

Supplementary Information

Table S1 Comparison of crystal parameters of compound **1** with the already reported compounds

| Crystal Parametres | 1 | CCDC 752079 | CCDC 1166932 | CCDC 2166801 |
|--|---|---|---|---|
| Emprical formula | C ₂₄ H ₁₈ ClCuN ₅ O ₄ | C ₁₂ H ₈ Cl _{0.50} Cu _{0.50} N _{2.50} O ₂ | C ₂₄ H ₁₈ ClCuN ₅ O ₄ | C ₂₄ H ₁₈ ClCuN ₅ O ₄ |
| Formula weight | 539.42 | 268.70 | 539.41 | 539.43 |
| Temperature (K) | 100.0 | 293(2) | 295 | 296(2) |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| <i>a</i> /Å | 9.6570(9) | 9.7359(6) | 11.128(1) | 9.771(2) |
| <i>b</i> /Å | 10.8732(10) | 11.1382(7) | 12.026(4) | 11.148(2) |
| <i>c</i> /Å | 11.9997(11) | 12.0067(8) | 9.738(2) | 12.052(2) |
| α ° | 68.329(2) | 67.739(6) | 108.84(2) | 67.823(2) |
| β ° | 70.758(2) | 71.020(5) | 108.54(2) | 71.034(2) |
| γ ° | 71.247(2) | 71.484(5) | 67.83(2) | 71.423(2) |
| Volume (Å ³) | 1076.48(17) | 1111.0(12) | 1113.23 | 1120.5(4) |
| Z | 2 | 4 | 2 | 2 |
| Calculated density (g/cm ³) | 1.664 | 1.606 | 1.609 | 1.599 |
| Absorption coefficient (mm ⁻¹) | 2.965 | 1.146 | Not available | 1.138 |
| F(000) | 550.0 | 546.0 | Not available | 550 |
| Crystal size (mm ³) | 0.45×0.21×0.21 | 0.40×0.38×0.36 | Not available | 0.30×0.26×0.23 |
| Index ranges | -11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 14 | -11 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 13, -13 ≤ <i>l</i> ≤ 16 | Not available | -13 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16 |
| Reflections collected | 27524 | 5800 | Not available | 5715 |
| Unique data(<i>R</i> _{int}) | 3909 (0.0523) | 3607 | Not available | 4035 |
| Refinement method | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² | Not available | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 3909 / 0 / 320 | 4824 / 0 / 316 | Not available | 5715 / 0 / 383 |
| Goodness-of-fit on F ² | 1.162 | 1.060 | Not available | 1.020 |
| Final R indices [<i>I</i> > 2σ (<i>I</i>)] R1/ wR2 | 0.0412/ 0.1047 | 0.0410/0.1182 | Not available | 0.0464/0.1194 |

Table S2 Comparison of crystal parameters of compound **2** with the already reported compound

| Crystal Parametres | 2 | CCDC 148860 |
|--------------------|--|--|
| Emprical formula | C ₂₀ H ₃₂ Cl ₄ Cu ₂ N ₈ | C ₂₀ H ₃₂ Cl ₄ Cu ₂ N ₈ |
| Formula weight | 653.41 | 653.42 |
| Temperature (K) | 111.0 | 173.0 |
| Crystal system | monoclinic | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> /Å | 8.6960(6) | 8.7137(8) |

| | | |
|---|---|--|
| $b/\text{\AA}$ | 13.4486(9) | 13.5493(14) |
| $c/\text{\AA}$ | 11.8533(8) | 11.8847(12) |
| α° | 90 | 90 |
| β° | 106.117(2) | 106.179(2) |
| γ° | 90 | 90 |
| Volume (\AA^3) | 1331.75(16) | 1347.6(2) |
| Z | 2 | 2 |
| Calculated density (g/cm^3) | 1.629 | 1.610 |
| Absorption coefficient (mm^{-1}) | 5.872 | 2.000 |
| $F(000)$ | 668.0 | 668.0 |
| Crystal size (mm^3) | 0.22 \times 0.152 \times 0.108 | 0.30 \times 0.25 \times 0.20 |
| Index ranges | -10 $\leq h \leq$ 8, -16 $\leq k \leq$ 16, -14 $\leq l \leq$ 14 | -11 $\leq h \leq$ 10, -17 $\leq k \leq$ 11, -15 $\leq l \leq$ 15 |
| Reflections collected | 8827 | 6096 |
| Unique data (R_{int}) | 2336 (0.0359) | 2985 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2528 / 0 / 205 | 2985 / 0 / 162 |
| Goodness-of-fit on F^2 | 1.188 | 1.057 |
| Final R indices [$I > 2\sigma(I)$] $R1$ / $wR2$ | 0.0435 / 0.1127 | 0.0455 / 0.1235 |

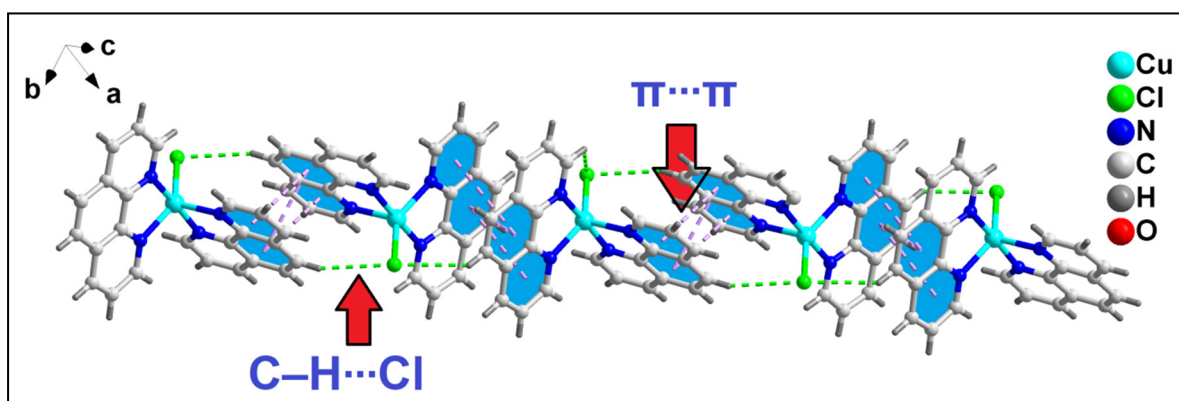


Figure S1 1D supramolecular chain of compound **1** assisted by C–H \cdots Cl and π -stacking interactions.

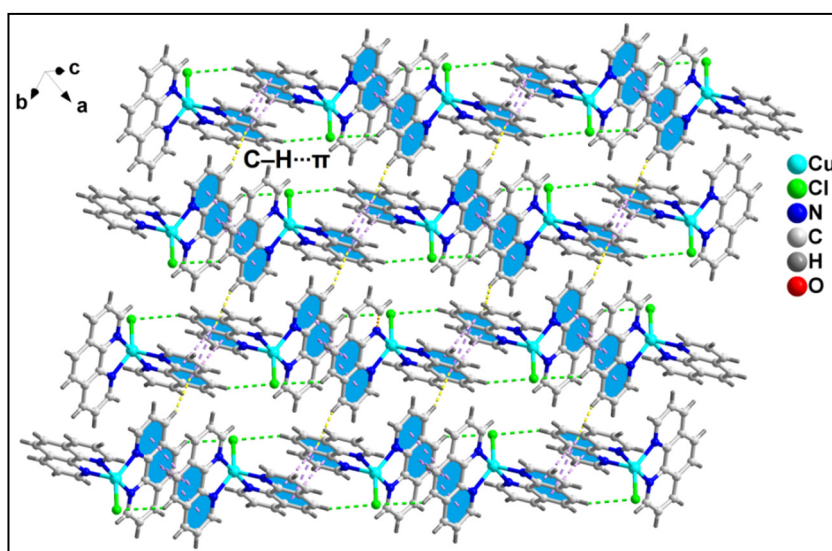


Figure S2 Layered assembly of compound **1** along the crystallographic ac plane.

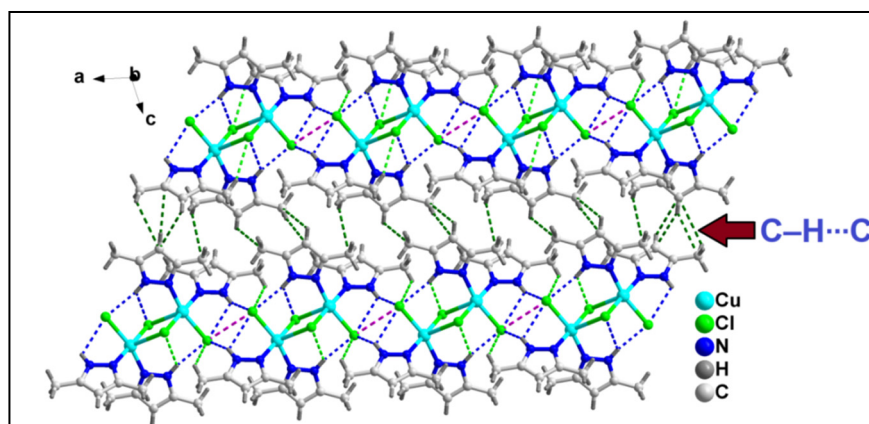


Figure S3 Layered assembly of compound **2** assisted by non-covalent C–H...C interactions.

Table S3 Selected parameters for C–H...C interactions in compound **2**.

| C–H...C | d(C–H) | d(C...C) | d(H...C) | Hybridization of C-atoms |
|----------------|--------|----------|----------|---|
| C51–H51E...C51 | 0.94 | 3.88 | 3.82 | C(sp ³)–H...C(sp ³) |
| C51–H51F...C51 | 0.94 | 3.88 | 3.25 | C(sp ³)–H...C(sp ³) |
| C31–H31B...C4 | 0.94 | 3.62 | 3.81 | C(sp ³)–H...C(sp ²) |
| C4–H4...C4 | 0.94 | 3.69 | 3.43 | C(sp ²)–H...C(sp ²) |
| C4–H4...C3 | 0.94 | 3.86 | 2.92 | C(sp ³)–H...C(sp ³) |
| C51–H51E...C31 | 0.94 | 3.60 | 3.36 | C(sp ³)–H...C(sp ³) |
| C51–H51D...C31 | 0.94 | 3.60 | 3.48 | C(sp ³)–H...C(sp ³) |
| C31–H31F...C51 | 0.94 | 3.52 | 3.60 | C(sp ³)–H...C(sp ³) |
| C31–H31D...C51 | 0.94 | 3.60 | 3.52 | C(sp ³)–H...C(sp ³) |
| C51–H51F...C31 | 0.94 | 3.60 | 3.69 | C(sp ³)–H...C(sp ³) |
| C51–H51B...C31 | 0.94 | 3.50 | 3.65 | C(sp ³)–H...C(sp ³) |
| C31–H31B...C51 | 0.94 | 3.60 | 3.49 | C(sp ³)–H...C(sp ³) |
| C51–H51B...C31 | 0.94 | 3.60 | 3.65 | C(sp ³)–H...C(sp ³) |
| C51–H51C...C31 | 0.94 | 3.60 | 3.58 | C(sp ³)–H...C(sp ³) |
| C31–H31C...C51 | 0.94 | 3.60 | 3.41 | C(sp ³)–H...C(sp ³) |

3.3 Spectral studies

3.3.3 FT-IR spectroscopy

The KBr phase FT-IR spectra of the compounds **1** and **2** were recorded in the frequency region of 4000-500 cm⁻¹ (Figure S4). The broad absorption band in the frequency region of 3200-3450 cm⁻¹ in the spectrum of the compound **1** can be assigned to $\nu(\text{O–H})$ stretching vibrations of the lattice water molecule [83]. The shifting of $\delta(\text{C–H})$ vibrations of phen in the FT-IR spectrum of the compound **1** can be attributed to the fact that phen donates a pair of electrons to the Cu(II) centre forming coordinate covalent bonds [84-85]. The absorption bands obtained at around 1145 cm⁻¹ in the FT-IR spectrum of **1** can be attributed to the

$\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ vibrations of coordinated phen [86]. The sharp absorption bands at 1382 cm^{-1} for compound **1** is due to the presence of uncoordinated nitrate ion [87]. In the FT-IR spectrum of compound **2**, the weak absorption bands obtained in the frequency region of $2924\text{--}2726\text{ cm}^{-1}$ can be assigned to the $\nu(\text{C}\text{--}\text{H})$ stretching vibrations of the coordinated Hdmpz moieties [88]. The ring stretching vibrations of Hdmpz moieties ($\text{C}\text{--}\text{N}$, $\text{N}\text{--}\text{N}$ and $\text{C}=\text{N}$ respectively) are obtained at 1466 , 1267 and 1160 cm^{-1} in the FT-IR spectrum of compound **2** [89].

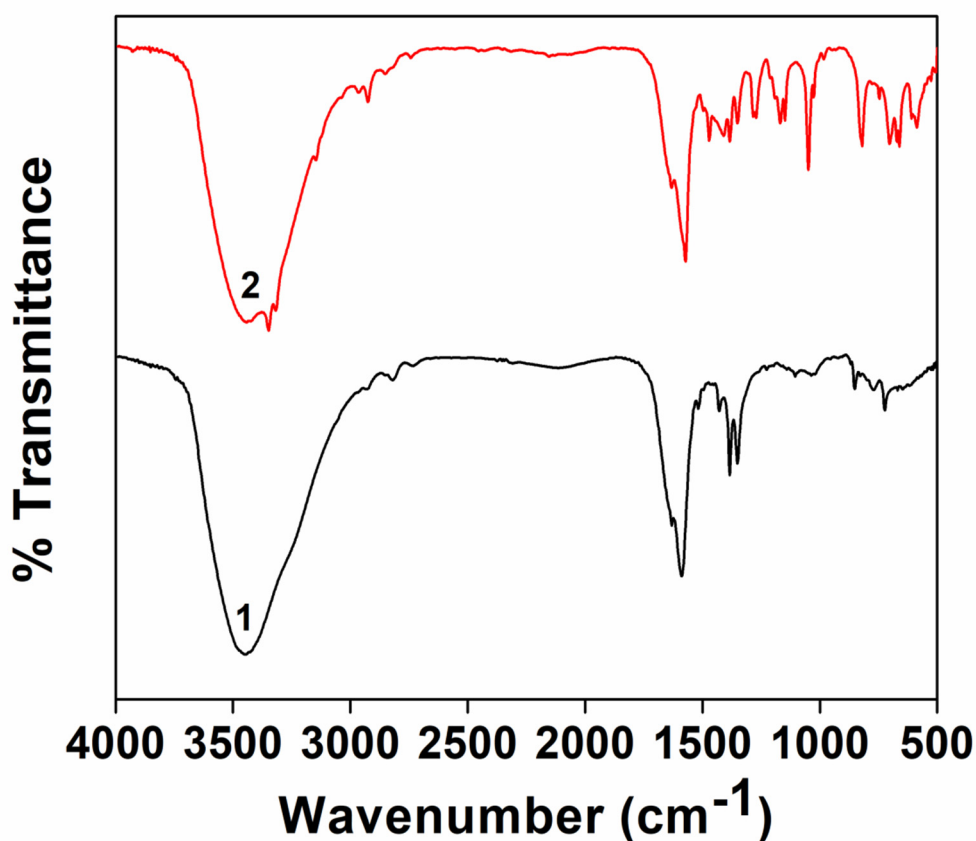


Figure S4 FTIR spectra of compounds **1** and **2**.

3.3.2 Electronic spectroscopy

The electronic spectra of the compounds have been recorded in both solid and in aqueous phases (Figures S5-S6). The broad absorption band in UV-Vis-NIR spectrum (Figure S5a) of **1** at 683 nm is due to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition, suggesting distorted square-

pyramidal geometry around the copper centre [1]. The UV band originating due to the $\pi \rightarrow \pi^*$ transition of the *phen* ligands is observed at 271 nm [2]. In the UV-Vis spectrum (Fig. S5b) in water, the absorption band due to $\pi \rightarrow \pi^*$ transition is observed at 273 nm. In the aqueous phase spectrum, the absorption band at 678 nm can be attributed to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition of the Cu(II) centers [3]. Similar electronic spectra for the compound **2** are also observed revealing the presence of Cu(II) centers in the compounds (Figure S6).

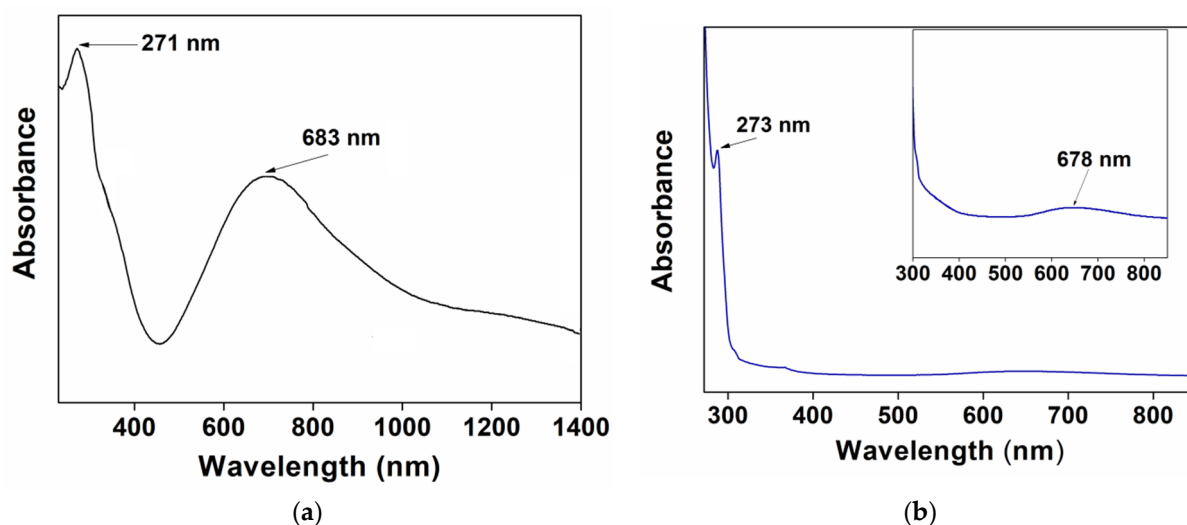


Figure S5(a) UV-Vis-NIR spectrum of **2** **(b)** UV-Vis spectrum of **2** in water

The observed similarities in the position of the absorption peaks in the solid and aqueous phase electronic spectra suggest that the bonding modes and geometries of the compounds do not undergo any distortion in aqueous phase [4].

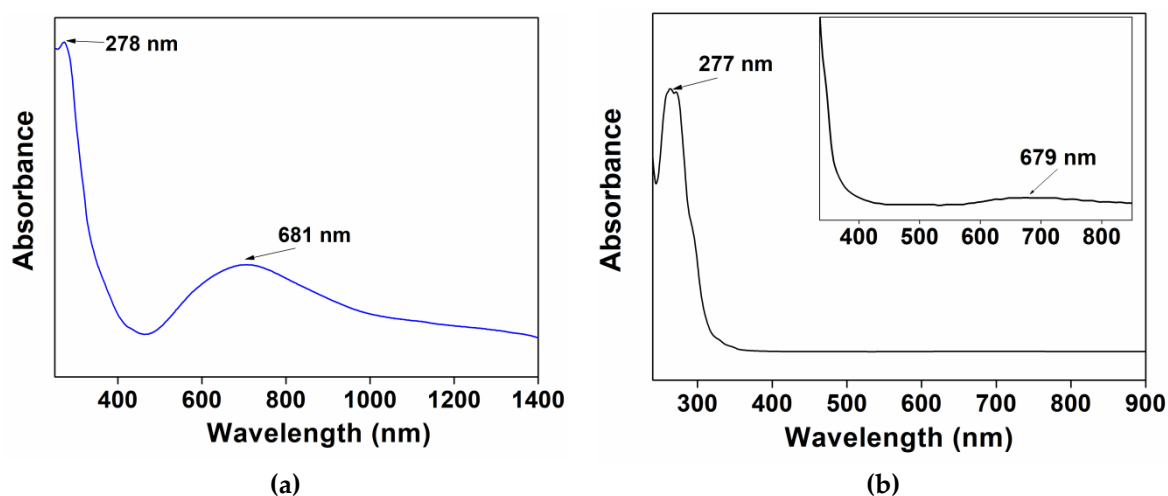
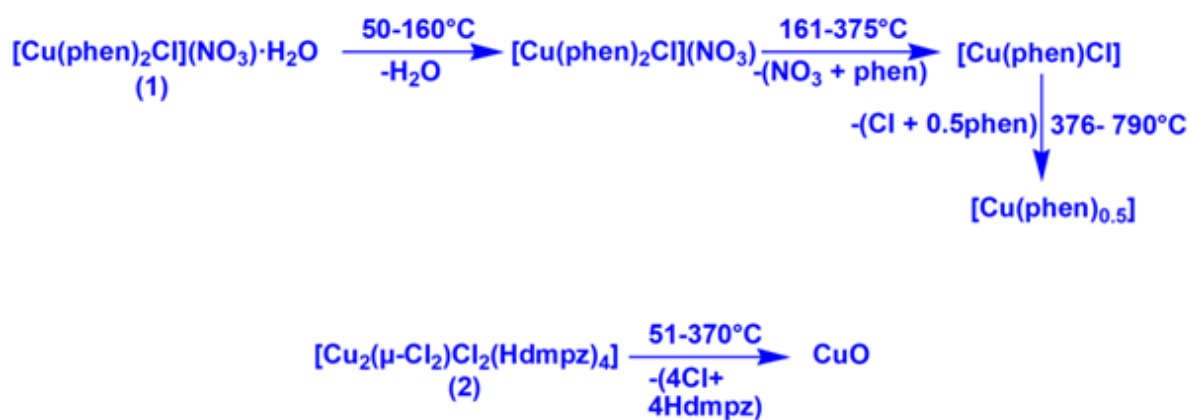


Figure S6(a) UV-Vis-NIR spectrum of **3** **(b)** UV-Vis spectrum of **3**.

Figure 1 is a TGA plot showing the thermal stability of polyimide 1 and polyimide 2. The x-axis represents Temperature in °C, ranging from 0 to 800. The y-axis represents % Weight Loss, ranging from 0 to 100. Curve 1 (red) represents polyimide 1, and Curve 2 (blue) represents polyimide 2. Both polymers exhibit high thermal stability up to approximately 300°C, followed by a rapid weight loss. Polyimide 1 shows a more gradual weight loss after 400°C compared to polyimide 2, which levels off at a lower weight loss percentage at 800°C.

| Temperature (°C) | % Weight Loss (Polyimide 1) | % Weight Loss (Polyimide 2) |
|------------------|-----------------------------|-----------------------------|
| 0 | 0 | 0 |
| 100 | 0 | 0 |
| 200 | 0 | 0 |
| 300 | 0 | 0 |
| 350 | ~60 | ~60 |
| 400 | ~50 | ~22 |
| 500 | ~45 | ~20 |
| 600 | ~38 | ~18 |
| 700 | ~32 | ~16 |
| 800 | ~25 | ~15 |

85
86
87
88
89
90



91
92
93
94
95
96

Supplementary references

1. Tandon, S.S.; Chen, L.; Thompson, L.K.; Bridson, J.N. Dinuclear copper(II) complexes of the tetradentate thiadiazole ligands BPMTD (2,5-bis((2-pyridylmethyl)thio)thiadiazole) and BPTD (2,5-bis(2-pyridylthio)thiadiazole). X-ray structures of $[\text{Cu}_2(\text{BPTD})(\mu_2\text{-Br})_2\text{Br}_2]$ and $[\text{Cu}(\text{BPMTD})\text{Cl}_2]_n$ and spectroscopic, electrochemical, and magnetic studies. *Inorg. Chem.* **1994**, *33*, 490-497.
2. Bhattacharyya, M.K.; Saha, U.; Dutta, D.; Frontera, A.; Verma, A.K.; Sharma, P.; Das, A. Unconventional DNA-relevant π -stacked hydrogen bonded arrays involving supramolecular guest benzoate dimers and cooperative anion- π/π - π/π -anion contacts in coordination compounds of Co(II) and Zn(II) phenanthroline: Experimental and theoretical studies. *New J. Chem.* **2020**, *44*, 4504-4518.
3. Kumar, S.; Sharma, R.P.; Venugopalan, P.; Aree, T.; Ferretti, V. Synthesis, spectroscopic characterization, single crystal X-ray analysis and DFT calculation of isomeric $\text{Cu}(\text{MR})_2(\beta/\gamma\text{-pic})_2$ complexes: First transition metal complexes of methyl red. *J. Mol. Struct.* **2018**, *1166*, 388-396.
4. Yenikaya, C.; Poyraz, M.; Sari, M.; Demirci, F.; Ilkimen, H.; Buyukgungor, O. Synthesis, characterization and biological evaluation of a novel Cu(II) complex with the mixed ligands 2,6-pyridinedicarboxylic acid and 2-aminopyridine. *Polyhedron* **2009**, *28*, 3526-3532.