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# Synthesis, structure, and properties of Cd(II) complexes generated from 2-phenylquinoline derivatives

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## HIGHLIGHTS

- Two dinuclear Cd(II) complexes are assembled from quinoline-based carboxylic acids.
- They show hydrogen-bonding driven 3D framework with **dia** topology.
- Luminescent and antibacterial properties of all compounds were investigated.
- Complexes show higher activities due to the increased lipotropism on complexation.

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## ABSTRACT

Carboxyl functionalized 2-phenylquinoline derivatives, 2-(4-fluorophenyl)quinoline-4-carboxylic acid (**HL$_1$**) and 2-(4-methoxyphenyl)quinoline-4-carboxylic acid (**HL$_2$**) were synthesized. Further reaction of these ligands with $Cd(CH_3COO)_2$ afforded new cadmium complexes, $[Cd_2(\mathbf{L_1})_4(CH_3OH)_4]\cdot 1.5H_2O$ (**1**) and $[Cd_2(\mathbf{L_2})_4(CH_3OH)_4]$ (**2**), respectively. These complexes were characterized by elemental analysis, infrared spectra, and single-crystal X-ray diffraction. The fluorescent behavior and antibacterial (*Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus aureus*) activities of these compounds have been studied.



## Introduction

The past decades witness numerous progress of metal complexes in the field of advanced material, owing to their potential application in catalysis, magnetic properties, gas adsorption and separation, chemosensor, and fluorescence imaging, etc. [1–5]. Since the successful use of cisplatin and related platinum complexes as anticancer agents, a renewed interest in complex-based therapy has been raised [6–8]. This can be ascribed to the fact that, on coordination, not only might bioactive ligands improve their bioactivity profiles, but also inactive ligands may acquire pharmacological properties [8,9]. In addition, the coordination effect can realize the slow-release of metal ions which can reduce the toxic side effects. In these regards, exploration of metal complex is an attractive approach to obtain drug candidates [10].

Quinoline derivatives are an important class of pharmaceutical compound showing broad spectrum of bioactivities, including antimicrobial [11], antimalarial [12] and anticancer [13]. To throw further light on the bioactive metal complex systems, we investigated the reaction of carboxyl modified quinoline derivatives with metal salts. The carboxylate ligands are of special interest because of their various of coordination modes, such as monodentate, bridging, chelating bidentate and bridging tridentate [14]. Moreover, they are endowed with hydrogen-bonding capabilities [15]. In this paper, 2-(4-fluorophenyl)quinoline-4-carboxylic acid (**HL$_1$**) and 2-(4-methoxyphenyl)quinoline-4-carboxylic acid (**HL$_2$**) are synthesized in high yields and fully characterized. Two Cd(II) complexes $[Cd_2(\mathbf{L_1})_4(CH_3OH)_4]\cdot 1.5H_2O$ (**1**) and $[(Cd_2(\mathbf{L_2})_4(CH_3OH)_4]$ (**2**) (Scheme 1) constructed by these two ligands and $Cd(CH_3COO)_2$, including their synthesis, crystal structures, fluorescence and antibacterial properties are described here.

## Experimental

### *Materials and instruments*

All the reactions were carried out under air atmosphere. All chemicals and solvents used in the synthesis were reagent grade without further purification.

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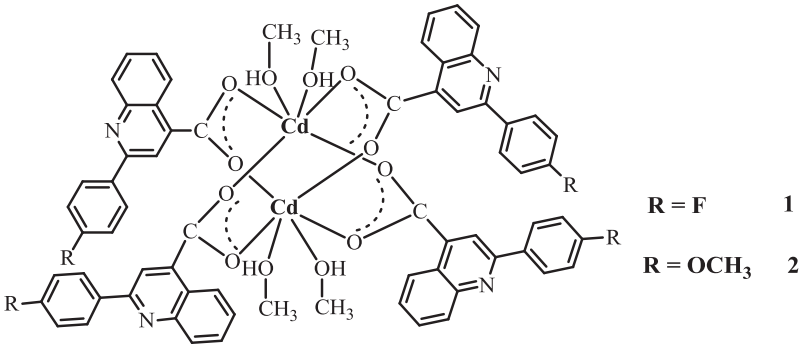


**Scheme 1.** Structure of complexes **1** and **2**.

The IR spectra were taken on a Vector22 Bruker spectrophotometer (400–4000 $cm^{-1}$) with KBr pellets. NMR spectra were measured on a Bruker AM 500 spectrometer. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyzer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

*Synthesis of 2-(4-fluorophenyl)quinoline-4-carboxylic acid (**$HL_1$**)*

A mixture of isatin (1.18 g, 8.00 mmol), 4-fluoroacetophenone (0.28 g, 2.00 mmol) and potassium hydroxide (2.24 g, 40.00 mmol) in 2 mL of ethanol and 18 mL of water was refluxed for 12 h. Then the orange solution was cooled to room temperature and then poured into 20 mL of water. The solution was adjusted to pH 5 with 1 M HCl. The resulting brown precipitate was filtered, washed with water and dried in vacuo to give the product. Yield: 0.31 g, 58%. IR (KBr, $cm^{-1}$): 3442, 3081, 2935, 2839, 1714, 1646, 1548, 1413, 1368, 1243, 1226, 1029, 860, 837, 806, 766, 696, 544, 516. $^1$H NMR (500 MHz, DMSO, δ): 8.63 (t, 1H), 8.42 (s, 1H), 8.35 (t, 1H), 8.26 (d, $J$ = 8.5 Hz, 1H), 8.13(q, 1H), 7.84 (q, 1H), 7.67 (m, 1H), 7.39 (t, 1H), 7.11 (d, $J$ = 8.5 Hz, 1H). Anal. Calcd for $C_{16}H_{10}FNO_2$: C, 71.91; H, 3.77; N, 5.24. Found: C, 72.05; H, 3.75; N, 5.26%.

*Synthesis of 2-(4-methoxyphenyl)quinoline-4-carboxylic acid (**$HL_2$**)*

Orange product **$HL_2$** was obtained with similar procedure for synthesizing **$HL_1$** by using 4-methoxyacetophenone instead of 4-fluoroacetophenone. Yield: 0.37 g, 66%. IR (KBr, $cm^{-1}$): 3440, 3077, 2936, 2840, 1713, 1651, 1602, 1521, 1425, 1374, 1247, 1189, 1077, 860, 836, 812, 761, 689, 540, 519. $^1$H NMR (500 MHz, DMSO, δ): 8.62 (d, $J$ = 8.5 Hz, 1H), 8.41 (s, 1H), 8.26 (d, $J$ = 8.5 Hz, 2H), 8.11(d, $J$ = 8.5 Hz, 1H), 7.82 (t, 1H), 7.66 (t, 1H), 7.11 (d, $J$ = 8.5 Hz, 2H), 3.86 (s, 3H). Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.01. Found: C, 73.41; H, 4.67; N, 5.03%

*Synthesis of $[Cd_2(L_1)_4(CH_3OH)_4]\cdot 1.5H_2O$ (1)*

A $CH_3OH$ solution (5 mL) of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.04 mmol, 10.7 mg) was added to a $CH_3OH$ solution (10 mL) of **$HL_1$** (0.04 mmol, 10.7 mg) with stirring. The mixture was stirred for 20 min at room temperature. The resulting solution was allowed to stand in air for three days. Colorless block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. Yield: 9.6 mg (67% on the basis of **$HL_1$**). IR (KBr, $cm^{-1}$): 3064, 2838, 1601, 1513, 1416, 1392, 1332, 1253, 1233, 1174, 1156, 905, 840, 812, 762, 665, 624, 552, 465. Anal. Calcd. for $C_{68}H_{55}N_4F_4O_{13.5}Cd_2$: C, 56.52; H, 3.83; N, 3.87. Found: C, 56.71; H, 3.81; N, 3.89%.

*Synthesis of $[Cd_2(L_2)_4(CH_3OH)_4]$ (2)*

Complex **2** was obtained with similar procedure for synthesizing **1** by using **$HL_2$** instead of **$HL_1$**. Yield: 10.7 mg (73% on the basis of **$HL_2$**). IR (KBr, $cm^{-1}$): 3060, 2937, 2836, 1603, 1516, 1419, 1394, 1333, 1253, 1212, 1173, 1114, 1033, 837, 813, 762, 683, 625, 547, 420. Anal. Calcd. for $C_{72}H_{64}N_4O_{16}Cd_2$: C, 58.98; H, 4.40; N, 3.82. Found: C, 59.21; H, 4.38; N, 3.83%.

*X-ray data collection and structure refinement*

Single crystals of all the complexes for X-ray diffraction analyses with suitable dimensions were mounted on the glass rod. The data were collected on a Bruker Smart Apex CCD diffractrometer equipped with graphite-monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation using a $\omega$–2$\theta$ scan mode at 273 K. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. The structure was solved by direct methods and refined by full-matrix least-squares methods on $F^2$ using SHELXTL-97. All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles, refined anisotropically. All the hydrogen atoms bonded to C atoms were generated geometrically and refined isotropically using the riding model. While hydroxyl H atoms of methanol molecules were first found in the Fourier map and then fixed at their ideal positions with O-H = 0.96 (2) Å and Uiso(H) = 1.5Ueq(O). Water H atoms were refined with distance restraints of O-H = 0.85 (2) Å, H···H = 1.44 (2) Å and Uiso(H) = 1.5Ueq(O).

*Bioassay conditions*

The antibacterial activity of the synthesized compounds was tested against *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* using MH medium (Mueller–Hinton medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL). The $IC_{50}$ (half minimum inhibitory concentrations) of the test compounds were determined by a colorimetric method using the dye MTT (3-(4,5-dimethylth-iazol-2-yl)-2,5-diphenyl tetrazoliumbromide). A stock solution of the synthesized compound (100 μg/mL) in DMSO was prepared and graded quantities of the test compounds were incorporated in specified quantity of sterilized liquid MH medium. A specified quantity of the medium containing the compound was poured into microtitration plates. Suspension of the microorganism was prepared to contain approximately 105 cfu/mL and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37 °C for 24 h. After the MICs were visually determined on each of the microtitration plates, 50 μL of PBS (phosphate

buffered saline 0.01 mol/L, pH 7.4, $Na_2HPO_4{\cdot}12H_2O$ 2.9 g, $KH_2PO_4$ 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg of MTT/mL was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed, and 100 μL of isopropanol containing 5% 1 mol/L HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 550 nm.

## Results and discussion

### *Synthesis and general characterization*

The carboxylic functionalized quinoline ligands **$HL_1$** and **$HL_2$** were prepared via the Pfitzinger reaction [16]. They can dissolve in strong polar solvents such as methanol and dimethyl sulfoxide (DMSO). Characterization of the ligands has been accomplished by IR, $^1$H NMR, and elemental analysis. In IR spectra, the typical stretching band $\nu$(C = O) of carboxylic group for **$HL_1$** and **$HL_2$** occurs at 1714 $cm^{-1}$ and 1713 $cm^{-1}$, respectively. While the broad stretching band $\nu$(O-H) of carboxylic group appears around 3442 $cm^{-1}$. The separation value $\Delta\nu$ ($\nu_{as}(COO^-)$–$\nu_s(COO^-)$ of the carboxylic based complex can be used to discriminate the coordination mode of the carboxyl group. $\Delta\nu < 200\ cm^{-1}$ indicates the bidentate mode, whereas $\Delta\nu > 200\ cm^{-1}$ indicates the monodentate mode. For the cadmium complexes **1** and **2**, the asymmetric stretching mode of carboxylate $\nu_{as}(COO^-)$ is located around 1601 $cm^{-1}$, while the symmetric stretching mode $\nu_s(COO^-)$ is around 1419 and 1416 $cm^{-1}$, respectively. Therefore, the $\Delta\nu$ values are 182 $cm^{-1}$ for **1** and 185 $cm^{-1}$ for **2**, which is in good agreement with their bridging bidentate coordination mode features shown by the results of crystal structures [17].

### *Crystal structures of complexes **1** and **2***

The solid structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction. Details of the crystal parameters, data collection, and refinement are summarized in Table 1; selected bond lengths and angles are listed in Table S1. Both of the two complexes are crystallized in tetragonal space group $I4_1/a$. The ORTEP drawing for them is shown in Fig. 1, the two complexes possess very similar paddlewheel dimeric structure formed by the bidentate coordination mode of the carboxyl groups.

**Table 1**
Crystallographic data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{68}H_{55}F_4N_4O_{13.5}Cd_2$ | $C_{72}H_{64}N_4O_{16}Cd_2$ |
| $M_r$ | 1444.96 | 1466.07 |
| Crystal system | Tetragonal | Tetragonal |
| Space group | $I4(1)/a$ | $I4(1)/a$ |
| $a$ (Å) | 22.4253(4) | 22.5144(3) |
| $b$ (Å) | 22.4253(4) | 22.5144(3) |
| $c$ (Å) | 12.0499(4) | 12.3995(5) |
| $V$ (Å$^3$) | 6059.8(3) | 6285.3(3) |
| $Z$ | 4 | 4 |
| Total reflections | 32,166 | 29,621 |
| Independent reflections | 3361 | 2786 |
| Observed reflections ($I > 2\sigma(I)$) | 2644 | 2231 |
| $\rho_c$ (g $cm^{-3}$) | 1.584 | 1.549 |
| $F$ (000) | 2924 | 2992 |
| $T$ (K) | 293(2) | 293(2) |
| $\mu$ (Mo Kα) ($mm^{-1}$) | 0.785 | 0.753 |
| GOF ($F^2$) | 1.044 | 1.040 |
| $R_1$[a], $wR_2$[b] (all data) | 0.0458, 0.0748 | 0.0410, 0.0626 |

[a] $R_1 = \Sigma||C| - |F_c||/\Sigma F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

Most of the paddle wheel carboxylate complexes found in CCDC have a coordination number 5, while for complexes **1** and **2**, two methanol molecules are coordinated to one $Cd^{II}$ center to achieve the coordination number 6. As shown in Fig. 1, the complexes are pseudo-octahedral, with the equatorial plane defined by methanol O atoms (O3 and O3A) and carboxylate O atoms (O2 and O2A), while the two axial positions come from the carboxylic O atoms (O1 and O1A). Of all the Cd-O bond lengths, the axial Cd1-O1distance is the shortest, 2.2118 (7) Å for **1**, and 2.2166 (7) Å for **2**. The tetracarboxylate bridging framework can accommodate metal–metal separation of up to 3.452 Å [18,19]. In complex **1**, the Cd···Cd separation of 3.4399(5) Å is shorter than this maximum, indicating of a degree of metal–metal interaction. While the corresponding Cd···Cd distance observed in complex **2** is longer being 3.4657(5) Å. The carboxylic ligands in complexes are twisted, as the phenyl ring (C(1)-C(6)) rotate by about 31.67(1)° for **1**, 30.40(1)° for **2**, respectively, with respect to the quinoline heterocycle. The coordination plane (Cd1, O1, C16, O2, Cd1A) and the plane of quinoline heterocycle are also non-coplanar, the dihedral angle between them amounts to 66.76(1)° for **1**, 66.10(1)° for **2**, respectively.

For both of the two compounds, the uncoordinated N1 atom of the quinoline ring serves as an acceptor to form intermolecular hydrogen bond O3-H3A···N1 with the coordinated methanol molecule. For **1**, H3A to N1 distance 1.859(2) Å, O3-H3A···N1 angle 165.53(5)°, symmetry code: $-y + 3/4$, $x + 1/4$, $z + 1/4$; for **2**, H3A to N1 distance 1.859(3) Å, O3-H3A···N1 angle 172.68(5)°, symmetry code: $-y + 7/4$, $x + 1/4$, $z + 1/4$. Therefore, each binuclear unit can be regarded as self-complementary module, with four H-bond donors (OH) and four acceptors (heteroaryl-N atoms). Aggregation of such modules generates the non-covalent 3D framework, with four-connected net nodes and **dia** topology (Fig. 2).

Besides the hydrogen bonding interactions, the structures of **1** and **2** are also stabilized by π···π interactions. In the solid state, the adjacent quinoline rings from different dinuclear units are approximately parallel to each other, the dihedral angle is 1.85(1)° for **1**, 1.92(1)° for **2**. The related parameters about the π···π interactions are summarized in Table 2 (Fig. 3) following the criteria of Janiak [20]. The distances between two quinoline planes range from 3.512 to 3.525 Å, indicating strong slipped π···π stacking interactions. The $C_{1,3}$ (centroid–centroid distances between pyridine and arene) values are less than 3.8 Å in complexes **1** and **2**. The values of $C_{1,4}$ (centroid–centroid distances between arene and arene) and $C_{2,3}$ (centroid–centroid distances between pyridine and pyridine) are all in the normal range found in the reported transition-metal quinoline fragments [20]. It is noteworthy to point out that the displacement angles of $\alpha$ in complex **1** and **2** (9.35° and 9.41°, respectively) are quite smaller than the usual values observed in literature (around 20°).

### *Photoluminescent properties of **$HL_1$**, **$HL_2$**, **1** and **2***

The photoluminescent properties of ligands **$HL_1$**, **$HL_2$**, and their corresponding Cd(II) complexes **1** and **2** in dimethylsulfoxide/methanol (1:1) solution were investigated. The emission spectra is shown in Fig. 3.

Upon excitation at 373 nm at room temperature, the carboxylic ligands exhibit broad structureless band at about 466 nm, resulting from the ligand-centered (LC) $\pi^*$–$\pi$ relaxations (Fig. 4). Referenced to that of **$HL_2$** having electron-donating group (–$OCH_3$), the relative luminescence intensity of electron-withdrawing group (–F) substituted ligand **$HL_1$** is about 0.61. For complex **1** and **2**, a blue shift in the emission maxima about 24 nm compared with the free ligands are observed. This is probably caused by the reduced $\pi$–$\pi$ conjugated effect upon coordination to the Cd(II). In the meantime, relative to the corresponding free ligands, the fluorescence intensity

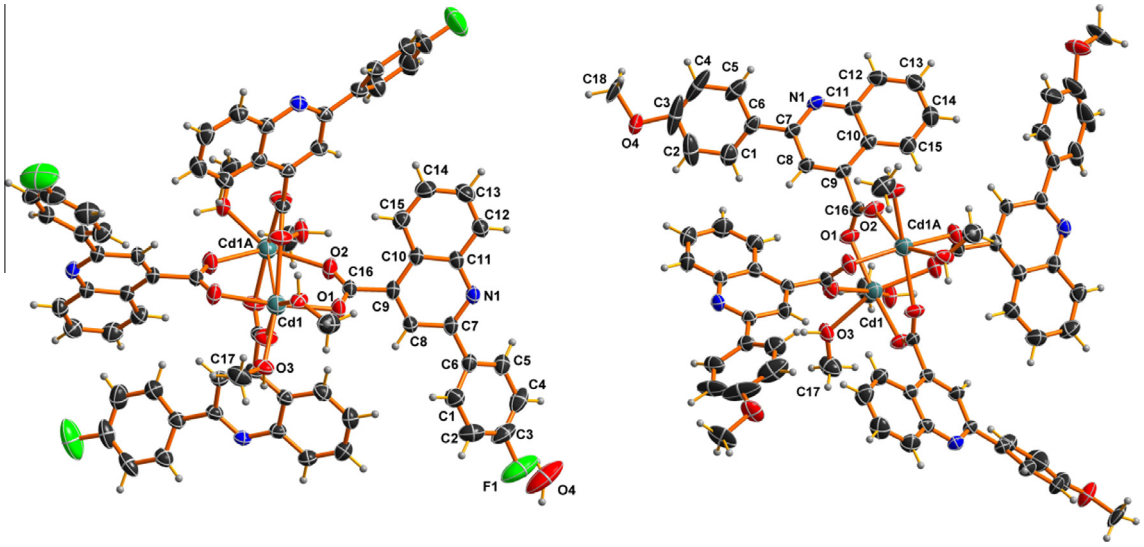


**Fig. 1.** Molecular structure of **1** (right) and **2** (left) at 50% probability displacement.

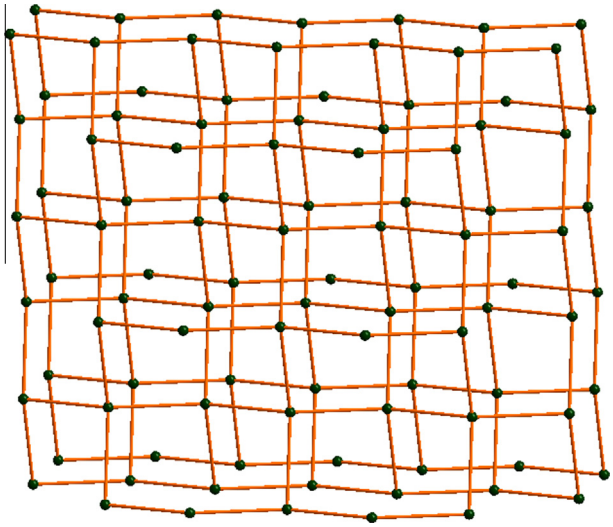

**Fig. 2.** The schematic representations of the uninodal 4-connected net of **1** and **2** with **dia** topology.

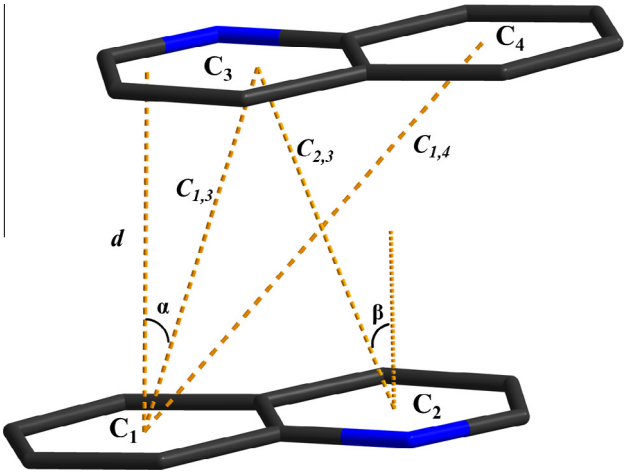


**Fig. 3.** Scheme for the parameters of π···π interactions. *d*, the distance between the two π planes; $C_{i,j}$, centroid–centroid distance of $C_i$ and $C_j$; *α*, *β*, the angle between the ring normal of quinoline plane and the centroid–centroid vector $C_{1,3}$, $C_{2,3}$.

**Table 2**
Parameters for the π···π interactions in 1 and 2.

| | *d* (Å) | $C_{1,3}$ (Å) | $C_{1,4}$ (Å) | $C_{2,3}$ (Å) | α (°) | β (°) |
|---|---|---|---|---|---|---|
| **1** | 3.525 | 3.678 | 4.959 | 3.739 | 9.35 | 28.38 |
| **2** | 3.512 | 3.660 | 4.935 | 3.660 | 9.41 | 28.41 |

of complexes are a little weaker because of the non-coplanar arrangement upon complexation.

### *Antibacterial Activities of **HL₁**, **HL₂**, **1** and **2***

Unlike Cu, Co, Ni or Zn which are essential for microorganisms as trace nutrients, Cd is a toxic heavy metal. While the research on the toxicology of $Cd^{2+}$ has shown that little cell-killing occurred at concentrations 50–150 μM for polymorphonuclear cells [21,22]. In addition, researches show that the cadmium complexes are less toxic than free $Cd^{2+}$. So several cadmium complexes have been reported for their antibacterial activity with good results, such as Schiff base cadmium complexes $[\{CdCl(HATtsc)\}_2(\mu\text{-}Cl)_2]\cdot 2H_2O$ (HATtsc = 2-acetyl-2-thiazoline thiosemicarbazone) [22], $[CdBr_2(3\text{-}TTSCH)_2]$ (3TTSCH = 3-thiophenaldehyde thiosemicarbazone) [23], and cadmium complexes with the quinolone antibacterial agent N-propyl-norfloxacin [24]. In the present study, the antibacterial activities of compounds **HL₁**, **HL₂**, **1**, **2** and salt $Cd(CH_3COO)_2$ are presented in Table 3. The antibacterial activity was performed against two Gram-negative bacterial strains: *E. coli* ATCC 35218 and *P. aeruginosa* ATCC 27853, two Gram-positive bacterial strains: *B. subtilis* ATCC 6633 and *S. aureus* ATCC 6538. Known antibiotic like streptomycin was used as positive control.

As shown in Table 3, against the all tested bacteria, free ligands **HL₁** or **HL₂** were inactive. The salt $Cd(CH_3COO)_2$ showed moderate activities against Gram-positive bacterial strains. While the complexes **1** and **2** exhibited an enhancement of antibacterial level against *B. subtilis* (HMIC = 3.80 and 12.23 μg/mL, respectively) and *S. aureus* (HMIC = 5.58 and 21.07 μg/mL, respectively). It should be noticed that complex **1** having electron-withdrawing substituent (F) exhibited higher activities than complex **2** having electron-donating substituent (OCH3). And the antibacterial level of complex **1** against *B. subtilis* and *S. aureus* was close to the

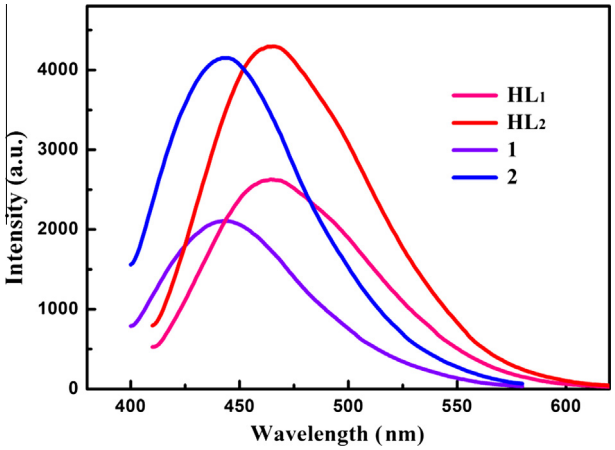


**Fig. 4.** Photoluminescence spectra of $\mathbf{HL_1}$, $\mathbf{HL_2}$, **1** and **2** in DMSO/$CH_3OH$ solution (1:1, v/v) at room temperature ($\lambda_{ex}$ = 372 nm).

**Table 3**
Antimicrobial activity of the tested compounds.

| Compounds | Half maximal inhibitory concentrations (μg/mL) | | | |
|---|---|---|---|---|
| | Gram-positive | | Gram-negative | |
| | *B. subtilis* | *S. aureus* | *E. coli* | *P. aeruginosa* |
| **1** | 3.80 | 5.58 | >50 | >50 |
| **2** | 12.23 | 21.07 | >50 | >50 |
| $\mathbf{HL_1}$ | >50 | >50 | >50 | >50 |
| $\mathbf{HL_2}$ | >50 | >50 | >50 | >50 |
| $Cd(OAC)_2$ | 37.58 | 36.43 | >50 | >50 |
| Streptomycin | 3.42 | 4.62 | 3.81 | >50 |

positive control streptomycin. Compared with the cadmium complexes reported previously [22,24], complex **1** showed similar activity against *B. subtilis* and higher activity against *S. aureus*.

As mentioned above, the ligands themselves do not inhibit the growth of the investigated bacterial strains, while the processes of complexation reduce the polarity and increase the lipophilic nature of the $Cd^{2+}$, which in turn favors its permeation through the lipid layer of the cell membrane of microorganism [23–28]. We propose that this might be the reason for the improvement of the antibacterial activity of these cadmium complexes.

## Conclusions

In this paper we reported the synthesis, characterization and photophysical studies of two new Cd(II) complexes based on carboxyl functionalized quinoline ligands. The X-ray crystallographic analysis reveals that the complexes exist as centrosymmetric bicyclic dimers constructed by the *syn-syn* bidentate bridging mode of the carboxylate groups. The free ligands and the complexes are luminescent with maximum emission wavelength at 466 nm and 442 nm, respectively. The bioassay results demonstrated that although the free ligands are inactive against the tested bacteria, the two complexes have good activity against *B. subtilis* and *S. aureus*. Further biological experiments in order to clarify the possible mechanism are under investigation.

## Acknowledgment

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.03.052.

## References

[1] C. Wang, J.L. Wang, W.B. Lin, J. Am. Chem. Soc. 134 (2012) 19895–19908.
[2] K. Qian, X.C. Huang, C. Zhou, X.Z. You, X.Y. Wang, K.R.A. Dunbar, J. Am. Chem. Soc. 135 (2013) 13302–13305.
[3] D.J. Tranchemontagne, J.L. Mendoza-Cortés, M. O'Keeffe, O.M. Yaghi, Chem. Soc. Rev. 38 (2009) 1257–1283.
[4] J.P. Ma, Y. Yu, Y.B. Dong, Chem. Commun. 48 (2012) 2946–2948.
[5] L. Zhu, W. Lv, S.J. Liu, H. Yan, Q. Zhao, W. Huang, Chem. Commun. 49 (2013) 10638–10640.
[6] B. Rosenberg, L.V. Camp, T. Krigas, Nature 205 (1965) 698–699.
[7] C.G. Hartinger, A.A. Nazarov, S.M. Ashraf, P.J. Dyson, B.K. Keppler, Curr. Med. Chem. 15 (2008) 2574–2591.
[8] D.S. Raja, N.S.P. Bhuvanesh, K. Nataraian, Eur. J. Med. Chem. 47 (2012) 73–85.
[9] V. Milacic, Q.P. Dou, Coord. Chem. Rev. 253 (2009) 1649–1660.
[10] M. Patra, G. Gasser, N. Metzler-Nolte, Dalton Trans. 41 (2012) 6350–6358.
[11] K.C. Skyrianou, E.K. Efthimiadou, V. Psycharis, A. Terzis, D.P. Kessissoglou, G. Psomas, J. Inorg. Biochem. 103 (2009) 1617–1625.
[12] D.A. Kocisko, B. Caughey, J. Virol. 80 (2006) 1044–1046.
[13] C. Pidathala, R. Amewu, B. Pacorel, G.L. Nixon, P. Gibbons, W.D. Hong, S.C. Leung, N.G. Berry, J. Med. Chem. 55 (2012) 1831–1843.
[14] J. Qin, N. Qin, C.H. Geng, J.P. Ma, Q.K. Liu, D. Wu, C.W. Zhao, Y.B. Dong, CrystEngComm. 14 (2012) 8499–8508.
[15] J. Qin, L. Cui, Inorg. Chem. Commun. 36 (2013) 170–173.
[16] W. Pfitzinger, J. Prakt. Chem. 56 (1897) 283–320.
[17] X.H. Bu, M.L. Tong, Y.B. Xie, J.R. Li, H.C. Chang, S. Kitagawa, J. Ribas, Inorg. Chem. 44 (2005) 9837–9846.
[18] T. Allman, R.C. Goel, N.K. Jha, A.L. Beauchamp, Inorg. Chem. 23 (1984) 914–918.
[19] Q.D. Zhou, T.W. Hambley, B.J. Kennedy, P.A. Lay, P. Turner, B. Warwick, J.R. Biffin, H.L. Regtop, Inorg. Chem. 39 (2000) 3742–3748.
[20] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885–3896.
[21] M.D. Enger, C.E. Hildebr, C.C. Stewart, Toxicol. Appl. Pharm. 69 (1983) 214–224.
[22] E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García, M.C. Fernánddez-Calderón, Eur. J. Med. Chem. 46 (2011) 150–159.
[23] K. Alomar, A. Landreau, M. Kempf, M.A. Khan, M. Allain, G. Bouet, J. Inorg. Biochem. 104 (2010) 397–404.
[24] E.K. Efthimiadou, G. Psomas, Y. Sanakis, N. Katsaros, A. Karaliota, J. Inorg. Biochem. 101 (2007) 525–535.
[25] D.U. Miodragović, D.M. Mitić, Z.M. Miodragović, G.A. Bogdanović, Ž.J. Vitnik, M.D. Vitorović, M.Đ. Radulović, B.J. Nastasijević, I.O. Jurnić, K.K. Anđelković, Inorg. Chim. Acta 361 (2008) 86–94.
[26] Z.H. Chohan, M. Ul-Hassan, K.M. Khan, C.T. Supuran, J. Enzyme Med. Chem. 20 (2005) 183–188.
[27] J.R. Anacona, C. Toledo, Transition Met. Chem. 26 (2001) 228–231.
[28] J.E. Weder, T.W. Hambley, B.J. Kennedy, P.A. Lay, D. MacLachlan, R. Delfs, C.D. Bramley, K.S. Murray, B. Moubaraki, B. Warwick, J.R. Biffin, H.L. Regtop, Inorg. Chem. 38 (1999) 1736–1744.