Supplementary Material

A series of new pyridine carboxamide complexes and self-assemblies with Tb(III), Eu(III), Zn(II), Cu(II) ions and their luminescent and magnetic properties

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Fig. S1 SEM images of compound 1

Fig. S2 SEM images of compound 5
**Compound 1**

$^1$H NMR (600 MHz, DMSO) $\delta$ 10.34, 8.85, 7.96, 7.49, 3.87, 3.34, 2.50.

**L1**

$^1$H NMR (403 MHz, DMSO) $\delta$ 10.83 (s, 1H), 9.06 (d, $J = 3.6$ Hz, 2H), 8.38 (d, $J = 6.3$ Hz, 2H), 8.03 (d, $J = 1.6$ Hz, 1H), 7.80 (dd, $J = 7.9$, 1.8 Hz, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 3.85 (s, 3H), 2.35 (s, 3H).
**Compound 5**

$^1$H NMR (403 MHz, DMSO) $\delta$ 9.77 (s, 1H), 8.70 (d, $J = 5.9$ Hz, 2H), 7.71 (d, $J = 5.4$ Hz, 2H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.57 − 6.41 (m, 1H), 5.82 (s, 1H), 3.34 (s, 6H water), 1.14 (s, 3H).

**L2**

$^1$H NMR (300 MHz, DMSO) $\delta$ 10.75 (s, 1H), 9.00 (d, $J = 6.3$ Hz, 2H), 8.27 (dd, $J = 5.1$, 1.3 Hz, 2H), 7.70 (dd, $J = 7.8$, 1.3 Hz, 1H), 7.56 (dd, $J = 7.8$, 0.9 Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 4.28 (s, N$^\text{H}$-proton fast chemical exchange with water molecules), 3.85 (s, 3H), 2.37 (s, 3H).

**Fig. S3** $^1$H NMR spectra of compounds 1, 5 and ligands L1 and L2
Taking for consideration the elemental analysis results, complex 4 presumably has adopted the structure similar to complex 7 ([Cu(L2)2Cl2]) with copper(II) ion coordinated by two ligands L1 via pyridine nitrogen donor atoms and two chloride anions. Thus in the complex 7 the same coordination mode of L2 was observed in the single crystal X-Ray diffraction analysis, but the FT-IR spectrum showed two different types of shifts for carbonyl stretching bands 1729 and 1690 or 1714 and 1671 cm⁻¹. Moreover for all compounds the presence of peptide group is indicated via ν(N-H) bands, which are doubled in this case at 3364 and 3291 cm⁻¹. It can be assumed that this is a reflectance of structural torsion of ligands L2 in relation to each other and as well as to the chloride ions, which are clarified by the single crystal X-Ray analysis.
The ν(C=O) bands were shifted to 1707 and 1685 cm\(^{-1}\) in coordination polymer 8 spectrum and it is probably caused by more intensive hydrogen bond interactions between neighboring zig-zag chains in the crystal structure.

The FT-IR spectrum of 5 showed the isonicotinic acid ν(C=O) stretching band shift to 1650 cm\(^{-1}\) and a symmetric and asymmetric deprotonated carboxylic group stretching bands occurred at 1530 and 1409 cm\(^{-1}\) as a result of ester decomposition [12a].

**Fig. S6** Emission spectra of benzene-1,3,5-tricarboxylic acid (BTC) and ligand L1 (solid state)

**Fig. S7** Excitation spectrum of complex 5 (solid state)
Fig. S8 Chromaticity diagram for compounds 1 and 5

Fig. S9 Luminescence lifetimes decay curves of complexes 1 and 5 (a, b) and changes of emission intensity of the $^5\text{D}_0-^7\text{F}_5$ (Tb$^{3+}$) and $^5\text{D}_0-^7\text{F}_2$ (Eu$^{3+}$) transition bands (at 545 nm, 618 nm) during UV-Vis radiation of complexes 1 and 5 with $\lambda_{ex} =$303 nm and 394 nm (c, d)
Fig. S10 TG-DTA analysis curves for compounds 1, 3, 4 and 5.
Fig. S11 XRD diagrams for compounds: **L1, BTC, 1 - 4** (a) and **L2, 5 – 8** (b), comparison of simulated and measured PXRD patterns for compounds **7 and 8** (c)
**Fig. S12** Hydrogen-bonded ring of complex molecules 2; hydrogen bonds are shown as dashed blue lines.

**Fig. S13** Two basic hydrogen-bonded motifs in the structure of 6: C22(6) (left) and R44(22) (right); cf. text.
Fig. S14 The N-H•••Cl and N-H•••O hydrogen bonds in the structure of complex 7

Fig.S15 N-H•••O hydrogen-bonded coordination polymers 8
**Fig. S16** Flexibility of ligand L2 molecules (structures are fitted onto pyridine rings)

**Fig. S17** Magnetic susceptibility and its reciprocal values vs temperature for complex 1
Fig. S18 Magnetic measurements for complex 7. Magnetic susceptibility $\chi_M(T)$ fitted with Eq. (5) for a singlet ground state and including the intra- and inter-dimer exchange coupling strength.

Fig S19. Magnetization curve $M(H)$ for complex 7

Fig.S20 Magnetic measurements for complex 3. Magnetic susceptibility $\chi_M(T)$ is fitted with Eq. (6) – red solid line. Inset: Magnetization curve $M(H)$
**Fig. S21** Magnetic measurements for complex 4. Magnetic susceptibility $\chi_M(T)$ is fitted with Eq. (2) – black solid line. The red dashed line is a fit with Eq. (5). Inset: Magnetization curve $M(H)$.

**Fig. S22** Magnetic measurements for complex 4: $(\chi_M T - \text{TIP})$ vs $T$ fitted with Eq. (4)
**CIF alert explanation for complex 2**

The explanation for Alert B occurrence: Flack parameter is 0.028(6) – so it is in fact larger than 3 sigmas, but it is certainly not much larger than 0. For reversed structure, the x is 0.969(6), and what’s more, R factor is almost two times larger (4.5%).

**CIF alert explanation for complex 6**

The explanation for Alert B occurrence: The reflections were cut because of beamstop position; Hirshfeld test reflects some inappropriateness of Uij tensor; however it is – in our opinion – not important enough to apply some kind of restraints (e.g. RIGU). Do cifów.