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A new cadmium(II) coordination polymer constructed from 2-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline and 1,3-benzenedicarboxylate: Synthesis, crystal structure, thermal behavior and luminescent properties

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Abstract: A new Cd(II) coordination polymer, namely, $[\text{Cd}_2(\text{Cl})(1,3\text{-BDC})_{1.5}(\text{L})_2] \cdot 1.25\text{H}_2\text{O}$ (**1**) ($\text{L} = 2\text{-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline}$ and 1,3-benzenedicarboxylate (1,3-BDC) was synthesized under hydrothermal conditions. The crystal of **1** belongs to orthorhombic, space group $P\text{bcn}$ with $a = 31.3116(19)\text{ \AA}$, $b = 13.5485(8)\text{ \AA}$, $c = 22.9850(15)\text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $\text{C}_{50}\text{H}_{28.5}\text{Cd}_2\text{Cl}_3\text{F}_2\text{N}_8\text{O}_{7.25}$, $M_r = 1226.46$, $V = 9750.8(10)\text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.671\text{ g cm}^{-3}$, $S = 1.038$, $\mu(\text{MoK}\alpha) = 1.106\text{ mm}^{-1}$, $F(000) = 4860$, $R = 0.0585$ and $wR = 0.1485$. Compound **1** exhibits a 1D-ladder structure. Furthermore, neighboring 1D-ladders are joined together by $\pi \cdots \pi$ interactions to result in a 2D supramolecular layer. The thermal behavior of **1** was characterized. Furthermore, its luminescent properties were studied in the solid state at room temperature.

Keywords: crystal structure; 1,3-benzenedicarboxylate; luminescence; 2-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline.

INTRODUCTION

Coordination polymers comprised of metal ions and bridging ligands have received much attention because of their fascinating motifs and potential applications as functional materials, ranging from catalysis, gas absorption, molecular recognition, optics, *etc.*^{1–3} The organic ligands play an important role in the construction of coordination polymers.^{4–6} In this regard, carboxylic acids exhibit diverse coordination modes, especially multi-carboxylic acids, such as benzenedicarboxylates, when used in the preparation of various coordination polymers.^{7–9} On the other hand, the intriguing structures of coordination polymers may be varied or tailored by incorporating different auxiliary ligands, in which conju-

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gated polycarboxylates are bridging ligands.¹⁰ 1,10-Phenanthroline (phen) and its various derivatives have become promising chelating ligands because of their potential ability to form supramolecular aggregates through π - π stacking interactions.^{11,12} Herein, the hydrothermal synthesis, crystal structure, thermal behavior and luminescent properties of $[\text{Cd}_2(\text{Cl})(1,3\text{-BDC})_{1.5}(\text{L})_2] \cdot 1.25\text{H}_2\text{O}$ (**1**), in which $\text{L} = 2\text{-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-}f\text{][1,10]phenanthroline}$ and 1,3-BDC = 1,3-benzenedicarboxylate.

EXPERIMENTAL

All the materials were of analytical reagent grade and used as received without further purification. The C, H and N elemental analysis were realized on a Perkin-Elmer 240C elemental analyzer. The crystalline structures of the as-synthesized products were investigated by X-ray diffraction analysis using $\text{CuK}\alpha$ radiation (XRD, BRUKER, D8 ADVANCE, Germany). The thermal stability experiment was performed on a TG SDT2960 thermal analyzer from room temperature to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} . The photoluminescent properties were measured on a Renishaw inVia Raman microscope at room temperature.

*General procedure for the synthesis of $[\text{Cd}_2(\text{Cl})(1,3\text{-BDC})_{1.5}(\text{L})_2] \cdot 1.25\text{H}_2\text{O}$ (**1**)*

A mixture of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol, 0.192 g), L (1 mmol, 0.300 g) and 1,3- H_2BDC (1 mmol, 0.166 g) were dissolved in 10 mL distilled water, followed by the addition of triethylamine until the pH value of the system was adjusted to between 4.5 and 5.5. Then the mixture was transferred and sealed in a 25 mL teflon-lined stainless steel container. The container was heated to 438 K and the temperature was held for 6 d. After the mixture had been cooled to room temperature at a rate of 10 °C h^{-1} , crystals of **1** were obtained. Yield: 15 %. Anal. Calcd. for $\text{C}_{50}\text{H}_{28.5}\text{Cd}_2\text{Cl}_2\text{F}_2\text{N}_8\text{O}_{7.25}$: C, 48.96; H, 2.34; N, 9.14 %. Found: C, 48.52; H, 2.21; N, 8.93 %.

X-Ray crystallography

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker-AXS Smart CCD diffractometer equipped with a graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation by using an ω - ϕ scan method at 293(2) K. The structure was solved by direct methods using the SHELXS-97 program and refined with SHELXL-97 by full-matrix least-squares techniques on F^2 .^{13,14} Non-hydrogen atoms of the compound were refined with anisotropic temperature parameters. All H atoms were positioned geometrically ($\text{C-H} = 0.93$ Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$. The water H atoms were not included in the model. A summary of crystallographic data and structure analysis is given in Table I. Selected bond lengths and bond angles are listed in Table II.

TABLE I. Crystal data and structure refinement for **1**

Compound	$[\text{Cd}_2(\text{Cl})(1,3\text{-BDC})_{1.5}(\text{L})_2] \cdot 1.25\text{H}_2\text{O}$
Chemical formula	$\text{C}_{50}\text{H}_{28.5}\text{Cd}_2\text{Cl}_3\text{F}_2\text{N}_8\text{O}_{7.25}$
Formula weight	1226.46
Wavelength, Å	0.71073
Temperature, K	293(2)
Crystal system	Orthorhombic
Space group	P bcn

TABLE I. Continued

$a / \text{\AA}$	31.3116(19)
$b / \text{\AA}$	13.5485(8)
$c / \text{\AA}$	22.9850(15)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	9750.8(10)
Z	8
$D_{\text{calc}} / \text{g cm}^{-3}$	1.671
μ / mm^{-1}	1.106
$F(000)$	4860
$(\theta_{\text{min}} - \theta_{\text{max}}) / ^\circ$	1.30–25.05
Diffraction measured fraction, θ_{max}	25.05
Refined difference density, max/min	1.845/–0.514
Reflection collected/unique (R_{int})	48689/8624 (0.0762)
Data/restraints/parameters	8624/6/668
Goodness-of-fit on F^2	1.038
R indices (all data)	$R_1 = 0.1000$, $wR_2 = 0.1694$
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0585$, $wR_2 = 0.1485$

TABLE II. Selected bond lengths and angles for **1**; symmetry transformations used to generate equivalent atoms: $^i x, y+1, z$

Bond lengths, $\text{\AA}$			
Cd(2)–N(1)	2.319(6)	Cd(2)–N(2)	2.323(6)
Cd(1)–N(5)	2.326(6)	Cd(1)–N(6)	2.403(5)
Cd(1)–O(1)	2.340(5)	Cd(1)–O(2)	2.409(5)
Cd(1)–O(3)	2.253(5)	Cd(2)–O(4)	2.220(5)
Cd(1)–Cl(3)	2.546(2)	Cd(2)–Cl(3)	2.585(2)
Cd(2)–O(6) ⁱ	2.221(5)	Cd(2)–O(5) ⁱ	2.573(5)
Bond angles, $^\circ$			
O(3)–Cd(1)–N(5)	84.5(2)	O(3)–Cd(1)–O(1)	83.0(2)
N(5)–Cd(1)–O(1)	120.0(2)	O(3)–Cd(1)–N(6)	139.58(19)
N(5)–Cd(1)–N(6)	70.4(2)	O(5) ⁱ –Cd(2)–Cl(3)	153.00(12)
O(3)–Cd(1)–O(2)	129.27(19)	O(6) ⁱ –Cd(2)–Cl(3)	99.49(13)
O(1)–Cd(1)–O(2)	54.59(17)	O(6) ⁱ –Cd(2)–O(5) ⁱ	53.88(17)
O(3)–Cd(1)–Cl(3)	92.17(16)	N(5)–Cd(1)–Cl(3)	142.52(16)
O(1)–Cd(1)–Cl(3)	96.48(16)	N(6)–Cd(1)–Cl(3)	89.54(15)
O(2)–Cd(1)–Cl(3)	116.56(13)	O(3)–Cd(1)–C(39)	106.8(2)
O(4)–Cd(2)–N(2)	155.8(2)	N(5)–Cd(1)–C(39)	108.8(2)
O(6) ⁱ –Cd(2)–N(2)	105.2(2)	O(1)–Cd(1)–C(39)	27.18(19)
N(1)–Cd(2)–N(2)	71.57(19)	N(6)–Cd(1)–C(39)	111.0(2)
O(4)–Cd(2)–O(5) ⁱ	96.6(2)	O(2)–Cd(1)–C(39)	27.41(18)
N(5)–Cd(1)–O(2)	93.4(2)	Cl(3)–Cd(1)–C(39)	107.89(17)
N(1)–Cd(2)–O(5) ⁱ	86.31(17)	O(4)–Cd(2)–O(6) ⁱ	99.0(2)
N(2)–Cd(2)–O(5) ⁱ	97.1(2)	O(4)–Cd(2)–Cl(3)	91.66(16)
N(6)–Cd(1)–O(2)	84.62(17)	N(1)–Cd(2)–Cl(3)	119.51(14)
O(1)–Cd(1)–N(6)	136.90(19)	N(2)–Cd(2)–Cl(3)	85.03(17)

Deposition for complex 1. CCDC-933986 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Crystal structure of **1**

The X-ray crystallographic analysis revealed that the asymmetric unit of **1** contains two Cd(II) atoms, two L ligands, one Cl anion, one and a half 1,3-BDC anions, and one and one fourth water molecules (Fig. 1).

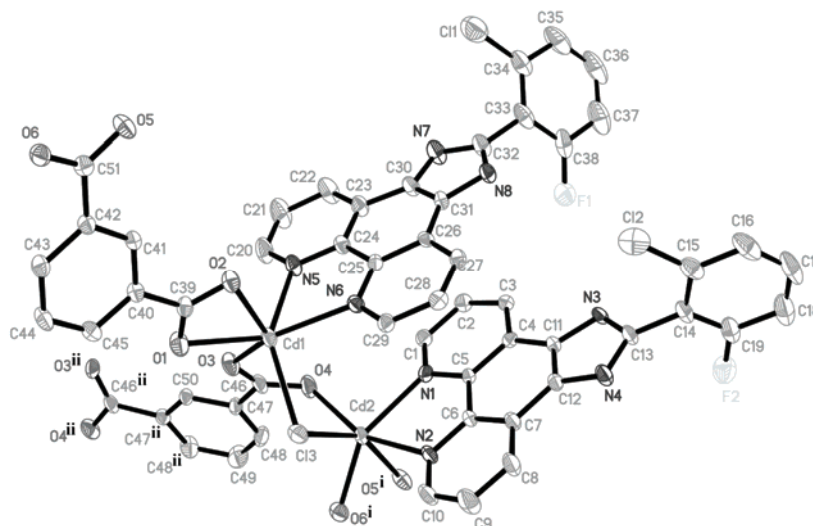
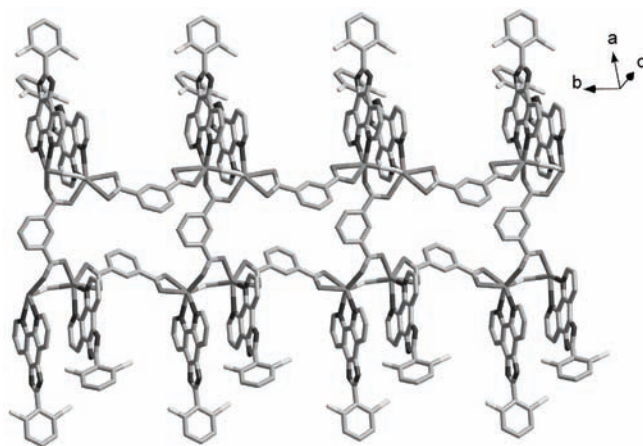
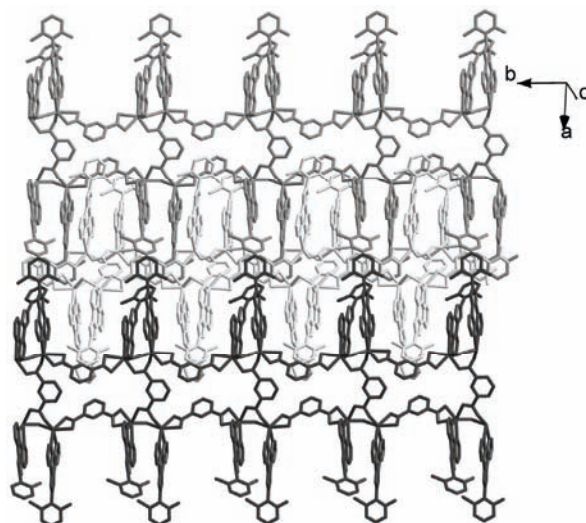


Fig. 1. View of the coordination environments of the Cd(II) atoms in complex **1**. All the hydrogen atoms have been omitted for clarity.

The two Cd(II) atoms show the same coordination geometries and coordination environments. Each Cd(II) atom is six-coordinated by three carboxylate oxygen atoms from two different 1,3-BDC anions, two nitrogen atoms from one L ligand, and one Cl anion in an octahedral sphere. The Cd–O and Cd–N distances of **1** (Table II) are very similar to those reported for another related complex $[\text{Cd}_2(\text{NDC})_2(\text{L}')_2(\text{H}_2\text{O})] \cdot 0.5\text{DMF}$ (NDC = 1,4-naphthalenedicarboxylate, $\text{L}' = \text{pyrazino}[2,3-f][1,10]\text{phenanthroline}$ and DMF = *N,N*-dimethylformamide).¹⁰ It is noteworthy that one Cl anion bridges two Cd(II) atoms to furnish a $[\text{Cd}_2\text{Cl}]$ dimer with a Cd···Cd distance of 3.737 Å. Further, neighboring dimers are linked by 1,3-BDC anions in tridentate and tetradentate modes to give rise to a 1D ladder structure (Fig. 2). The L ligands are alternately attached on both sides of the ladders (Fig. 2). Interestingly, π – π stacking interactions among neighboring L ligands in adjacent ladders exist. These π – π stacking interactions extend the ladders into a 2D supramolecular layer (Fig. 3).

Fig. 2. View of the 1D ladder structure of **1**.Fig. 3. View of the 2D supramolecular layer constructed by π - π interactions in **1**.

It should be stressed that some related complexes with phen derivatives have been reported.^{15–20} However, the structure of complex **1** is different from the reported ones. For example, in the related known complex $[\text{Cd}_2(\text{L})_2(1,3,5\text{-BTC})(\text{Cl})]\cdot\text{H}_2\text{O}$ ($1,3,5\text{-BTC} = 1,3,5\text{-benzenetricarboxylate anion}$),¹⁵ each $1,3,5\text{-BTC}$ anion connects five $\text{Cd}(\text{II})$ atoms to form a double chain. These chains are further extended into 2D supramolecular networks through π - π interactions.

Powder X-ray diffraction and thermal behavior

The powder X-ray diffraction (PXRD) pattern for compound **1** was recorded at room temperature to confirm its phase purity (Fig. 4). The experimental PXRD

pattern corresponds well to the simulated one from the respective single-crystal data, indicating that the synthesized bulk materials and the measured single crystals are the same.

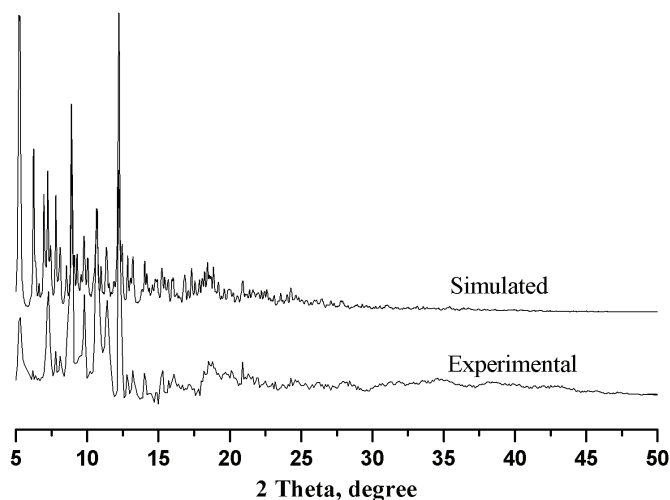
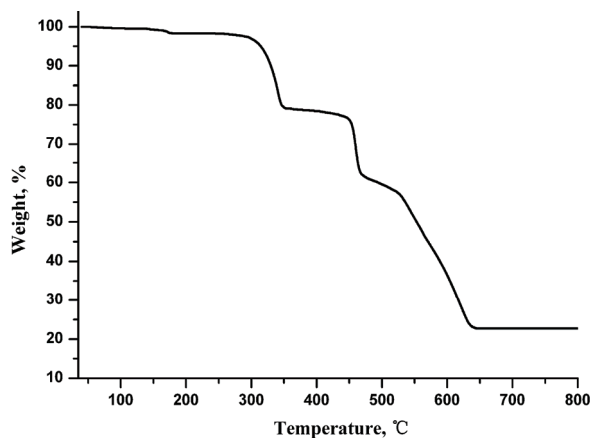
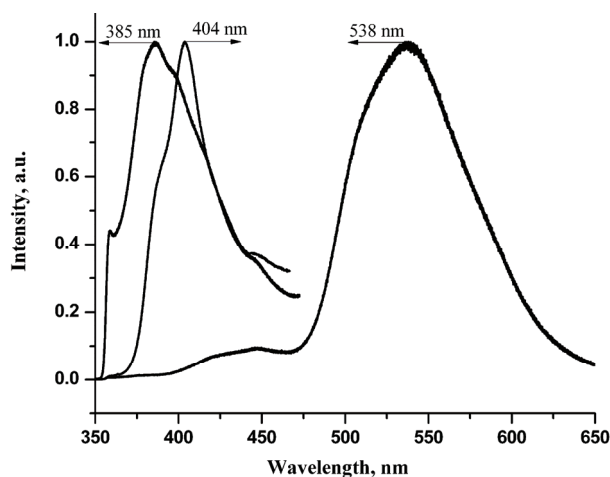


Fig. 4. Simulated and experimental powder X-ray diffraction patterns.

Thermogravimetric analysis of **1** was performed. The experiment was realized under a N_2 atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in the temperature range 40 to $800\text{ }^{\circ}\text{C}$. As illustrated in Fig. 5, the first mass loss of 1.7 % between 54 and $178\text{ }^{\circ}\text{C}$ corresponds to the loss of free water molecules (Calcd. 1.8 %). The second weight loss could be assigned to the decomposition of the 1,3-BDC ligand in the temperature range $245\text{--}353\text{ }^{\circ}\text{C}$ (observed 19.2, Calcd. 20.1 %). The final weight loss from 371 to $644\text{ }^{\circ}\text{C}$ may be attributed to the decomposition of L ligand (obsd 56.1 %, calcd. 56.9 %).

Luminescent properties

Coordination polymers with d^{10} metals have received intensive attention because of their various applications in photochemistry, chemical sensors, and electroluminescent (EL) displays.¹² In this work, the luminescent properties of the free organic ligands and compound **1** were investigated in the solid state at room temperature (Fig. 6). The free L and 1,3- H_2 BDC showed emission bands centered at 404 nm ($\lambda_{\text{ex}} = 325\text{ nm}$) and 385 nm ($\lambda_{\text{ex}} = 325\text{ nm}$), respectively. As previously reported, these emissions can be attributed to the $\pi^*\text{--n}$ or $\pi^*\text{--}\pi$ transitions. Compound **1** showed an emission at about 538 nm ($\lambda_{\text{ex}} = 325\text{ nm}$). In comparison with the emission of 1,3- H_2 BDC, a red shift was observed for compound **1**. The emission of **1** may be attributed to the synergetic contribution of a charge-transfer transition and the intraligand transition.¹²

Fig. 5. TG curve of **1**.Fig. 6. Emission spectra of 1,3-H₂BDC, **L** and **1** (observed down the direction of increasing wavelength) in the solid state at room temperature.

CONCLUSION

A new Cd(II) coordination polymer was prepared from the phen derivative **L** and 1,3-benzenecarboxylate under hydrothermal condition. In compound **1**, the 1,3-BDC anions bridge the [Cd₂Cl] dimers to form a 1D-ladder structure. Furthermore, neighboring 1D-chains are joined together by $\pi \cdots \pi$ interactions to give a 2D supramolecular layer. In addition, compound **1** showed good luminescent properties in solid state at room temperature.

SUPPORTING INFORMATION

Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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ИЗВОД

НОВИ КООРДИНАЦИОНИ ПОЛИМЕР КАДМИЈУМА(II) КОЈИ САДРЖИ
2-(2-ХЛОРО-6-ФЛУОРОФЕНИЛ)-1H-ИМИДАЗО[4,5-f][1,10]ФЕНАНТРОЛИН И
1,3-БЕНЗЕНДИКАРБОКСИЛАТ: СИНТЕЗА, КРИСТАЛНА СТРУКТУРА, ТЕРМИЧКО
ПОНАШАЊЕ И ЛУМИНИСЦЕНТНА СВОЈСТВА

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У овом раду је синтетизован нови координациони полимер кадмијума(II), $[\text{Cd}_2(\text{Cl})(1,3\text{-BDC})_{1,5}(\text{L})_2] \cdot 1,25\text{H}_2\text{O}$ (**1**) (L = 2-(2-хлоро-6-флуорофенил)-1H-имидазо[4,5-f][1,10]фенантролин и 1,3-BDC = 1,3-бензендикарбоксилат). Полимер **1** кристалише у просторној групи *P* бсп орторомбичног кристалног система, при чему су параметри јединичне ћелије: $a = 31,3116(19) \text{ \AA}$, $b = 13,5485(8) \text{ \AA}$, $c = 22,9850(15) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $\text{C}_{50}\text{H}_{28,5}\text{Cd}_2\text{Cl}_3\text{F}_2\text{N}_8\text{O}_{7,25}$, $M_r = 1226,46$, $V = 9750,8(10) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1,671 \text{ g cm}^{-3}$, $S = 1,038$, $\mu(\text{MoK}_\alpha) = 1,106 \text{ mm}^{-1}$, $F(000) = 4860$, $R = 0,0585$ и $wR = 0,1485$. Полимер **1** има 1D структуру налик на лестве, при чему су суседни 1D мотиви повезани $\pi \cdots \pi$ интеракцијама у 2D супрамолекулске слојеве. Испитано је термичко понашање полимера **1**, као и његове луминисцентне особине у чврстом стању и на собној температури.

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