

X-ray structure, magnetic and fluorescence characteristics of new Cu(II) complexes with Schiff bases derived from 2-(2-aminoethyl)pyridine and 2-hydroxy-1-naphthaldehyde; morphology and fluorescence of their thin films

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Supplementary Materials

Figure S1. Structural formula and atomic numbering scheme for 1-[(2-pyridin-2-yl-ethylimino)-methyl]-naphthalen-2-ol (HPEMN) **L1**.

Figure S2. TG-DTA traces of [Cu(II)(PEMN))(CH₃COO)]CH₃Cl **1**.

Figure S3. TG-DTA traces of [Cu(II)(PEMN)Cl] **2**.

Figure S4. TG-DTA traces of [Cu(II)(PEMN)NO₃] **3**.

Figure S5. TG-DTA traces of [Cu(II)(PEMN)CH₃COO] CH₃Cl **1**. under nitrogen

Figure S6. TG-DTA traces of [Cu(II)(PEMN)Cl] **2**. under nitrogen

Figure S7. TG-DTA traces of [Cu(II)(PEMN)NO₃] **3** under nitrogen.

Figure S8. The Uv-vis spectrum of a) complex **3**, b) **1**, c) **2** in the solution (blue) and in the solid state (pink).

Figure S9. AFM image of [Cu(II)(PEMN)(CH₃COO)]CH₃Cl **1**/Si/PMMA, 2000 rpm, 5s x5, a) height, b) phase, c) amplitude scan size 10 μm. Phase images map material property including mechanical, chemical, and viscoelastic. Amplitude- the image of height, in which the dimension of z axis was reduced.

Figure S10. AFM image of [Cu(II)(PEMN))Cl] **2**/Si/PMMA, 2000 rpm, 5s x5, a) height, b) phase, c) amplitude scan size 10 μm.

Synthesis of ligand HPEMN L1

To 2-hydroxy-1-naphthaldehyde 1.722 g (10 mmol) dissolved in dichloromethane 1.19 ml (10 mmol) of 2-(2-pyridyl)ethylamine was added. The mixture was stirred during 1 h, color was changed from yellow to orange. The slow evaporation of the solvent resulted in the orange oil.

^1H [ppm]: 3.31 (t, 2H) CH_2 -, 4.05 (t, 2H) CH_2 -, 6.93 (d 1H), 7.15-7.23 (m, 2H) Ar-H; 7.28 (s, 1H), 7.31 (d, 1H), 7.35-7.37 (m, 1H) Ar-H; 8.61-8.62 (m, 1H) Ar-H; 8.67 (s, 1H) -NCH-; 14.41 (s, 1H) -OH.⁶

^{13}C [ppm]: 172.7 (HC8N), 170.1 (C10), 158.3 (C11), 149.2 (C14, 15), 136.9 (C13), 135.2 (C12), 133.2 (C11), 128.5 (C3), 125.1 (C1), 126.8 (C5, 4), 124.8 (C16), 124.3 (C17), 122.1 (C18), 121.8 (C19), 110.9 (C2), 45.8 (C7), 38.1 (C6). ^{15}N -68.86 ppm, -181.84 ppm. (Figure 1).

Selected FT-IR data (KBr, cm^{-1}) 3055 ν_{OH} , 2930 ν_{CH_2} , 2723, 2635 $\nu_{\text{C-H}_{\text{Ar}}}$, 1618 $\nu_{\text{C=N}}$, 1592, 1550, 1475, 1435 $\nu_{\text{C=C}_{\text{Ar}}}$, 1346, 1280 $\nu_{\text{C-N}_{\text{py}}}$, 1247 $\nu_{\text{Ph-O}}$, 1210, 956. Uv-Vis MeCN [nm]: 311, 397.

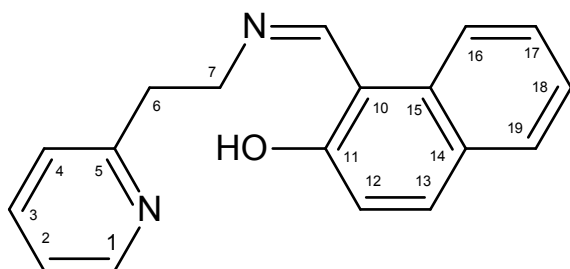


Figure S1. Structural formula and atomic numbering scheme for 1-[(2-pyridin-2-yl-ethylimino)-methyl]-naphthalen-2-ol (HPEMN) **L1**.

Infrared spectroscopy

The IR spectra of ligand (HPEMN) **L1** exhibits band from -N=CH- stretching vibrations at 1618 cm^{-1} . Additionally, spectrum of **L1** exhibits the Ph-O stretching vibration band at 1247 cm^{-1} , whereas the -OH stretching vibration band was noted at 3055 cm^{-1} . Upon complexation, the Ph-O stretching vibration band was shifted towards higher frequencies (1282 cm^{-1} for **1**, 1256 cm^{-1} for **2** and 1250 cm^{-1} for **3**), while ν_{OH} bands disappeared.

Moreover, the band from azomethine stretching vibrations in **1** was noted at 1603 cm^{-1} , $\Delta_{\text{coord}} = \Delta_{\text{comp}} - \Delta_{\text{lig}} = -17\text{ cm}^{-1}$ for **2** and -13 for **3**, what confirms the copper binding by the -N=CH- group.

In the spectra of $[\text{Cu(II)(PEMN)CH}_3\text{COO}]$ **1** the bands from symmetrical and asymmetrical stretching vibrations of the carboxylate group at 1419 cm^{-1} ν_{COO^-} and 1619 cm^{-1} ν_{asCOO^-} were registered,¹⁻² suggesting the monodentate coordination.

The band from Cu-O stretching vibrations appeared at 543 cm^{-1} for **1**, at 541 cm^{-1} for **2** and at 545 cm^{-1} for **3**.³ Additionally, the band from Cu-Cl stretching vibrations were registered at: 349 cm^{-1} $[\text{Cu(II)(PEMN)Cl}]$ **2**.¹ The presence of the bands from Cu-O, Cu-N and Cu-Cl stretching vibrations confirms the coordination *via* Ph-O, N and Cl ions, respectively. The nitrate anions in the IR spectrum of **3** revealed a split $\text{E}_1(\nu_3)$ doubly degenerated asymmetric stretching of the NO bond at 1365 and 1508 cm^{-1} frequencies. The calculated splitting parameter, Δ_{coord} , for **3** was 143 cm^{-1} . According to Nakamoto¹, the observed magnitude of Δ_{coord} can be related to the bidentately bonded NO_3^- ion. The values of Δ_{coord} reported in the literature were larger in the case of bidentate coordination of the NO_3^- ion than those in the monodentate mode.^{1,4-5} Summarizing IR results for the studied complexes it is evident that the copper(II) ions coordinate with the ligand *via* N or O atoms and Cl^- , CH_3COO^- or NO_3^- ions.

Thermal analysis

For all complexes the thermal decomposition studies were performed under air or under nitrogen. The thermal decomposition process was significantly different in dependence on the analysis atmosphere. When reaction was carried under nitrogen only one mass loss has been seen on the TG curves. (Figures S2-S7). The final product of decomposition was mixture of copper and copper oxide.

When the thermal decomposition was carried out under air the decomposition process was more complex.

Thermogram of compound $[\text{Cu(II)(PEMN)(CH}_3\text{COO)}]\text{CH}_3\text{Cl}$ **1** reveals three peaks of the decomposition on DTG curve, which can be assigned to CHCl_3 , acetate ion and piridine amine derivative ($\text{C}_7\text{H}_8\text{N}_2$) molecules detachment (exp. 56.86%, cal. 56.8%). (Figure S2) Second DTG peak corresponds to 25.47% mass loss, what can be related to the rest molecule decomposition, followed by mixture of Cu and CuO formation at 707°C . The first endothermic peak appeared at 143°C , the next two endothermic at 197°C , 261°C , and finally two exothermic peaks at 409°C and 475°C were noted.

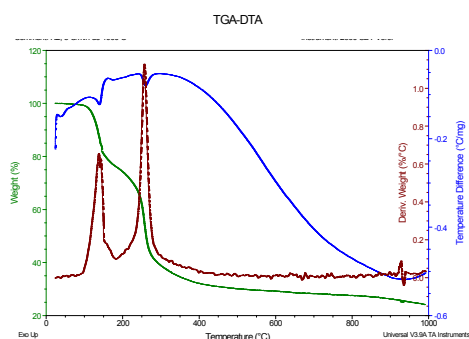


Figure S2. TG-DTA traces of $[\text{Cu(II)(PEMN)}](\text{CH}_3\text{COO})\text{CH}_3\text{Cl}$ **1**.

Thermogram of **2** (Figure S3) exhibits seven DTG peaks with maxima at 185, 251, 231, 358, 388, 461 and 561°C, which on TG curve reveal two stages with 41.04 and 44.83% sample mass loss. The partial mass loss in the first step corresponds to the detachment of chloride ion and pirydyne amine derivative ($\text{C}_7\text{H}_8\text{N}_2$) (cal. 41.58%). Further sample mass reduction is connected with the naphthyl molecule detachment (found 44.83%; cal. 44.6%) and copper oxide formation at 650°C.

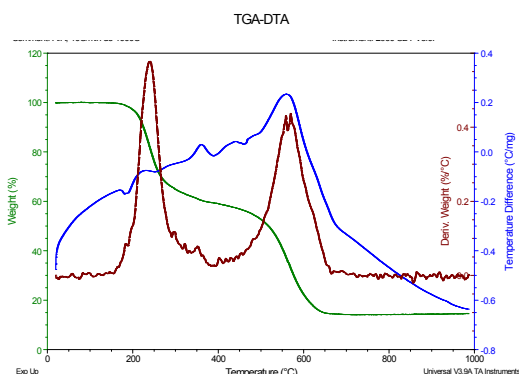


Figure S3. TG-DTA traces of $[\text{Cu(II)(PEMN)Cl}]$ **2**.

Thermogram of **3** (Figure S4) over 123°C presents on TG curve continuous mass loss, starting from 123°C to 591°C, whereas the first endothermic stage can be observed on DTA curve at 161°C. Additionally, one endothermic peak at 227°C and two exothermic peaks at 261 and 469°C were noted. The mass loss corresponds the NO_3^- and pyridine derivative dissociation. Further sample mass reduction is connected with the naphthalene ring molecule detachment ($\text{C}_{11}\text{H}_8\text{O}$, found 39.52%; cal. 39.96%) and mixture of copper and 0.5 CuO formation (25.34/25.56%) at 591°C.

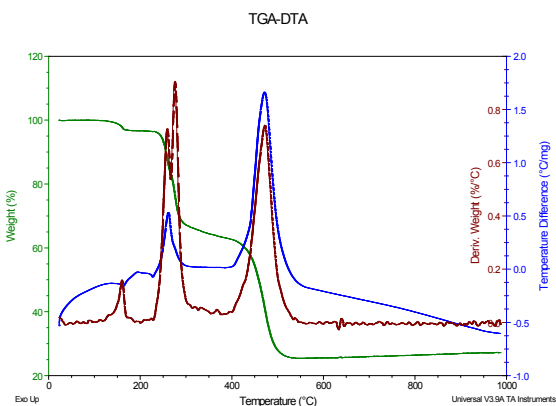


Figure S4. TG-DTA traces of $[\text{Cu(II)(PEMN)NO}_3]$ **3**.

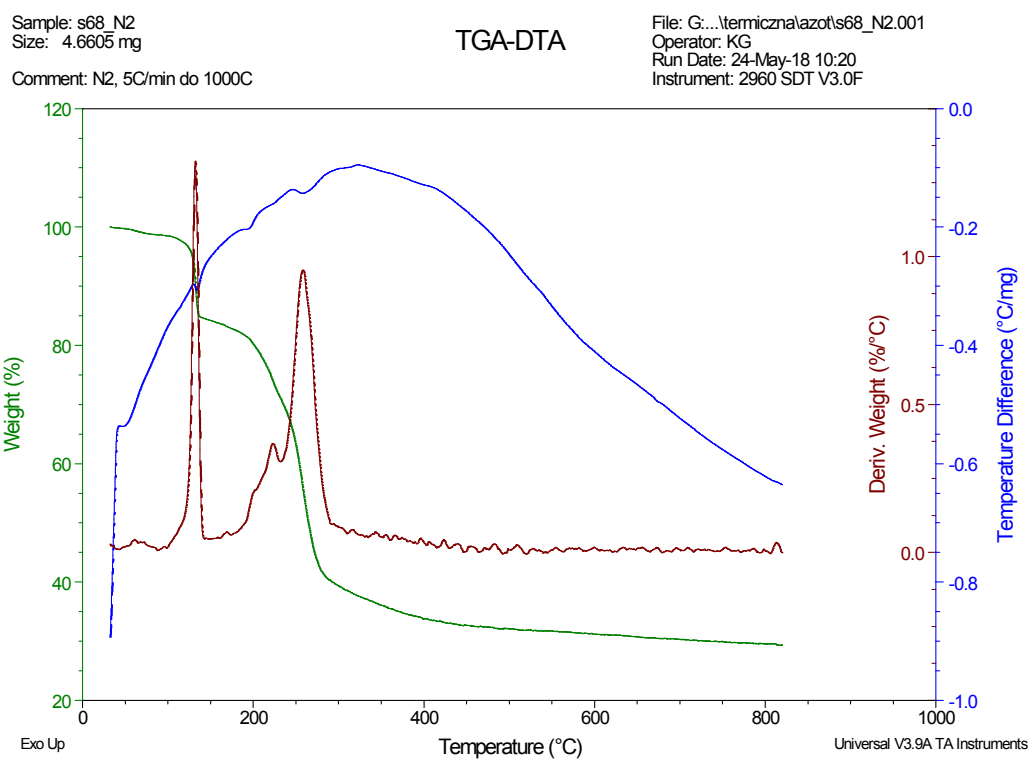


Figure S5. TG-DTA traces of $[\text{Cu(II)(PEMN)CH}_3\text{COO}]\text{CH}_3\text{Cl}$ **1**. under nitrogen

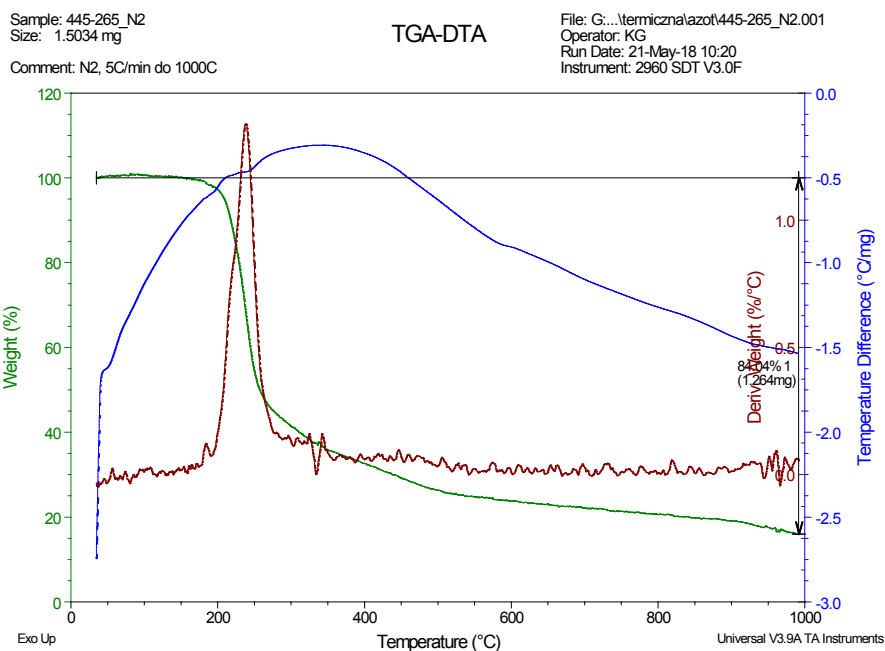


Figure S6. TG-DTA traces of $[\text{Cu(II)(PEMN)Cl}] \mathbf{2}$ under nitrogen

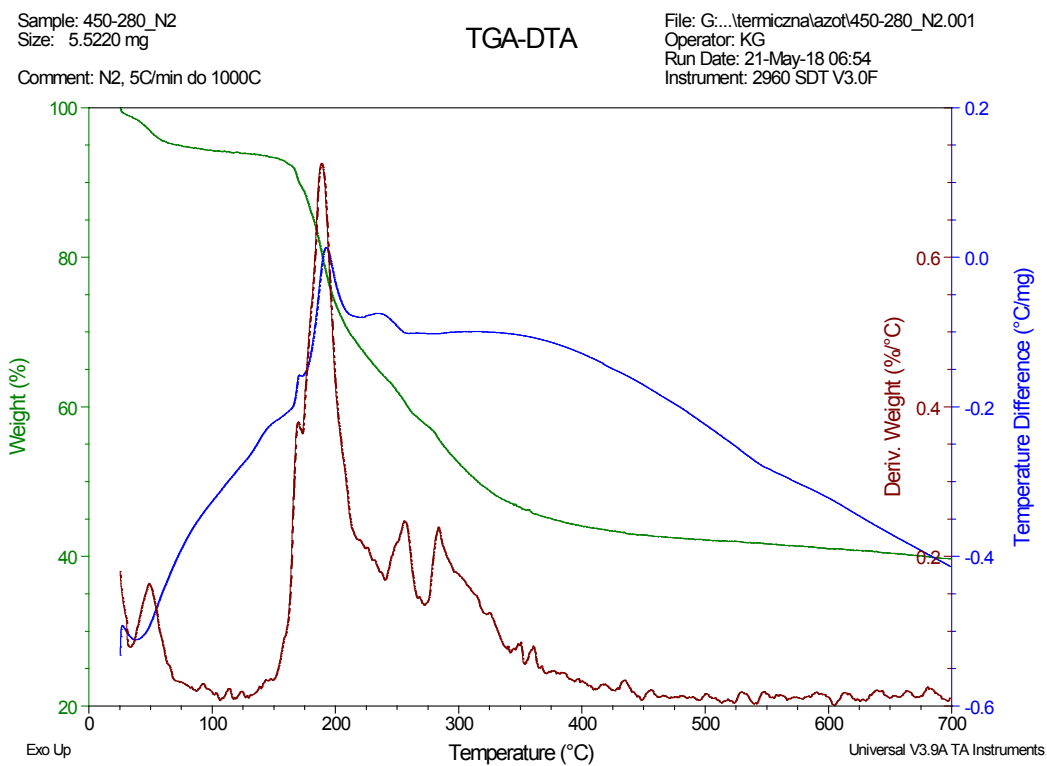


Figure S7. TG-DTA traces of $[\text{Cu(II)(PEMN)NO}_3] \mathbf{3}$ under nitrogen.

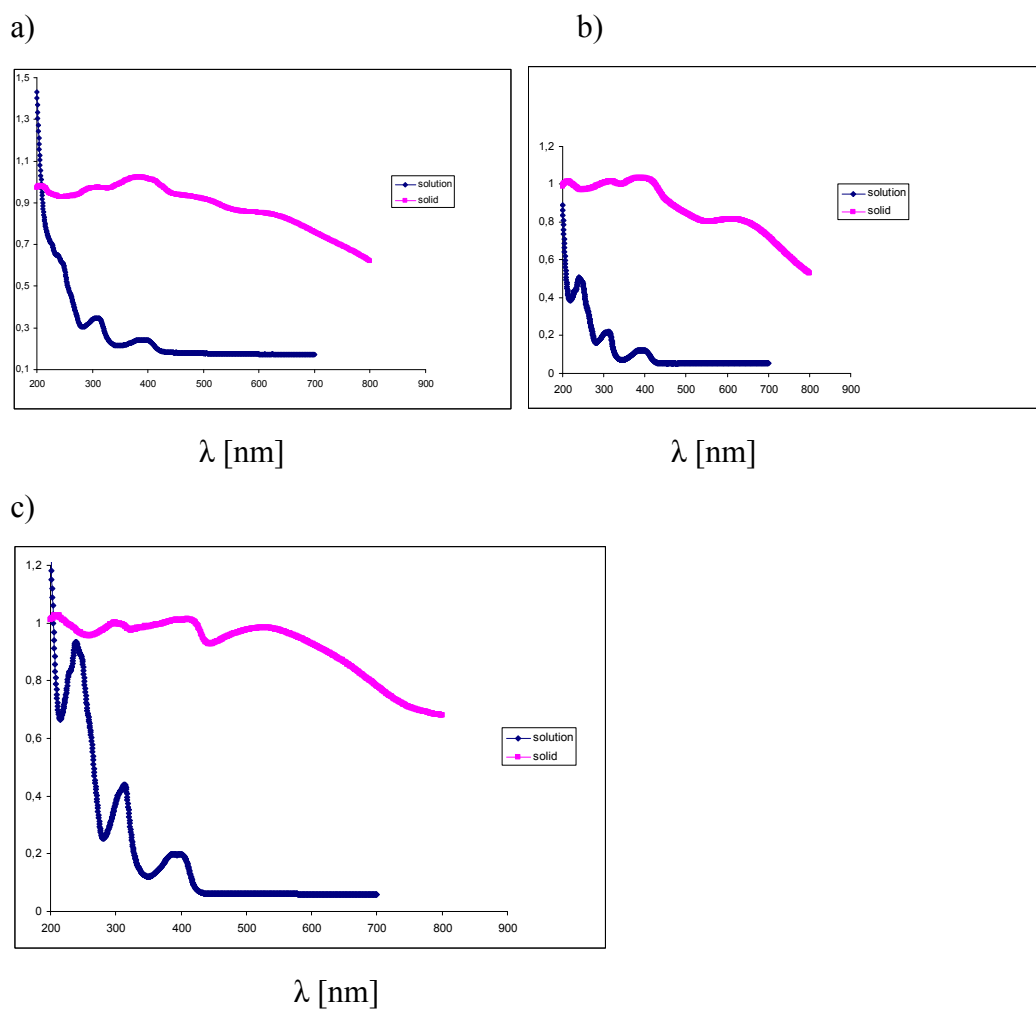


Figure S8. The Uv-vis spectrum of a) complex **3**, b) **1**, c) **2** in the solution (blue) and in the solid state (pink).

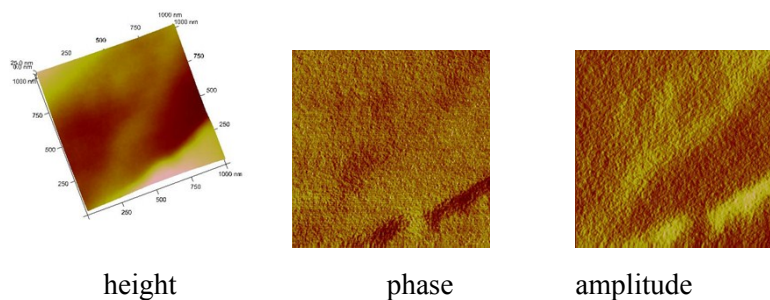


Figure S9. AFM image of $[\text{Cu(II)(PEMN)(CH}_3\text{COO)}]\text{CH}_3\text{Cl 1/Si/PMMA}$, 2000 rpm, 5s x5, a) height, b) phase, c) amplitude scan size 10 μm . Phase images map material property including mechanical, chemical, and viscoelastic. Amplitude- the image of height, in which the dimension of z axis was reduced.

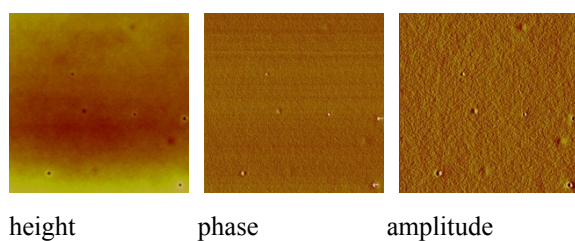


Figure S10. AFM image of $[\text{Cu(II)(PEMN))Cl}] \text{ 2/Si/PMMA}$, 2000 rpm, 5s x5, a) height, b) phase, c) amplitude scan size 10 μm .

References

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