



Metal cation complexation studies of 4-arylvinyl-2,6-di(pyridin-2-yl)pyrimidines: Effect on the optical properties

Caroline Hadad^a, Sylvain Achelle^a, Isabel López-Solera^{a,1}, Joaquín C. García-Martínez^b, Julián Rodríguez-López^{a,*}

^aFacultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela 10, 13071 Ciudad Real, Spain

^bFacultad de Farmacia, Universidad de Castilla-La Mancha, 02071 Albacete, Spain

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ABSTRACT

An extensive qualitative study of the complexation properties of 4-arylvinyl-2,6-di(pyridin-2-yl)pyrimidines has been performed by UV–vis and fluorescence spectroscopy. All of the materials coordinate with a wide variety of metal ions, leading to noteworthy bathochromic shifts in the absorption spectra and diverse responses in the emission spectra (*i.e.* fluorescence quenching or increases in the fluorescence intensity) depending on the arylvinyl moiety and the cation. Quantitative studies demonstrated a 1:1 stoichiometry for the Zn²⁺ and Sn²⁺ complexes with remarkably high binding constants although poor selectivity for Zn²⁺ over other competitive metal ions such as Ca²⁺. The crystal structure of the **2h**–Zn complex shows coordination of the cation through the di(pyridin-2-yl)pyrimidine moiety. The ligands easily detected Zn²⁺, Sn²⁺, and Ca²⁺ in aqueous solution in a proof-of-concept study, thus making these molecules and their derivatives attractive propositions for sensory applications.

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1. Introduction

2,2':6',2''-Terpyridine and its derivatives are tridentate nitrogen-containing ligands that are widely used in coordination chemistry since they offer planar, convergent and well-defined triple chelation [1,2]. For many years, a considerable number of terpyridine derivative complexes with various transition metals have been synthesized and characterized [3,4]. The rich coordination chemistry of these systems and their remarkably high binding affinities toward most transition metal ions, through $d\pi \rightarrow p\pi^*$ bonding, make them highly attractive building blocks for the construction of complex metallo-supramolecular architectures, which have found applications in catalysis [5–7], electrochemistry [8–10], photochemistry [11–14] or in the recognition of G-quadruplex–DNA [15–17]. It is known that the terpyridine unit is able to coordinate with several kinds of metal ions [18–20], especially Zn²⁺ and Cu²⁺, and this causes fluorescence changes in the original ligands [21–25].

Di(pyridin-2-yl)pyrimidine ligands have been less widely reported in the literature. However, the higher π -acidity and the presence of more than one heteroatom in the pyrimidine ring play an important role in its coordination chemistry compared to that of pyridine [26]. This structural difference leads to greater metal to ligand charge transfer. Oligotridentate ligands with alternating pyridine and pyrimidine units have been studied by Lehn and co-workers [27–29] and these materials were used to form supramolecular fibers [30], rigid organometallic arrays [8,31] and ion-controlled fluorescence resonance energy transfer (FRET) systems [32]. Tetrapyrindyl-4,4'-bipyrimidine has also been reported and a ruthenium complex of this ligand exhibits an unusually long-lived emission and a high quantum yield [33,34].

In a previous article [35], we described the straightforward preparation of a series of 2,6-di(pyridin-2-yl)pyrimidines, functionalized with phenylenevinylene groups at the 4-position, from the methyl derivative **1** (Chart 1). The synthetic protocol allows not only the incorporation of electron-donating and electron-withdrawing groups at the end of the π -conjugated system but also the functionalization with water soluble groups and dendritic wedges. The interesting solvatochromism and pH sensing properties of these systems suggest that suitable design of this type of material could enable promising colorimetric and luminescence pH sensors to be developed. On the other hand, the presence of the

* Corresponding author. Tel.: +34 926295300; fax: +34 926295318.
E-mail addresses: mabel.lopez@uclm.es (I. López-Solera), julian.rodriguez@uclm.es (J. Rodríguez-López).

¹ To whom inquiries regarding the X-ray structural determination should be addressed.

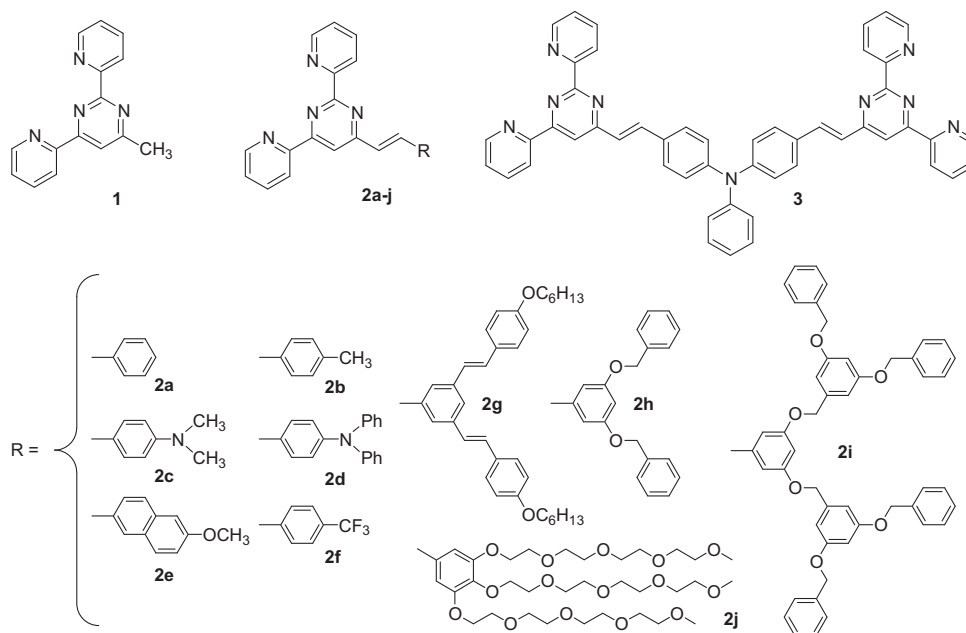


Chart 1. 4-Arylviny-2,6-di(pyridin-2-yl)pyrimidine ligands.

2,6-di(pyridin-2-yl)pyrimidine moiety allows the coordination of different families of metal cations. Herein we describe the ability of these molecules to act as binding ligands. Both qualitative and quantitative studies have been carried out by UV/vis and fluorescence spectroscopy to evaluate the influence that the cation and the substituent present on the di(pyridin-2-yl)pyrimidine ligand have on the photophysical properties of the metal complexes. The stoichiometry was determined by applying the Job method and was confirmed by NMR studies. Several Zn^{2+} complexes were isolated and the structure of one of them was unequivocally resolved by X-ray diffraction analysis. Moreover, the selectivity of these ligands for Zn^{2+} over other competitive metal ions was also examined along with their potential as chemosensors.

2. Experimental

2.1. General

The general experimental conditions were reported previously [35].

2.2. Synthesis of complex 2c–Zn

Ligand **2c** (33 mg, 0.087 mmol), $ZnCl_2$ (12 mg, 0.087 mmol) and degassed ethanol (20 mL) were placed in a 50 mL round-bottom flask. The reaction mixture was heated under reflux with stirring. After cooling, the solid was filtered off and washed with cold CH_2Cl_2 and ethanol to give 35 mg (75%) of the complex **2c–Zn** as a dark purple powder. Mp > 315 °C. 1H NMR (500 MHz, $CDCl_3$) δ : 3.11 (s, 6H, NCH_3), 6.75 (d, 2H, $J = 8.0$ Hz, p - $Me_2N-C_6H_4$), 6.96 (d, 1H, $J = 15.5$ Hz, $CH=$), 7.55 (d, 2H, $J = 8.5$ Hz, p - $Me_2N-C_6H_4$), 7.59 (t, 1H, $J = 6.5$ Hz, Pyr-H), 7.62–7.66 (m, 1H, Pyr-H), 7.90–7.98 (m, 3H, Pyr-H and pyrimidine-H), 8.14–8.20 (m, 2H, Pyr-H and $CH=$), 8.70 (d, 1H, $J = 8.5$ Hz, Pyr-H), 9.03 (d, 1H, $J = 4.5$ Hz, Pyr-H), 9.12 (d, 1H, $J = 5.0$ Hz, Pyr-H). ^{13}C NMR (125 MHz, $DMSO-d_6$) δ : 112.0, 113.9, 118.8, 122.2, 122.9, 123.1, 128.5, 128.6, 130.4, 140.5, 140.7, 142.9, 145.9, 147.2, 148.7, 149.0, 152.0, 154.5, 157.1, 168.8. IR (ATR) ν : 1578, 1662, 1473, 1368, 1167, 1020, 761 cm^{-1} . Anal. Calcd for

$C_{24}H_{21}N_5Cl_2Zn$: C, 55.89; H, 4.10; N, 13.58. Found C, 55.51; H, 4.07; N, 13.27. MALDI–TOF (dithranol) m/z : 478.5 $[M-Cl]^+$.

2.3. Synthesis of complex 2h–Zn

This complex was prepared from ligand **2h** (34 mg, 0.062 mmol) and $ZnCl_2$ (8 mg, 0.062 mmol) using the same procedure as described above. The solid was filtered off and washed with cold ethanol to give 25 mg (59%) of **2h–Zn** as a yellow powder. Mp 255–256 °C. 1H NMR (500 MHz, $CDCl_3$) δ : 5.12 (s, 4H, CH_2), 6.66 (s, 2H, Ar-H), 6.90 (d, 1H, $J = 15.5$ Hz, $CH=$), 7.13 (t, 1H, $J = 5.5$ Hz, Pyr-H), 7.38–7.55 (m, 10H, Pyr-H, Ar-H and Ph-H), 7.81 (d, 1H, $J = 16.0$ Hz, $CH=$), 7.86 (d, 1H, $J = 8.0$ Hz, Pyr-H), 8.01 (s, 1H, Pyrimidine-H), 8.35 (d, 1H, $J = 7.5$ Hz, Pyr-H), 8.72 (br d, 1H, $J = 4.5$ Hz, Pyr-H), 8.98 (br d, 1H, $J = 4.0$ Hz, Pyr-H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ : 70.0 (CH_2), 105.1 (CH), 107.4 (CH), 113.3 (CH), 122.1 (CH), 123.0 (CH), 124.1 (CH), 127.6 (CH), 127.9 (CH), 128.3 (CH), 128.8 (CH), 136.1 (C), 136.5 (C), 139.1 (CH), 139.1 (CH), 141.9 (CH), 144.9 (C), 146.4 (C), 148.9 (CH), 149.6 (CH), 155.1 (C), 157.7 (C), 159.8 (C), 168.0 (C). IR (ATR) ν : 1585, 1444, 1371, 1141, 1049, 825, 736, 694 cm^{-1} . Anal. Calcd for $C_{36}H_{28}N_4O_2Cl_2Zn$: C, 63.13; H, 4.12; N, 8.18. Found C, 62.79; H, 3.95; N, 7.88. MALDI–TOF (dithranol) m/z : 647.4 $[M-Cl]^+$.

2.4. Synthesis of complex 3–Zn

This complex was prepared from ligand **3** (33 mg, 0.043 mmol) and $ZnCl_2$ (13 mg, 0.094 mmol) using the same procedure as described above. The solid was filtered off and washed with cold ethanol to give 28 mg (63%) of **3–Zn** as a yellow powder. Mp > 315 °C. 1H NMR (500 MHz, $DMSO-d_6$) δ : 7.10 (d, 4H, $J = 7.0$ Hz, p - $N-C_6H_4$), 7.25 (d, 2H, $J = 8.0$ Hz, Ph-H), 7.27–7.35 (m, 3H, $CH=$ and Ph-H), 7.49 (t, 2H, $J = 8.0$ Hz, Ph-H), 7.73 (br d, 4H, p - $N-C_6H_4$), 7.88 (br s, 4H, Pyr-H), 8.18–8.36 (m, 6H, $CH=$, Pyr-H and pyrimidine-H), 8.63 (d, 2H, $J = 7.5$ Hz, Pyr-H), 8.71–8.86 (m, 8H, Pyr-H). ^{13}C NMR (125 MHz, $DMSO-d_6$) δ : 114.5, 123.1, 123.2, 125.6, 126.5, 128.7, 129.4, 130.0, 130.2, 140.8, 141.1, 145.7, 147.0, 148.6, 148.8, 149.1, 155.2, 157.2, 168.4. IR (ATR) ν : 1580, 1566, 1503, 1473, 1384, 1284, 1174, 1012, 759 cm^{-1} . Anal. Calcd for $C_{50}H_{35}N_9Cl_4Zn_2$: C, 58.05; H,

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