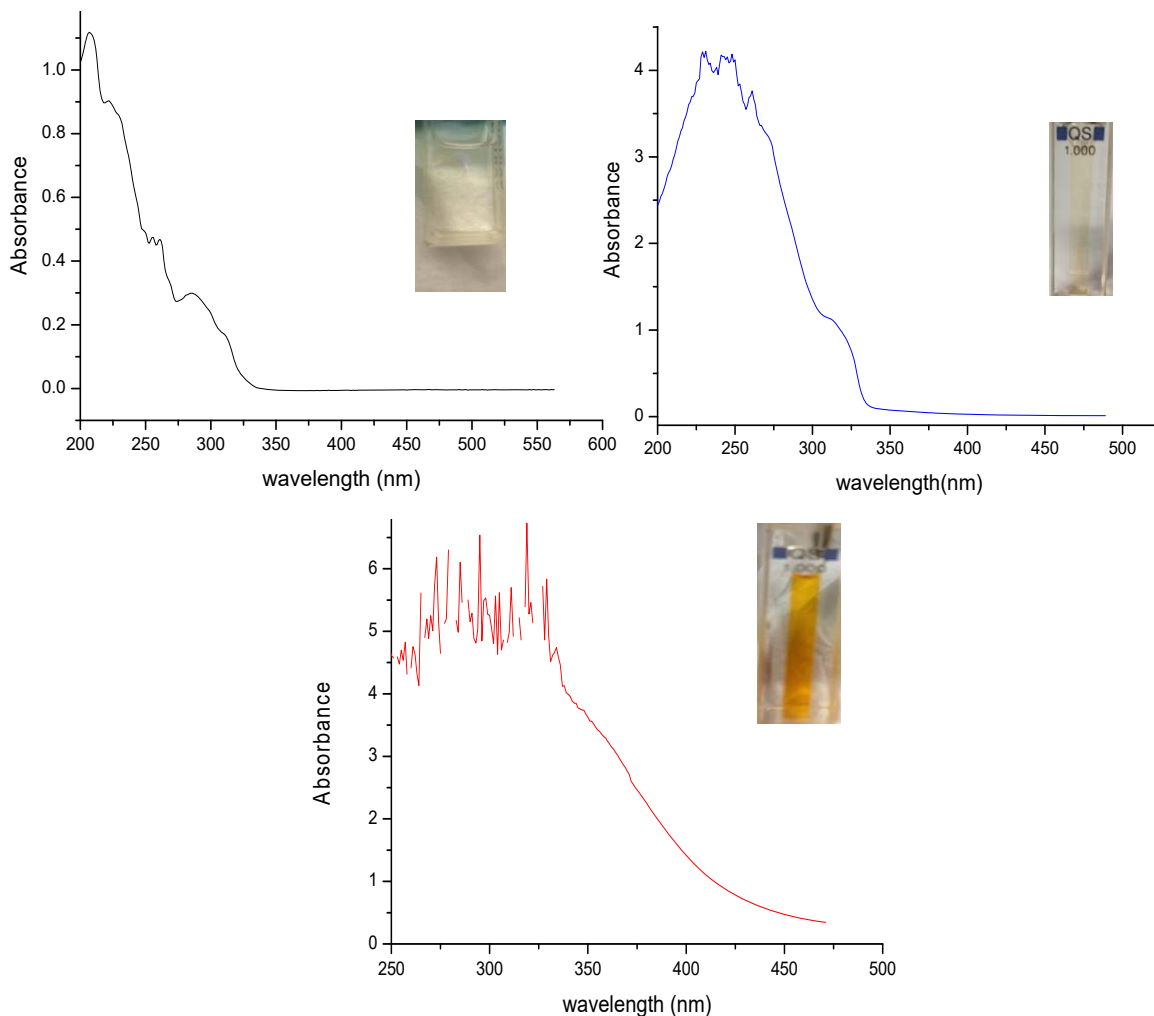


Figure S1. Absorption spectra at different concentrations -- 1×10^{-5} M (black), 1×10^{-3} M (blue) and 1×10^{-2} M (red) -- of complex **1** in acetonitrile.

Figure S2 shows intense absorption spectra for complex **2** in the UV and visible region using different concentrations. Due to ligand $\pi\text{-}\pi^*$ transitions, the absorption in the UV region appears at similar wavelengths to those for the free pyrazine ligand at low concentration, 10^{-5} M, whereas due to MLCT the absorption bands appear at longer wavelengths in the near-UV into the onset of the visible region at high concentration, 10^{-3} and 10^{-2} M .

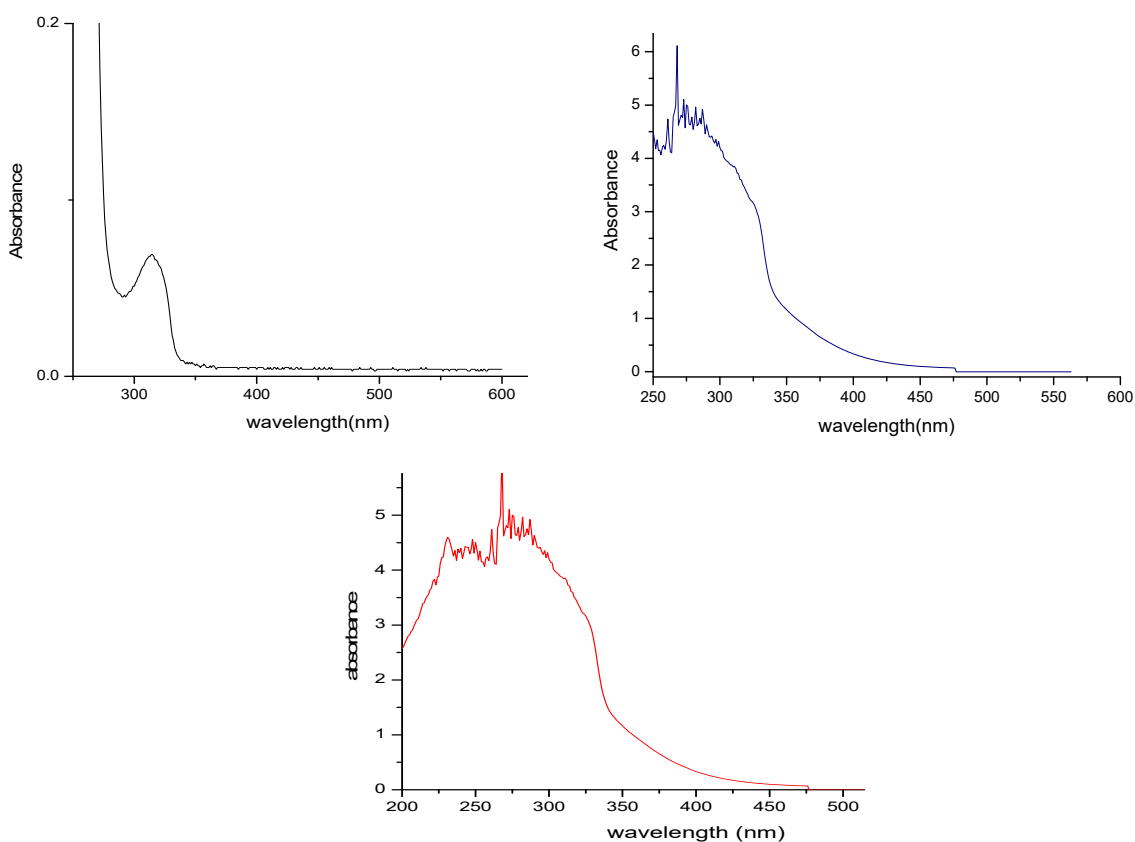


Figure S2. Absorption spectra at different concentrations -- 1×10^{-5} M (black), 1×10^{-3} M (blue) and 1×10^{-2} M (red) -- of complex **2** in acetonitrile.

Figure S3 shows intense absorption spectra for complex **3** in the UV region due to ligand-centered π - π^* transitions at $\lambda < 300$ nm and MLCT transitions in the near-UV region at $\lambda > 300$ nm.

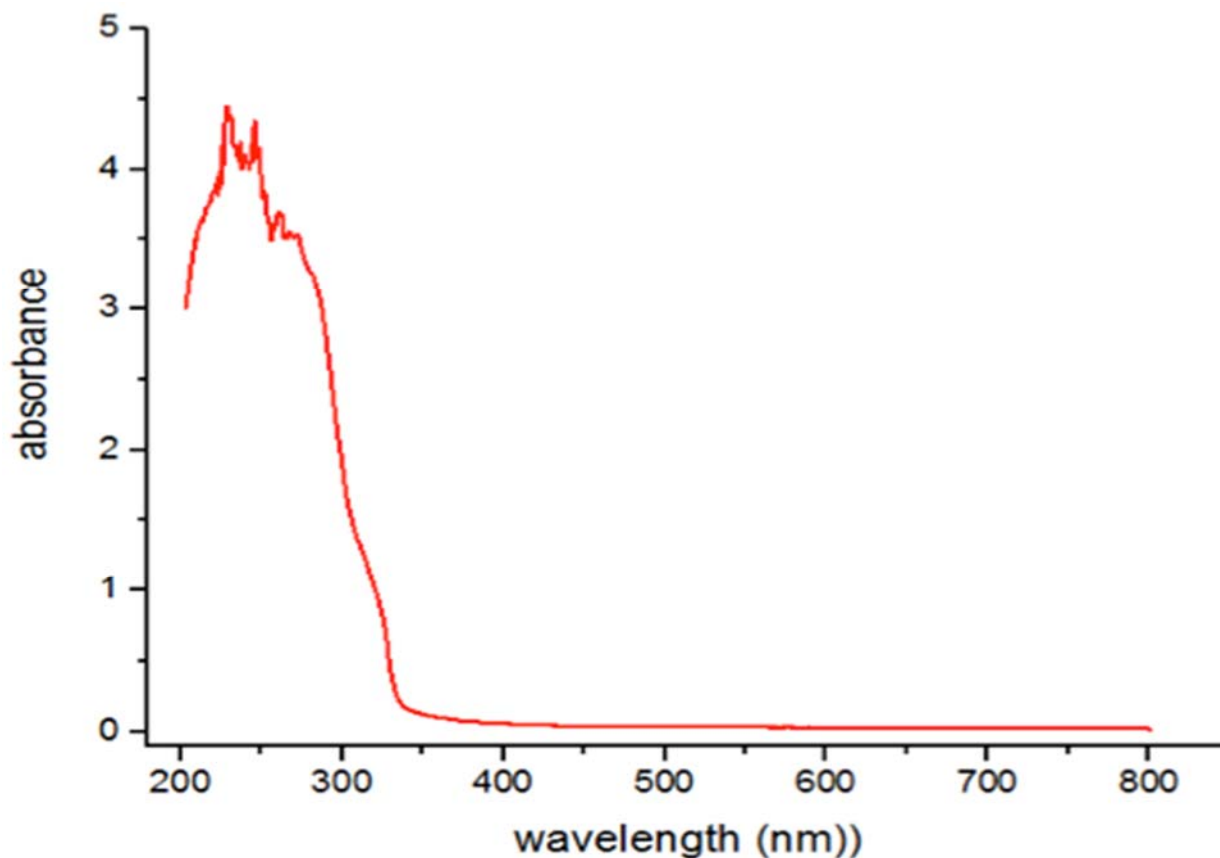


Figure S3. Absorption spectrum for complex **3** at 1×10^{-5} M in acetonitrile.

Figure S4 shows intense absorption bands for complex **4** in both the UV region -- due to ligand-centered π - π^* transitions at $\lambda < 300$ nm -- and metal-to-ligand charge transfer transitions in the near-UV region at $\lambda > 300$ nm -- due to MLCT. The broad MLCT band in this complex is more resolved than the analogous MLCT bands in the previous complexes, allowing the calculation of an extinction coefficient as high as $1.5 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ for complex **4**.

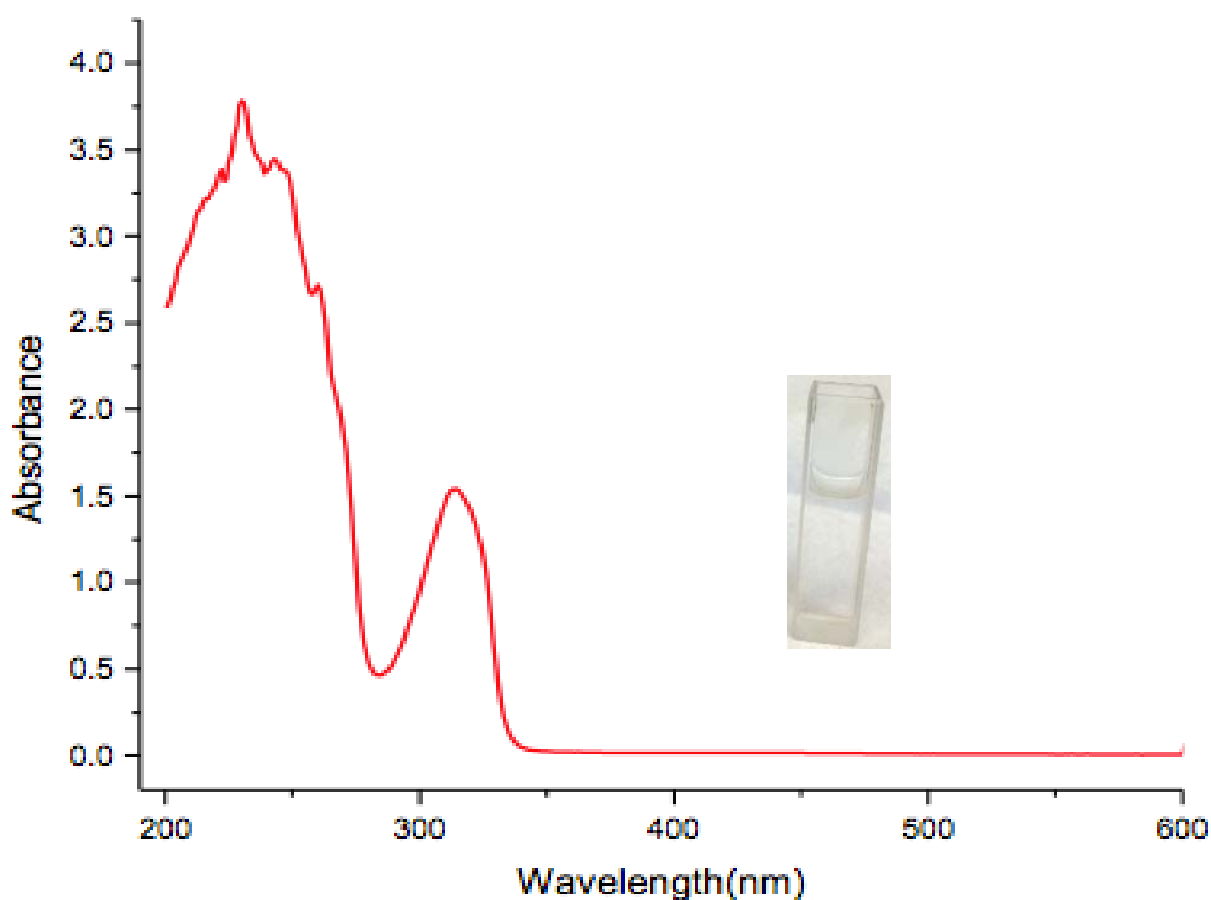


Figure S4. Absorption spectrum of complex **4** at 1×10^{-5} M in acetonitrile.

Figure S5 shows intense absorption band for complex **5** only in the UV region but not the near-UV as in the previous complexes. This observation is consistent with the piperazine being only a σ -donor but not π -acceptor -- unlike the pyrazine which is both a good σ -donor and excellent π -acceptor. Despite the presence of the pyrazolate, which is only a moderately good π -acceptor but excellent σ -donor (due to the negative charge associated with its lone pairs in its Pz^- instead of the PzH form), both the MLCT and π - π^* transitions associated with it in **5** are significantly blue-shifted vs those for the pyrazine in the previous complexes **1-4**.

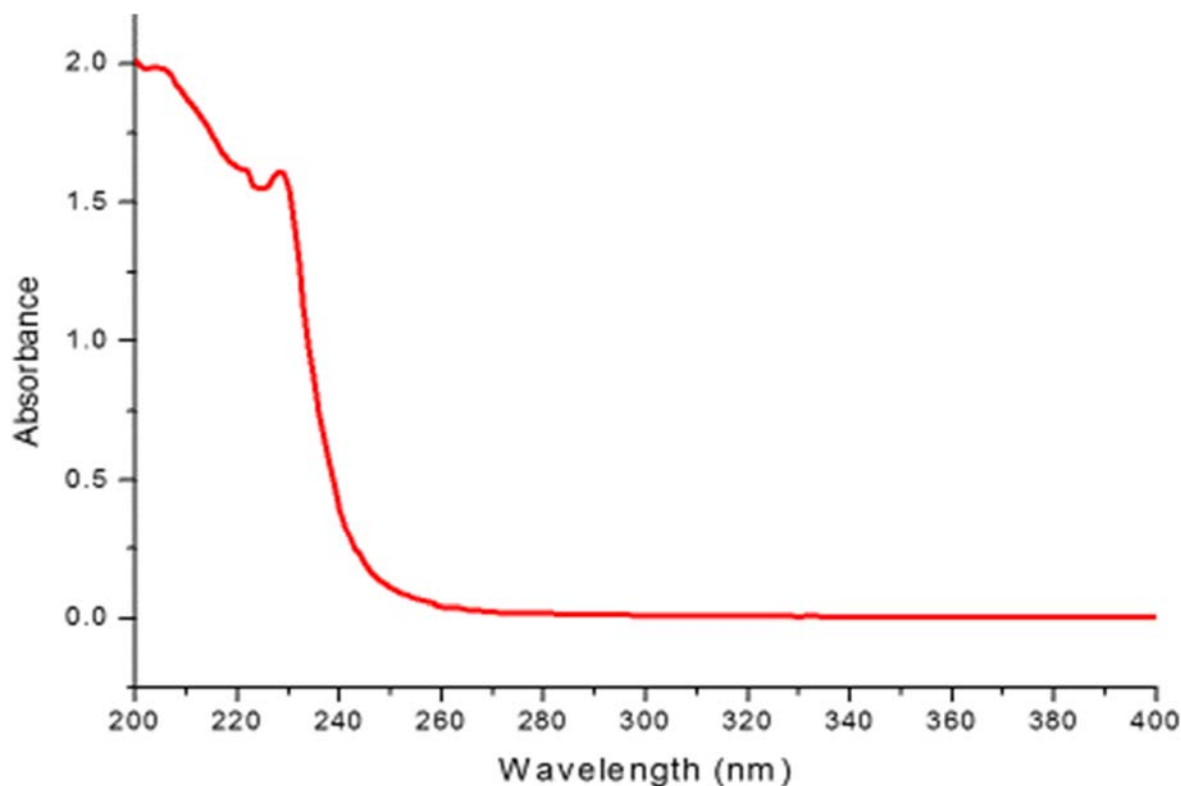


Figure S5. Absorption spectrum of complex **5** at 1×10^{-5} M in acetonitrile.

Figure S6 shows the solution absorption spectra for complex **6** in acetonitrile. Due to ligand $\pi\text{-}\pi^*$ transitions, the absorption in the UV region appears at similar wavelengths to those for the free pyrazine ligand at low concentration, 10^{-5} M. Although the spectral profile and band assignment for complex **6** are similar to those for complexes **1-4**, a unique feature for the spectrum of complex **6** is the high resolution of the $\pi\text{-}\pi^*$ transition so as to show the vibronic fine structure. This is likely attributed to the presence of only a single chromophoric imine ligand, pyrazine, as this is the only complex that does not contain a pyrazolate ligand among all six complexes in this investigation. We are also able to calculate accurate extinction coefficients for both transitions as the $\pi\text{-}\pi^*$ transition is not opaque at 10^{-5} M, giving rise to $\varepsilon = 1.06 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ and $1.19 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ for the $\pi\text{-}\pi^*$ and MLCT transitions, respectively, in complex **6**. Finally, by dissolving the solid in acetonitrile, the complex generates a *colorless* solution. However, evaporating the solvent

re-generates the yellow-colored solid as a powder or, upon drop-casting onto a glass slide, forms a thin film.

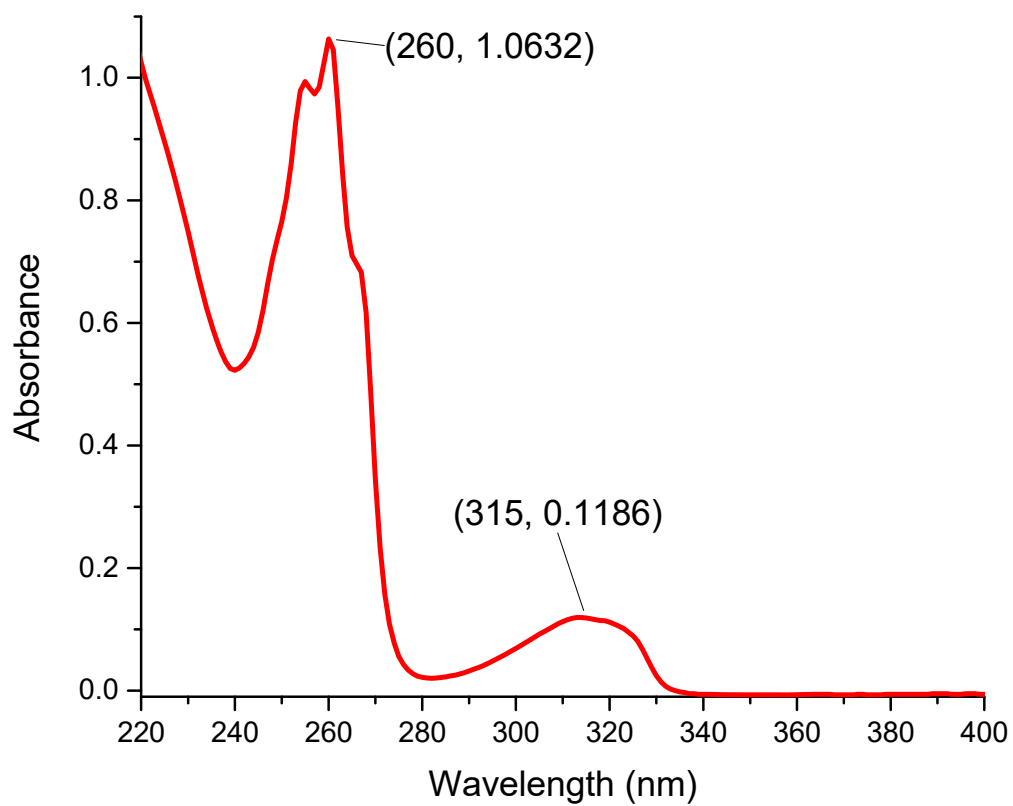


Figure S6. Absorption spectrum of complex **6** at 1×10^{-5} M in acetonitrile.

S3. Thermogravimetric Analysis (TGA):

Figure S7 shows the TGA for the solventless powder of compound **1**. The weight loss of 19.79% represents loss of both adsorbed moisture and pyrazine. Accounting for water loss of ~1.3 g, pyrazine loss would then be estimated to represent ~2.3 g or ~13.9% of the remaining weight of the dry sample – reasonably close to the theoretical 13.04% pyrazine content in the formula weight of the dry, unsolvated compound **1** (i.e., $\{\text{Cu}_6[3,5\text{-(CF}_3)_2\text{Pz}]_6(\text{Pyz})_3\} = \text{C}_{42}\text{H}_{18}\text{Cu}_6\text{F}_{36}\text{N}_{18}$; FW= 1839.93 g/mol). The next loss step represents the sublimation of the remaining $\{[3,5\text{-(CF}_3)_2\text{Pz}]\text{Cu}\}_3$ trimer, whose TGA profile is shown in Figure S8. The temperature profile of the onset and end of sublimation at ~ 175 and 230 °C, respectively, is rather similar for the 2nd loss step for the solventless product **1** in Figure S7 to that for the cyclotrimer alone in Figure S8.

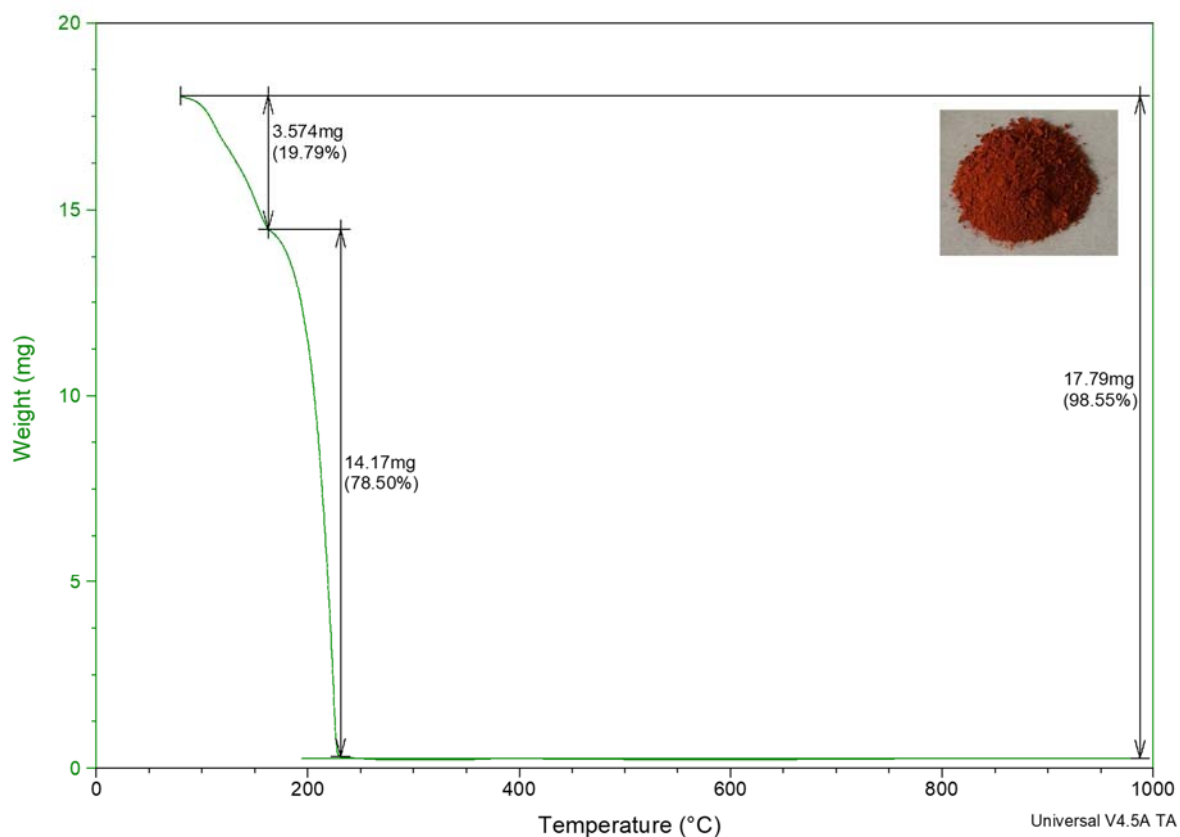


Figure S7. TGA for the solventless powder of compound **1**.

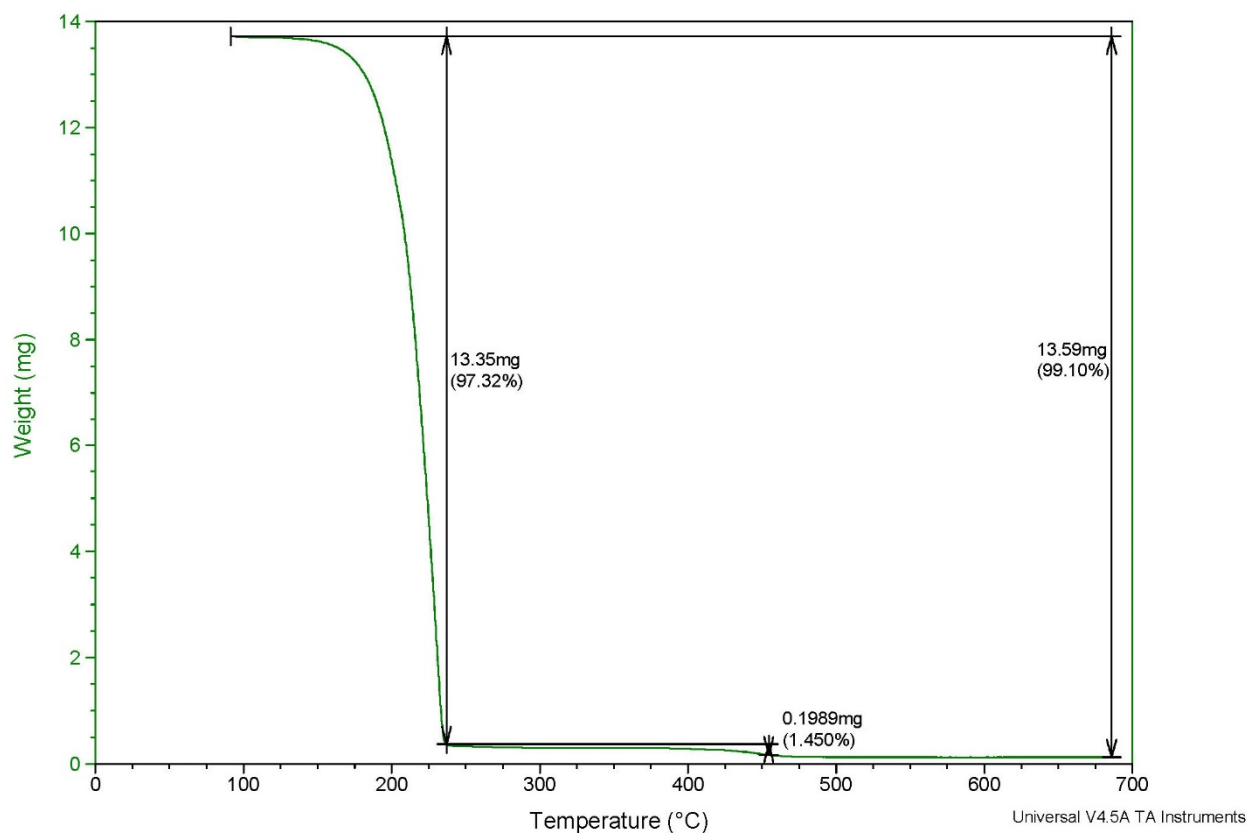


Figure S8. TGA for the {[3,5-(CF₃)₂Pz]Cu}₃ cyclotrimer precursor used in the synthesis of compounds **1-3**.

Figure S9 shows the TGA for the solvent-mediated powder product of compound **1** after reaction workup using dichloromethane. The 1st weight loss step of 11.85% represents loss of primarily pyrazine in addition to traces of adsorbed dichloromethane. Accounting for dichloromethane in the formula weight of compound **1**•CH₂Cl₂ (i.e., {Cu₆[3,5-(CF₃)₂Pz]₆(Pyz)₃}•CH₂Cl₂ = C₄₃H₂₀ Cl₂Cu₆F₃₆N₁₈; FW= 1924.91 g/mol) would make the theoretical pyrazine loss 12.46% to slightly reduce the error in the aforementioned 1st weight loss step vs the 13.04% theoretical value for the dry product. In either case, such absolute errors of 1-2% are acceptable in TGA, especially given that the pyrazine loss step terminates at a close temperature range as the onset of sublimation of the copper trimer seen in the 2nd loss step.

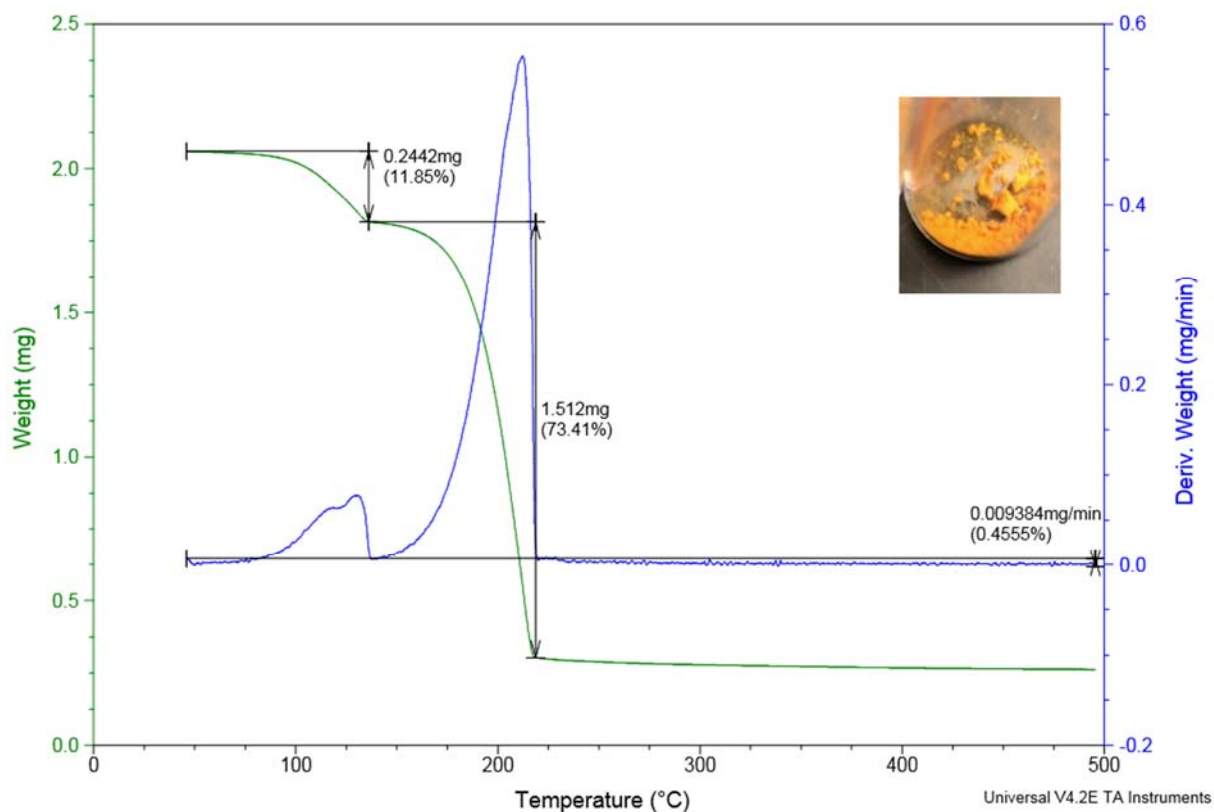


Figure S9. TGA for the solvent-mediated powder of compound **1**.

Figure S10 shows the TGA for four different forms of compound **2**, including: (a) bulk powder product after solvent-mediated synthesis; (b) freshly-grown maroon-colored single crystals from toluene; (c) solid sample resulting from air-drying the maroon single crystals under ambient laboratory conditions for a few days; and (d) solid sample resulting from drying the maroon single crystals in a vacuum oven for 1 hr and 30 mins at 50°C. Pyrazine loss from the wet ($\{\text{Cu}_2[3,5-(\text{CF}_3)_2\text{Pz}]\}_2(\text{Pyz})_2 \bullet \text{toluene}\} = \text{C}_{25}\text{H}_{18}\text{Cu}_2\text{F}_{12}\text{N}_8$; FW= 785.55 g/mol) and dry ($\{\text{Cu}_2[3,5-(\text{CF}_3)_2\text{Pz}]\}_2(\text{Pyz})_2\} = \text{C}_{18}\text{H}_{10}\text{Cu}_2\text{F}_{12}\text{N}_8$; FW= 693.41 g/mol) accounts for 20.39% and 23.10% of the formula weight, respectively. Thus, the bulk powder of compound **2** exhibits a weight loss of 10.76%, which corresponds to only approximately one-half the pyrazine content (Figure S10a). We attribute this discrepancy to be largely due to the presence of the $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ trimer during the synthesis while attempting to obtain a mixed-metal product. Toluene loss from the

freshly-grown maroon-colored single crystals accounts for 14.30% experimentally (Figure S10b) vs 11.73% theoretically, probably due to interference with the subsequent pyrazine loss. With that accounted for to add the difference to the pyrazine weight loss in the 2nd step, we obtain 19.1% for pyrazine loss experimentally vs 20.39% theoretically – a reasonable agreement. For the air-dried crystals in Figure S10c, toluene loss is greatly reduced but not completely eliminated, whereas pyrazine loss remains close to theory (~18%). Finally, the TGA for the vacuum oven-dried sample in Figure S10d exhibits ~10% 1st weight loss step, approximately half the theoretical pyrazine content. This suggests the possible removal of one equivalent of pyrazine from the molecular formula – which is reasonable to propose given the volatility of pyrazine and the formation of other constitutional isomers (compounds **1** and **3**) with half the pyrazine content found in **2**.

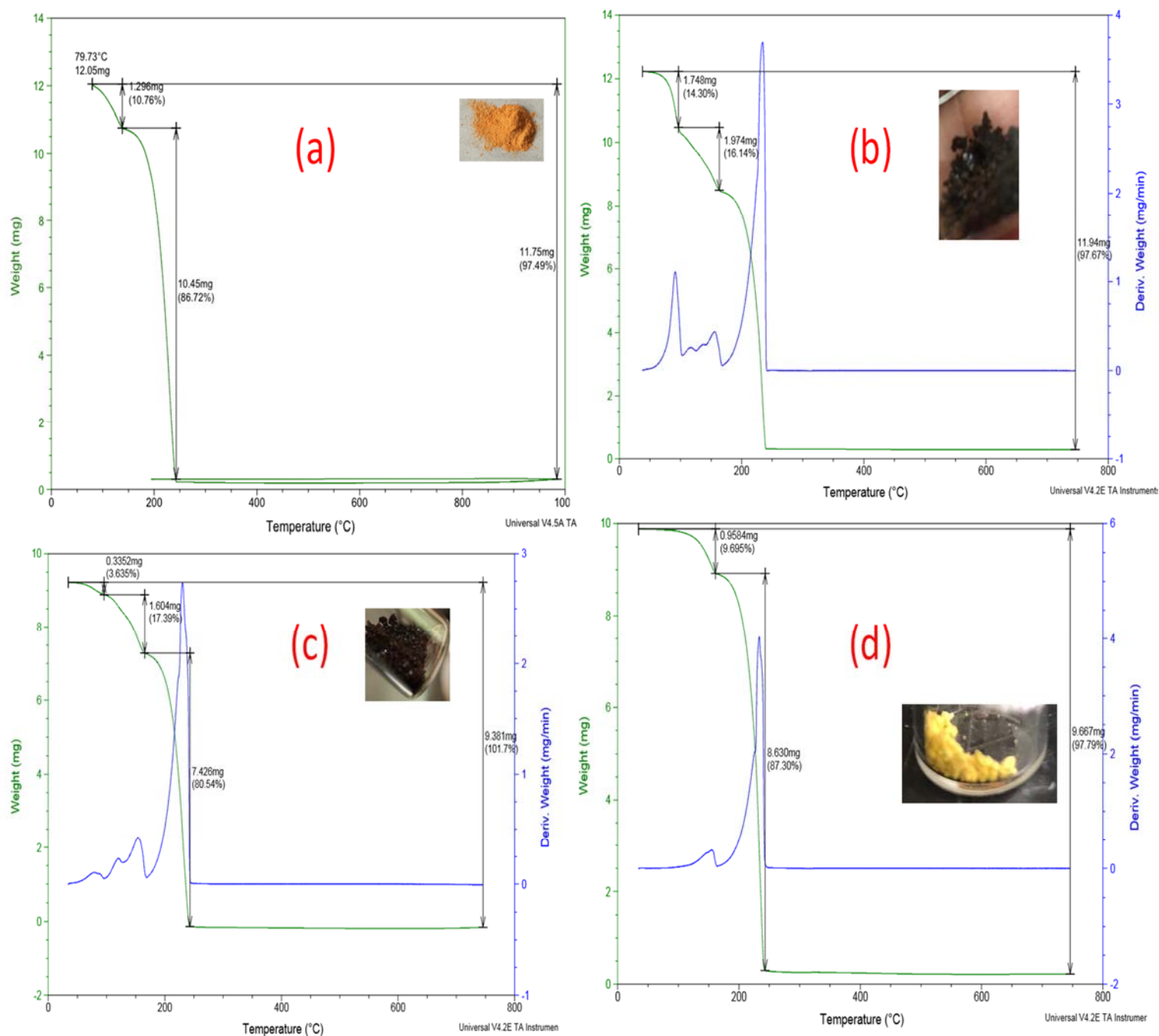


Figure S10. TGA for four different forms of compound **2**: (a) bulk powder product after solvent-mediated synthesis; (b) freshly-grown maroon-colored single crystals from toluene; (c) solid sample resulting from air-drying the maroon single crystals under ambient laboratory conditions for a few days; and (d) solid sample resulting from drying the maroon single crystals in a vacuum oven for 1 hr and 30 mins at 50°C.

Finally, Figure S11 shows the TGA for solventless powder of compound **6**, which reveals successive removal of acetonitrile and pyrazine molecules in three steps. The more significant weight loss in the final step, unlike the behavior for the other complexes illustrated above, is not associated with sublimation, as some 23% of the initial weight remains even at 800 °C. This is consistent with the complex being ionic such that the last step would leave the CuBF₄ salt.

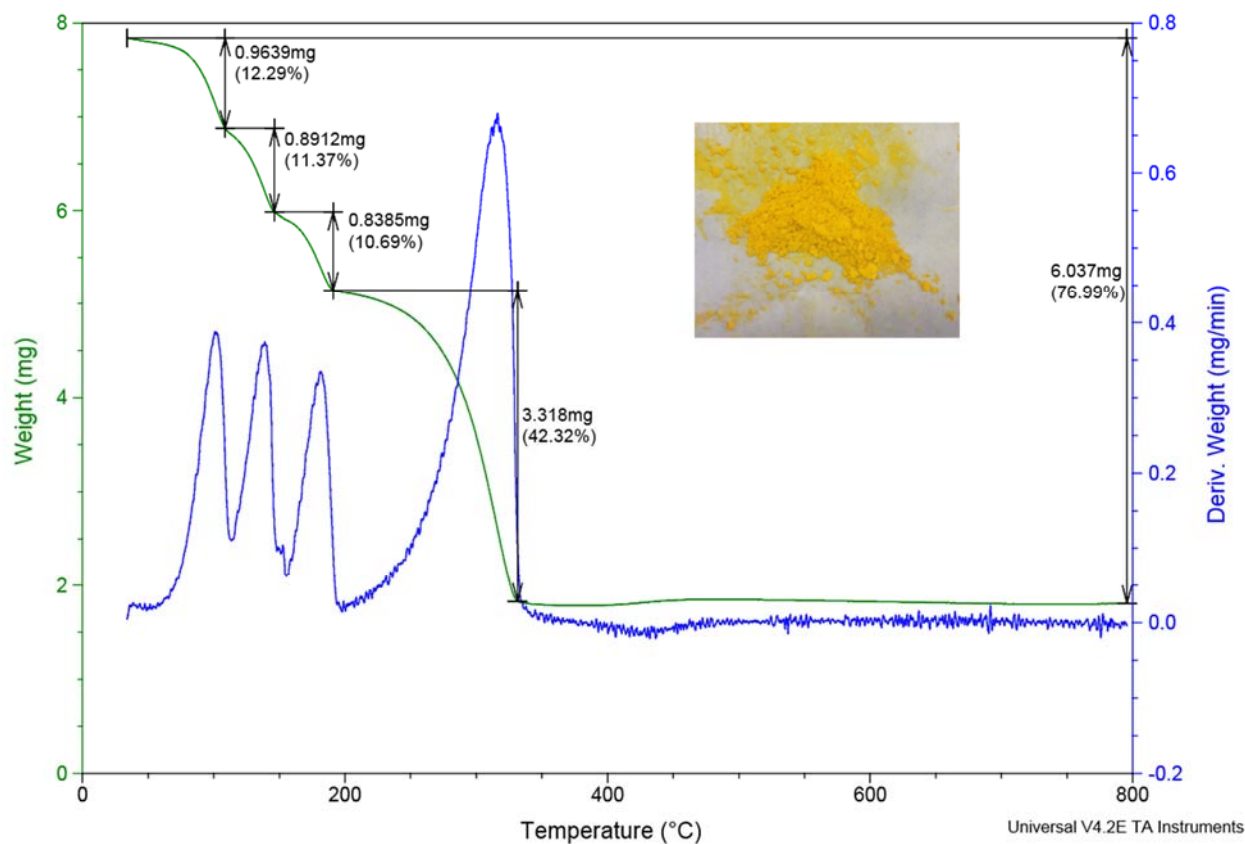


Figure S11. TGA for the solventless powder of compound **6**.