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Anion Recognition in Aqueous Solution by Cyclic Dinuclear 1

Square Cage-shaped Coordination Complexes 2

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7 **ABSTRACT:** Three cyclic dinuclear complexes, namely $[M_2(H_2L)_2](ClO_4)_4$ [M = Co²⁺ (1), Ni²⁺ (2), Zn²⁺ (3), H₂L = (1,2)-bis-N'-(pyridin-2-2)-b 8 ylmethylene)benzohydrazide hydrazine, C26H22N8O2], containing amide and hydrazine groups were synthesized and characterized. 9 Each central metal ion is coordinated with two oxygen atoms and four nitrogen atoms from carbonyl, and pyridine and imine, 10 respectively. The metal ion is six-coordinated and has a slightly deformed octahedral geometry. X-ray crystallographic analyses 11 showed that all the three cyclic dinuclear complexes crystallize in the orthorhombic system, and belong to the C222 space group, 12 with two molecules in each unit cell. The cyclic dinuclear molecule is linked by two H₂L ligands with a Z-form -HN-NH- bridge, nearly 13 forming a square coordination cage with edges of length around 8.4 Å. The cyclic dinuclear complexes can recognize acetate and 14 fluoride anions in an acetonitrile solution containing 60% volume water. Recognition is governed by electrostatic interactions in 15 cooperation with the cage structure effect with the mechanism of anion displacement reaction. The results show that the recognition 16 of anions in acetonitrile aqueous solution is an exothermic and entropy-reducing reaction. This suggests that the enthalpy change 17 plays an important role in the presence of highly polar water and highlights the importance of positively charged cage structure 18 effect. A color change from light yellow to dark yellow was clearly observed for complex 3 on addition of acetate or fluoride anions 19 in acetonitrile aqueous solution containing 60% water. Complex 3 can be used for colorimetric "naked eye" recognition of acetate or 20 fluoride anions in acetonitrile aqueous solution. Theoretical calculations based on time dependent density functional theory (TD-21 DFT) show the agreement between the theoretical results and experimental data. 22 Keywords: Anion recognition; Cyclic dinuclear coordination complexes; Square cage

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1. Introduction 24

25 Anion recognition continues to be one of the most active fields in supramolecular chemistry because of its wide 26 applications in areas such as sensing, 1-5 extraction, 6,7 self-assembly, 8-13 transmembrane transport, 14-19 and 27 catalysis.²⁰⁻²³ The design of receptors capable of anion binding in aqueous media is a widely researched topic 28 because the effects of water on the affinities and selectivities of such receptors are still not completely understood. 29 ²⁴⁻²⁸ Considerable efforts have been made to design various recognition receptors that are effective in water. Such 30 receptors are mainly based on combinations of non-covalent interactions such as hydrogen-bonding, electrostatic, 31 $\pi-\pi$, hydrophobic, and coordination interactions. ^{26, 28-35} Single hydrogen-bonding or other interactions do not 32 provide efficient receptors for anions in aqueous solution because of competition between the receptor and protic 33 solvents, particularly water. Protonated bicyclic receptors, ³⁶ quaternary ammonium cages, ^{37, 38} cyclic or bicyclic 34 polyamines, ³⁹ cryptands, ^{40, 41} guanidinium-based receptors, ⁴² and cyclopeptides⁴³ and other synthetic receptors^{44, 45} 35 can perform in anion recognition well in aqueous media. Another successful strategy for anion recognition in water 36 involves the use of metal-based coordination interactions combined with electronic and/or hydrogen-bonding 37 interactions. ^{26, 32,43-47} Binding studies performed with these receptors have greatly increased our understanding of 38 anion coordination chemistry. Thermodynamic studies of anion recognition in water are currently divided into two 39 main areas: endothermic complexation by a favorable entropy change (positive ΔH^{0} and positive $T\Delta S^{0}$) and the

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40 opposite thermodynamic behavior (i.e., negative ΔH^{0} and negative $T\Delta S^{0}$).²⁴⁻²⁶ It would be interesting to extend 41 these investigations to other types of receptor to gain more information on the binding modes that allow anion 42 recognition in water. On the basis of these reports, we investigated the design of cyclic dinuclear complexes with 43 molecular cages. Such metal-ligand coordinated molecular cages are potential size- and shape-selective synthetic 44 receptors with various responses to guest molecules. 48-50 In this study, we designed a ligand containing amide and 45 hydrazine groups, i.e., (1,2)-bis-N'-(pyridin-2-ylmethylene)benzohydrazide hydrazine (H₂L), it generally exists in E-46 form (Scheme 1). The oxygen atom from carbonyl and two nitrogen atoms from pyridine and imine can chelate 47 metal ions. Two Z-form H₂L ligands in an -HN-NH- group can easily react with two six-coordinated metal ions to 48 form a square coordination cage, i.e., $[M_2(H_2L)_2]^{4+}$, with a saturated coordination metal center. The total four 49 positive charges on the metal centers make the complex soluble in polar solvents. The cage rim and its cavity 50 provided by the two H₂L ligands is capable of efficient binding of guests. We reasoned that these amide and 51 hydrazine groups in the positively charged cages could provide the static geometric requirements for specific anion 52 recognition. The anion recognition properties of pure H₂L and its cyclic dinuclear complexes in pure acetonitrile 53 solution and acetonitrile aqueous solutions containing 40%, 50%, and 60% volume water were therefore 54 investigated. All three cyclic dinuclear complexes can recognize acetate (CH₃COO⁻) and fluoride (F⁻) anions in 55 acetonitrile solution, even containing 60% water. UV-vis spectroscopy and ¹H NMR titrations showed that the 56 binding force in anion recognition mainly arises from electrostatic interactions in cooperation with the cage 57 structure effect in acetonitrile aqueous solution. Thermodynamic data showed that anion recognition in acetonitrile 58 aqueous solution is an exothermic and entropy-reducing reaction. The zinc cyclic complex can be used for 59 colorimetric "naked eye" recognition of CH₃COO ⁻ and F⁻ anions in acetonitrile aqueous solution.

60 **2. Experimental Section**

61 **2.1** Materials and Methods.

62 Analytical-grade reagents were purchased from the Sinopharm Chemical Reagent Co. (Shanghai, China) and used 63 as received. Metal(II) perchlorate hexahydrate $[M(ClO_4)_2 \cdot 6H_2O, M = Co, Ni, Zn]$ and tetrabutylammonium with 64 various anions were purchased from Alfa Aesar (Tetrabutylammonium phosphate undergoes protonation (pKa₃ = 65 12.67) in neutral water or aqueous solutions and is identical to tetrabutylammonium hydrogenphosphate). Melting 66 points were determined with an X-4 micromelting point apparatus without correction. Elemental analyses were 67 performed with a Vario EL III elemental analyzer. Positive electrospray ionization mass spectrometry (ESI MS) data 68 were obtained with a Bruker ESQUIRE-3000 Plus LC-MS/MS spectrometer, with methanol as the solvent. IR spectra 69 (KBr pellets) were recorded with a Nicolet AVATAR FT-IR 330 spectrometer. Solution ¹H NMR spectra were recorded 70 at 400 MHz with a Bruker ADVANCE 400 spectrometer at room temperature, i.e., about 25 °C. The chemical shifts 71 (ppm) were reported relative to tetramethylsilane as an internal reference. UV-vis absorption spectra were recorded 72 with a Shimadzu UV224012PC absorption spectrometer. Thermal experiments were performed by placing a 1 cm 73 cuvette in the thermostated cell of a spectrophotometer, and the spectrum was recorded; the temperature error 74 was controlled to ±1 °C.

75 **2.2** General Protocol for UV-vis Spectrophotometric Titrations.

The concentrations of stock solutions of H₂L and complexes **1–3** were all 5.0×10^{-4} mol/L; the solvent was DMSO or acetonitrile (depending on the solubility of the substance). A microsyringe was used to pipette the stock solution (50.0 µL) into a 1 cm cuvette containing acetonitrile (2.50 mL) to obtain a 1.0×10^{-5} mol/L solution for analysis. Solutions (5.0×10^{-3} mol/L) of anions as tetrabutylammonium salts were added in microvolumes to the cuvette, followed by thorough mixing. UV-vis spectra were recorded at each concentration of the added anion.

81 **2.3** ¹H NMR Titrations.

- 82 Tetrabutylammonium fluoride or acetate was dissolved in 9:1 acetonitrile-d₃/DMSO-d₆ to prepare a 0.20 mol/L 83 stock solutions. The host acetonitrile- d_3 /DMSO- d_6 (9:1) solution (0.01 mol/L, 0.50 mL) was added to an NMR tube. A 84 certain equivalent amount of tetrabutylammonium fluoride or acetate solution was microsyringed into the tube, 85 followed by thorough mixing. Spectra were recorded at 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, and 6.0 anion 86 equivalents. 87 2.4 DFT and TD-DFT Calculations. 88 DFT Calculations were performed using Gaussian 09b program.⁵¹ The structure of complex 3 was fully optimized 89 and frequency verifications were performed in acetonitrile using the B3LYP hybrid density functional with the default 90 PCM solvent model and its crystallographic coordinates. The LANL2DZ basis set was employed for Zn with effective 91 core potential, and the 6-31 G(d, p) basis set was used for other atoms.⁵²Then the energies of each molecules 92 were calculated at the optimized geometries by TD-DFT with the same basis set. 93 2.5 Determination of $[Co_2(H_2L)_2](CIO_4)_4$ (1), $[Ni_2(H_2L)_2](CIO_4)_4$ (2), and $[Zn_2(H_2L)_2](CIO_4)_4$ (3) 94 structures. 95 Diffraction data for 1 and 3 were collected with a Bruker SMART Apex CCD diffractometer with graphite-96 monochromated Mo K α (λ = 0.71073 Å) radiation in ω scan mode at -100 °C. Crystal data integration and 97 reduction were performed with SAINT software.⁵³ The data for 2 were collected with an Oxford Gemini S 98 Ultra CCD area detector at -70 °C. Absorption correction was performed with the multiscan CrysAlis Red 99 program.⁵⁴ The structures were solved by direct methods with SHELXS-2014 and refined by full-matrix least-100 squares calculations with SHELXL-2014, based on $F^{2.55}$ All non-hydrogen atoms were refined anisotropically. 101 Least-squares refinement of hydrogen atoms was mixed: some were constrained and others were 102 independent. For the constrained case, hydrogen atoms were placed at the calculated positions using the 103 riding model. Hydrogen atoms in water were not determined. For complexes 2 and 3, the unit cell included 104 a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. 105 PLATON/SQUEEZE was used to remove the diffused electron density from these solvent molecules and to 106 produce a set of solvent-free diffraction intensities. The generated data were then used to refine the 107
- structures again. Data for the crystal structures of complexes 1-3 have been deposited at the Cambridge
- 108 Crystallographic Data Centre (CCDC 1831733 for 1, 1831731 for 2, and 1831732 for 3).

109 2.6 Ligand Synthesis.

110 2.6.1 (E)-4,4'-Azobenzenedicarboxylic acid diethyl ester (LA).

111 Ethyl p-aminobenzoate (0.50 g, 3.0 mmol), sodium iodide (0.90 g, 6.0 mmol), and anhydrous ether (30.0 112 mL) were added to a flask. tert-Butyl hypochlorite (0.66 g, 6.0 mmol) was added and the mixture was stirred 113 at room temperature for 3 h under nitrogen. Sodium thiosulfate solution (60.0 mL, 1.0 mol/L) was added to 114 the solution. The aqueous solution was extracted three times with dichloromethane. The combined organic 115 layers were treated with anhydrous sodium sulfate and filtered. The collected solution was concentrated 116 under reduced and purified by silica gel chromatography with petroleum pressure 117 ether/dichloromethane/ethyl acetate (20/10/1) as the eluent. LA (0.34 g, yield 70%) was obtained as an 118 orange–red solid. mp 135–136 °C; ESI(+) MS m/z (methanol) 327.0 [M⁺]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 119 8.24 (s, 4H), 8.02 (s, 4H), 4.45 (s, 4H), 1.46 (d, J = 2.9 Hz, 6H).

- 120 2.6.2 (E)-1,2-Azodibenzoydrazide (LB).
- 121 LA (0.98 g, 3.0 mmol) and hydrazine hydrate (85%, 20.0 mL) were added to a flask. The solution was refluxed
- 122 at 110 °C for 10 h under vigorous stirring. Deionized water (50.0 mL) was added to the solution. The mixture
- 123 was stored in a refrigerator for 24 h and a pale-yellow solid formed. The precipitate was filtered and washed

- 124 with 1:1 ethanol/water. LB (0.71 g, yield 80%) was obtained as a pale-yellow solid. mp > 300 °C; ESI(+) MS m/z 125 (methanol) 300.6 [M⁺]; ¹H NMR (400 MHz, DMSO- d_6) δ (ppm) 9.39 (s, 2H), 8.21 (s, 2H), 7.63 (d, J = 8.8 Hz, 4H), 126 6.69 (d, J = 8.8 Hz, 4H), 4.39 (s, 4H). 127 2.6.3 1,2-Bis-(N'-pyridin-2-ylmethylene)benzohydrazide hydrazine (H₂L). 128 LB (0.30 g, 1.0 mmol) and 2-pyridinecarbaldehyde (0.21 g, 2.0 mmol) were dissolved in methanol (50.0 mL). 129 The solution was refluxed at 60 °C for 24 h under vigorous stirring. The precipitate was filtered off and washed 130 with methanol. H₂L (0.38 g, yield 70%) was obtained as a yellow solid. mp 189–190 °C; ESI(+) MS m/z 131 (methanol) 501.0 [M + Na⁺]; ¹H NMR (400 MHz, DMSO) δ (ppm) 11.75 (s, 2H), 8.63–8.58 (m, 2H), 8.45 (d, J = 132 18.2 Hz, 4H), 7.94 (s, 2H), 7.88 (dd, J = 7.5, 1.3 Hz, 2H), 7.80 (d, J = 8.8 Hz, 4H), 7.40 (ddd, J = 7.3, 4.9, 1.2 Hz, 133 2H), 6.81 (d, J = 8.8 Hz, 4H); FT-IR (KBr, cm⁻¹) 3423 (w, O–H), 1638 (s, C=O), 1571 (m, C=C), 1281 (s, C–N), 829, 134 782, 758 (m, Ph–H). Anal. Calcd for C₂₆H₂₂N₈O₂(H₂O)₄: C, 56.72; H, 5.49; N, 20.35. Found: C, 56.36; H, 5.08; N,
- 135 20.36.

136 **2.6.4** Synthesis of Complexes 1–3.

All three complexes were synthesized by the following method. Ligand H₂L (0.048 g, 0.1 mmol) and M(ClO₄)₂·6H₂O (0.1 mmol, M = Co, Ni, Zn) were dissolved in a mixed solvent (12.0 mL acetonitrile and 8.0 mL chloroform). The solution was stirred at room temperature for 24 h. Single crystals of complexes **1–3** were obtained by anhydrous diethyl ether diffusion into the reaction solution.

- 145 $[Ni_2(H_2L)_2](ClO_4)_4$ (2). Yellow block crystal (yield 60%); mp > 300 °C; ESI(+)-MS m/z (methanol) = 268.2146 $([Ni_2(H_2L)_2]^{4+})$, 357.5 ($[Ni_2(H_2L)_2-H^+]^{3+}$), 535.9 ($[Ni_2(H_2L)_2-2H^+]^{2+}$). FT-IR (KBr, cm⁻¹): 3434 (w, O–H), 1600 (s,147C=O), 1563 (m, C=C), 1293 (s, C–N), 1255 (s, N–N), 834, 775, 755 (m, Ph–H). Anal. Calcd for148 $Ni_2C_{52}H_{44}N_{16}O_{20}Cl_4(H_2O)_5(CH_3CN)_2(CHCl_3)$: C, 38.82; H, 3.49; N, 14.29. Found: C, 38.84; H, 3.35; N, 14.34.
- 149 [Zn₂(H₂L)₂](ClO₄)₄ (3). Yellow block crystal (yield 65%); mp > 300 °C; ESI(+)-MS m/z (methanol) = 271.8
- 150 ([Zn₂(H₂L)₂]⁴⁺), 361.9 ([Zn₂(H₂L)₂-H⁺]³⁺), 542.7 ([Zn₂(H₂L)₂-2H⁺]²⁺). ¹H NMR (400 MHz, DMSO) δ ppm = 12.08 (s, 2H),
- 151 8.60 (d, J = 4.2 Hz, 4H), 8.47 (s, 2H), 7.97 (s, 4H), 7.83 (d, J = 8.5 Hz, 4H), 7.47 (s, 2H), 6.82 (d, J = 8.6 Hz, 4H). FT-IR
- 152 (KBr, cm^{≥1}): 3434 (w, O-H), 1618 (s, C=O), 1571 (m, C=C), 1289 (s, C⊇N), 1255 (s, N⊇N), 834, 773, 708 (m, Ph⊇H). Anal.
- $153 \qquad \mathsf{Calcd for } \mathsf{Zn_2C_{52}H_{44}N_{16}O_{20}Cl_4(H_2O)_6(CH_3CN)_2(CHCl_3): C, 38.14; H, 3.54; N, 14.04. \ \mathsf{Found:} \ \mathsf{C}, 38.21; H, 3.40; N: 13.96.$
- 154 **3.** Results and Discussion

155 **3.1** X-ray Crystallographic Analysis.

- Crystals of [Co₂(H₂L)₂](ClO₄)₄ (**1**), [Ni₂(H₂L)₂](ClO₄)₄ (**2**), and [Zn₂(H₂L)₂](ClO₄)₄ (**3**) were grown by diethyl ether vapor diffusion into chloroform and acetonitrile binary solutions. The molecular geometries of their crystal structures were determined by single-crystal X-ray crystallography. Table 1 gives the crystallographic parameters of the three cyclic complexes. The important bond lengths and angles of the three compounds are listed in Table S1.
- 160 The perspective view of the molecular structure of complexes **1-3** is shown in Figure 1 and Figures S1-3. The crystal 161 structures show that the three complexes have similar structures and all belong to the orthorhombic system, in the 162 C222 space group, and form cationic square shape structures. Each *Z*-form H₂L ligand acts as a bridge between two 163 metal ions to form two edges, leading to a nearly square coordination cage. The coordination mode of the two central

164 metal ions in each complex is the same, i.e., they are coordinated to two oxygen atoms from carbonyl and four 165 nitrogen atoms from pyridine and imine, forming a stable structure with coordination number six, and the geometry 166 of the coordination polyhedron is a slightly deformed octahedron. The diagonal M···M separations are 12.878, 12.790, 167 and 12.923 Å for Co…Co, Ni…Ni, and Zn…Zn, respectively. The average diagonal N4A…N4A (or N5A…N5A) separations 168 are 11.829, 11.917, and 11.735 Å in complex 1, 2, and 3, respectively. The lengths of the four edges from the metal 169 center to the first nitrogen atom of the hydrazine group are all around 8.4 Å for the three complexes. This shows that 170 the three complexes almost form molecular square coordination cages. The total of +4 charges on the metal ions is 171 balanced by four perchlorate anions outside the cavity of the square. In addition, there are solvent acetonitrile 172 molecules and water molecules inside the square cavity. The Co-O, Ni-O, and Zn-O bond lengths range from 2.112 173 to 2.146, 2.093 to 2.141, and 2.133 to 2.198 Å, respectively. The Co-N, Ni-N, and Zn-N bond lengths are 2.041–2.149, 174 1.972–2.108, and 2.045–2.141 Å, respectively. These M–O and M–N bond lengths are similar to those reported in the 175 literature for the same coordination mode. ⁵⁶ Furthermore, the hydrogens at the imine carbon, amide nitrogen, and 176 hydrazine can form intermolecular hydrogen bonds with solvent water molecules or the perchlorate counter anion. 177 The hydrogen-bond parameters are summarized in Table S2. The crystal structures directly indicate the presence of 178 multiple hydrogen-bonding sites in this series of cyclic dinuclear square coordination cages.

179 **3.2** UV-vis Spectroscopy Titrations.

180 The designed H₂L ligand has amide –CONH and hydrazine –HN–NH– groups (Scheme 1). It normally forms 181 hydrogen bonds with fluorine, oxygen, or nitrogen atoms, similarly to other neutral anion receptors. First, we 182 examined the recognition properties of the H₂L ligand for anions in organic solvents. The UV-vis absorption 183 spectra of H₂L and H₂L with addition of 10 equiv of various anions in acetonitrile solution were recorded. 184 Figure 2 shows that H₂L has a maximum absorption peak at 322 nm (ε = 5.9 × 10⁴ L mol⁻¹ cm⁻¹). The UV-vis 185 absorption spectrum of H₂L changed to different extents on addition of 10.0 equiv of F⁻, CH₃COO⁻, Cl⁻, Br⁻, 186 ClO₄⁻, NO₃⁻, H₂PO₄⁻, PO₄³⁻, HSO₄⁻, and BF₄⁻ in tetrabutylammonium salts. The clearest change in the UV-vis 187 absorption spectrum was observed for addition of F-. The intensity of the absorption peak at 322 nm 188 decreased significantly and the peak red shifted. A new absorption peak appeared at 425 nm. Addition of 189 CH₃COO⁻ to the H₂L solution resulted in a slight increase in the intensity of the absorption peak at 322 nm 190 and a new absorption peak appeared at 415 nm. Addition of other anions to the H₂L solution did not cause 191 significant changes in the UV-vis absorption spectrum. The inset in Figure 2 shows the changes in the 192 absorbance at 322 nm after addition of 10.0 equiv of various anions. The intensity changes show that the 193 order of the degree of interactions between H_2L and the anions is $F^- > CH_3COO^- > BF_4^- > Br^- > ClO_4^- >$ 194 $HSO_4 > NO_3 > PO_4^{3-} > H_2PO_4^{-} > Cl^{-}$. The changes in the UV-vis absorption spectrum of H₂L in acetonitrile 195 solution as a function of F⁻ anion concentration were monitored. With increasing addition of F⁻, the intensity 196 of the absorbance of H₂L at 322 nm gradually decreased and red shifted, and a new absorption peak appeared 197 at 425 nm, with an isosbestic point at 336 nm. These results indicate that H₂L forms a stable hydrogen-bonded 198 complex with F⁻. Similar changes were observed on addition of CH₃COO⁻ anion, even on addition of the 199 strong base OH⁻ anion in tetrabutylammonium salt; but other anions, i.e., BF₄⁻, Br⁻, ClO₄⁻, HSO₄⁻, NO₃⁻, 200 H₂PO₄⁻, PO₄³⁻ and Cl⁻ did not change the UV-vis spectrum (Figures S4 and S5 in the electronic supplementary 201 information). H₂L behaves similarly to most neutral anion receptors but does not occur a deprotonation 202 process; it recognizes anions in pure organic solvents but recognition is poor in solutions containing water 203 (Figure S6).

 $\begin{array}{ll} & H_2L \mbox{ reacts easily with } Co^{2+}, \mbox{ Ni}^{2+}, \mbox{ and } Zn^{2+} \mbox{ to form cyclic complexes } 1-3. \mbox{ These complexes are nearly square} \\ & 205 \mbox{ cationic coordination cages, } [M_2(HL)_2]^{4+}, \mbox{ with each Z-form hydrazine of H_2L bridging two metal ions to form} \\ \end{array}$

206 two edges. Unlike H_2L , complexes 1–3 interact strongly with various anions in acetonitrile solution. Taking 207 complex **3** as an example, Figure 3 shows the changes in the UV-vis absorption spectrum of complex **3** in the 208 presence of 10 equiv of various anions in acetonitrile solution. The UV-vis spectrum of 3 in acetonitrile 209 solution shows two strong absorption bands, at 283 nm (ε = 3.8 \times 10⁴ L mol⁻¹ cm⁻¹) and 363 nm (ε = 1.0 \times 210 10^5 L mol⁻¹ cm⁻¹). The UV-visible absorption spectrum of **3** in acetonitrile changed to different degrees on 211 addition of 10 equiv of F⁻, Ac⁻, Cl⁻, Br⁻, ClO₄⁻, NO₃⁻, $H_2PO_4^{-}$, PO_4^{3-} , HSO_4^{-} , and BF_4^{-} anions in 212 tetrabutylammonium salts. A comparison of these spectra shows that addition of F⁻ and CH₃COO⁻led to red 213 shifts of both bands, to 302 and 398 nm, with a decrease in the intensity of the shorter-wavelength band and 214 an increase in the intensity of the longer-wavelength band. In contrast, on addition of PO_4^{3-} , $H_2PO_4^{-}$, CI^- , 215 HSO_4^- , and Br⁻, the band at 283 nm red shifted to around 320 nm and its intensity increased, and the intensity 216 of the band at 363 nm decreased. On addition of CIO_4^- , NO_3^- , and BF_4^- anions to the solution, the intensity of 217 the band at 363 nm decreased. These results show that complex 3 can interact with various anions in 218 acetonitrile solution. Similar phenomena were observed for complexes 1 and 2 in acetonitrile solution 219 (Figures S7–S9). It was not observed the occurrence of deprotonation process even for the interaction of 220 complexes with the strong base OH⁻ anion in tetrabutylammonium salt.

221 These complexes can interact with various anions because the complex cages have an internal cavity with 222 a cationic charge, and amide and hydrazine multiple recognition sites for anions, therefore the cage complex 223 can easily interact with anions through electrostatic, hydrophobic, and/or hydrogen-bonding interactions 224 with anions. It is well-known that the intensity of hydrogen bonding of an anion to a receptor becomes weaker 225 as the dielectric constant of the solvent increases. 35, 57 Water has one of the highest dielectric constants of 226 all solvents and different anions show different solvation properties in water.⁵⁸ We therefore hypothesize 227 that the three complexes have different binding abilities and will show selectivity for certain anions in solvent 228 mixtures with high water contents.

The anion recognition abilities of complexes **1–3** in acetonitrile solutions containing 40%, 50%, and 60% volume water were therefore examined. The experimental results show that the anion recognition abilities of the three complexes were similar; complex **3** was selected as an example.

232 The changes in the UV-vis absorption spectrum of complex 3 on addition of 10 equiv of various anions in 233 acetonitrile solution containing 40% water (Figure 4) show that the UV-vis absorption spectrum changes most 234 on addition of CH₃COO⁻, with F⁻ coming second. On addition of CH₃COO⁻ or F⁻, a new absorption peak 235 appeared at around 380 nm, and the intensity of the absorption peak at 332 nm decreased significantly. 236 However, addition of other anions did not cause obvious changes to the absorption bands of complex 3. 237 Complex 3 can selectively recognize CH₃COO⁻ and F⁻ in acetonitrile solution containing 40% water and 238 responds little to other anions such as Cl^- , Br^- , ClO_4^- , NO_3^- , $H_2PO_4^-$, PO_4^{3-} , HSO_4^- , and BF_4^- . Figure 5 shows 239 the changes in the UV-vis absorption spectrum of complex $\bf{3}$ as a function of the CH₃COO⁻ anion 240 concentration in acetonitrile solution containing 40% water. During the titration, a new absorption peak 241 appeared at 380 nm, accompanied by an isosbestic point at 350 nm; this indicates the formation of stable 242 complexes of **3** with CH₃COO⁻. The changes in the UV-vis absorption spectrum of complex **3** as a function of 243 the F^- anion concentration are similar to those with CH₃COO⁻ (Figure S10).

The changes in the UV-vis absorption spectra of the three complexes on addition of various anions in acetonitrile solution containing 50% and 60% water were also investigated (Figures S11–19). The results show that the anion recognition properties are similar to those in acetonitrile solution containing 40% water. However, the binding ability of the complexes to anions becomes weaker with increasing water content

because anion solvation becomes easier when more water is present. The hydrogen-bonding interactions between complexes and anions are generally inhibited, and the recognition ability decreases, with increasing water content.

251 On addition of 10.0 equiv of CH_3COO^- or F^- , the light yellow solution of complex **3** in pure acetonitrile, in 252 acetonitrile containing 40%, 50%, or 60% water solutions (Figures 6 and S20), all immediately became dark 253 yellow. However, such color changes for complexes **1** and **2** cannot be observed in acetonitrile containing 254 40%, 50%, or 60% water solutions (Figure S21). Complex **3** can be used for colorimetric "naked eye" 255 recognition of acetate or fluoride anions in acetonitrile aqueous solution.

256 **3.3** ¹H NMR Titrations.

257 ¹H NMR spectroscopy is a versatile tool for determining whether interactions between anions and 258 receptors involve hydrogen bonding or deprotonation of the receptor. $^{59\text{-}61}$ ^1H NMR spectra of H_2L and 259 complex 3 in the presence of various concentrations of anions were therefore recorded, with 9:1 acetonitrile-260 d_3 /DMSO- d_6 as the solvent owing to their solubilities are low in acetonitrile and better in DMSO. Figures 7 261 and 8 show the corresponding ¹H NMR spectra of H₂L and complex **3** with various concentrations of CH₃COO⁻ 262 anions in acetonitrile- d_3 /DMSO- d_6 mixed solvents. The chemical shift of H_d (δ , ppm) in the amide group 263 (-CONH_d) of H₂L is 11.56. This signal gradually broadened and shifted downfield with increasing concentration 264 of CH₃COO⁻. At the same time, the chemical shift of H_a (δ , 8.03 ppm) in the hydrazine group (–NH_aNH_a–) was 265 broadened and accompanied by a little upfield shift. This shows that H_d and H_a in in H_2L complexed with 266 anions to form hydrogen bonds.

267 The chemical shift of H_d (δ ppm) in the amide group (–CONH_d) of complex **3** is 12.03, a little downfield of 268 that for free H₂L, because of coordination of the metal ion with oxygen of the amide group carbonyl, and the 269 chemical shift of H_a in the hydrazine group (-NH_aNH_a-) is the same as that for H_2L . The chemical shifts of H_d 270 in complex 3 became a little narrow on introduction of various amounts of CH₃COO⁻. The chemical shift of 271 H_a (δ , 8.03 ppm) was also broadened and shifted upfield a little. These results show that complex **3** may 272 interact with anions through H_d or H_a proton in pure organic solvent. Furthermore, the NMR spectrum of 273 complex **3** with addition of F^- and CH₃COO⁻ in acetonitrile- d_3 containing of 40% D₂O was also examined. The 274 NMR signals of complex 3 did not change on introduction of these two anions (Figure S22 in the supporting 275 information). There is therefore no clear evidence of hydrogen bonding in acetonitrile aqueous solution. 276 The anion may interact with the positively charged square coordination cage by electrostatic interactions in 277 cooperation with the cage structure effect.

278 During the NMR titrations in pure acetonitrile- d_3 solvent, an orange precipate was observed on addition of a 279 large excess of anions. The precipate was separated by filtration and its positive electrospray ionization mass 280 spectrum was examined. The highest peak in the ESI mass spectrum appears at 542.8, corresponding to $[Zn_2(H_2L)_2-$ 281 2H²⁺, which is the same peak observed in pure complex **3**. Addition of F⁻ or CH₃COO⁻ to the complex solution 282 precipates the similar positively charged cage with a different counter anion. This indicates that ClO_4^- is probably 283 displaced by F⁻ or CH₃COO⁻ (inside or outside the cavity) or any complex-anion adduct is formed similar with the 284 title compound, which leads to the formation of a less soluble positively charged square coordination cage. 285 However, it can not be excluded that metal ions can be involved in the interaction with the anions although they are 286 saturated coordination metal centers. At any rate, the complexes are not inert toward ligand substitution and the 287 "saturated coordination" is reached by involving amide oxygen atom, whose donor properties would be expected to

288 be weak. Therefore, it can not be ruled out that anions may displace one or more ligand binding sites and directly

interact with metal ions.

290 **3.4** Enthalpy/entropy Compensation of Complex 3 in Acetonitrile Solutions Containing Water.

291 Job plots showed that the stoichiometry of H_2L binding to F^- or CH_3COO^- anions was 1:2, with the 292 maximum molar fractions at 0.33. The maximum molar fractions in the Job plots for complexes 1-3 with 293 F[−] and CH₃COO [−]Danions are within the range of 0.33 ~ 0.5. (Figure S23) For some supramolecular systems, a 294 maximum shift to 0.45 may indicate 1:2 complex formation; even more complicated cases are also possible. 295 62, 63. In the UV-vis spectroscopy titrations, the UV-vis spectrum was unchanged after the ratio of the 296 concentration of anion to that of receptor molecule reached 2, especially for F⁻ as shown in Figure S24. 297 Therefore our approach was to fit the raw data to 1:2 model and calculated the binding constant between 298 the receptor and the anion by non-linear fitting of changes in the UV-vis absorption spectra, according to 299 equation 1.64

300

$\mathcal{A} = (C^2 \times K \times A_{im} + A_0) / (1 + C^2 \times K) \quad (1)$

Equation 1 is the non-linear fitting equation for the formation of a 1:2 complex between a receptor molecule and an anion; *A* and A_{lim} are the absorbance and maximum absorbance of the new absorption peak in the UV-vis absorption spectrum of the receptor molecule in the presence of an anion; A_0 is the absorbance of the receptor molecule without an anion; *C* is the concentration of the receptor molecule; and *K* is the general binding constant. The anion concentration was plotted against the absorbance by non-linear fitting to equation 1. The results show good fitting, which indicates that 1:2 anion complexes are present in the solution (Figure S25). The calculation results of binding constant (log K) are shown in Table 2.

308 The anion-binding constants of H_2L in pure acetonitrile and of the three complexes in acetonitrile solutions 309 containing different amounts of water were compared. The results show that the binding constants of the three 310 complexes with anions in different solutions are almost all greater than those of H_2L in pure acetonitrile. This indicates 311 that the designed cyclic dinuclear complexes easily associate with anions.

A comparison of the anion-binding constants of the complexes in different aqueous solutions shows that the binding constants decreased with increasing water content. This is mainly because a higher water content enhances anion solvation by water molecules, therefore the interactions between the receptor molecules and anions are inhibited, which weakens the ability of the receptors to recognize anions. This further proves that the interactions between the complex and the anion are mainly caused by electrostatic interactions in cooperation with cage cavity effect.

317 The mechanism of complex binding with anions in aqueous solutions was elucidated by performing UV-vis titration 318 spectroscopy of H_2L in acetonitrile solution with F_{-} , and of complex 3 in acetonitrile containing 40% water with 319 CH₃COO and F-, at 30.0 and 35.0 °C. The effects of temperature on the binding constants can be used to 320 approximately determine the enthalpy and entropy of the recognition reaction. 65 The data in Table 3 shows that 321 recognition by H₂L of F⁻ in acetonitrile solution is an endothermic reaction ($\Delta H > 0$) and the entropy is favorable ($\Delta S >$ 322 0). As the temperature increases, the change in free energy (ΔG) gradually decreases and the reaction at higher 323 temperatures is favorable for recognition. Similarly, the recognition reactions of complex 3 with F⁻ and CH₃COO⁻ in 324 acetonitrile solution are endothermic ($\Delta H > 0$), with a favorable entropy term ($\Delta S > 0$). As the temperature increases, 325 ΔG gradually decreases and appropriate higher temperatures are beneficial to the recognition reaction. However, the 326 recognition reaction of complex **3** in acetonitrile containing 40% water is an exothermic reaction ($\Delta H < 0$) but with an 327 unfavorable entropy term ($\Delta S < 0$). As the temperature rises, ΔG gradually increases. Higher temperatures are 328 therefore unfavorable for anion recognition reactions in aqueous solution. These results show that anion 329 desolvation plays an important role in anion recognition in pure acetonitrile solvent (the entropy-driven term makes 330 an important contribution). In contrast, the recognition of anions in acetonitrile aqueous solutions is an exothermic

331 and entropy- decreasing reaction. This suggests that the enthalpy change plays an important role in the presence of 332 highly polar water.

333 We also tried to determine the binding mode by DFT calculations. The structure of complex 3 was fully optimized 334 and frequency verifications were performed in acetonitrile using the B3LYP hybrid density functional with the default 335 PCM solvent model and its crystallographic coordinates. The initial geometry of the fluoride and acetate counter ion 336 atoms in [Zn₂(H₂L)₂]⁴⁺ was retrieved by placing the counter ion atoms on the basis of the optimized structure of the 337 complex 3. Various starting structures were generated by changing the counter ion position. The possible structures 338 of [Zn₂(H₂L)₂]F₄(I), [Zn₂(H₂L)₂]F₄(II), [Zn₂(H₂L)₂] (CH₃COO)₄, [Zn₂(H₂L)₂] (F)₂ (CIO₄)₂ and [Zn₂(H₂L)₂] (CH₃COO)₂ (CIO₄)₂ were 339 separately calculated and the minimum energy structure was compared with that of [Zn₂(H₂L)₂](ClO₄)₄. The calculation 340 results are shown in Table S3. The energy of the optimized structure of complex 3 is the lowest and the $[Zn_2(H_2L)_2]F_4$ 341 complexes is the highest. The energies of $[Zn_2(H_2L)_2]$ (Anion)₂(ClO₄)₂ are between the parent complex 3 and 342 $[Zn_2(H_2L)_2](Anion)_4$ of which displaces four ClO_4^- anions The energy of the complex $[Zn_2(H_2L)_2]F_4(II)$ with two fluoride 343 anions inside its cavity and two outside the cavity is the same as that of $[Zn_2(H_2L)_2]F_4(I)$ with all four fluoride anions 344 outside the cavity. These results indicate that it is possible for the small anion enter the cage cavity. However, the UV-345 vis and NMR titration results suggest that the fluoride or acetate anions displace the two counter perchlorate anions 346 to form a similar cage-like complex. The theoretical UV-vis spectra of the possible structures of $[Zn_2(H_2L)_2]$ (F)₂ (ClO₄)₂ 347 and $[Zn_2(H_2L)_2]$ (CH₃COO)₂ (ClO₄)₂ calculated by TD-DFT are the most similar to the experimental spectra of complex **3** 348 on addition of fluoride or acetate anions (see Figure 9). TD-DFT calculations can descript a detail molecular orbitals 349 involved in the electronic transitions (Table 4). The calculations show that the highest energy occupied orbital (HOMO) 350 of complex 3 is centered at the two azodibenzoydrazide moleties of the ligands, while the highest energy occupied 351 orbital (LUMO) localizes on the four N'-pyridin-2-ylmethylene moieties. In case of complexes [Zn2(H2L)2] (F)2 (ClO4)2 352 and $[Zn_2(H_2L)_2]$ (CH₃COO)₂ (ClO₄)₂, HOMO is centered at the π orbital of one of the ligands and their LUMOs are rather 353 different and complicated (see in Table S4). Furthermore, the HOMO-LUMO energy gap of complexes [Zn₂(H₂L)₂] F₂ 354 (CIO₄)₂ and [Zn₂(H₂L)₂] (CH₃COO)₂ (CIO₄)₂ is 3.11 and 3.19 eV, respectively, smaller than that of complex 3 (3.38 eV). 355 This demonstrates that the interaction of complex 3 with fluoride or acetate anions in aqueous acetonitrile solution 356 can induce strong changes in its UV-vis spectrum and prove the experimental results.

357 Some recent reports on the dinuclear metal complexes as chemosensors show that they are excellent hosts toward 358 certain anions, mainly through metal-ligand interactions, anions include N₃⁻, NCS⁻, Cl⁻, HPO₄²⁻, nucleoside 359 monophosphates, oxalate, succinate, and citrate.^{44,46,47,50, 65-68} Our three cyclic dinuclear complexes are different from 360 the reported dinuclear metal complexes in that the metal ions in our designed complexes are all six-coordinated, with 361 normally no more coordinate sites for anions, as in the case for first-row transitional metals. These cyclic dinuclear 362 complexes can bind strongly with a wide range anions in pure acetonitrile solution. The binding constants with anions 363 are high of the order 10⁹, i.e., one to three orders higher than most values reported in the literature.^{46,47,50} They can 364 identify acetate and fluoride anions in an acetonitrile solution containing 60 % water, but fail to identify certain anion 365 at higher water contents. We suppose that the enthalpy change plays an important role in the presence of highly polar 366 water and this highlights the importance of the effects of positively charged cage structures on different anion-binding 367 abilities.

368 **4.** Conclusions

369 In summary, we synthesized three cyclic dinuclear (Co²⁺, Ni²⁺, and Zn²⁺) complexes with square positively charged 370 cavities. The complexes contained multiple recognition sites, including amide and hydrazine groups. X-ray 371 crystallographic analyses showed that all three cyclic complexes crystallized in the orthorhombic system, and belonged

372 to the C222 space group, with two molecules in each unit cell. The cyclic dinuclear molecule was linked by two Z-form 373 ligands to form a square coordination cage. The cyclic dinuclear complexes easily associated with various anions in 374 pure acetonitrile as the solvent, without anion selectivity. The cyclic dinuclear complexes selectively recognized 375 acetate and fluoride anions in acetonitrile containing 60% water, mainly governed by electrostatic interactions in 376 cooperation with cage structure effect. The mechanism of anion recognition can be assumed as anion displacement 377 reaction. TD-DFT calculations show the agreement between the theoretical results and experimental data. Anion 378 recognition in acetonitrile aqueous solution is an exothermic and entropy-reducing reaction. The enthalpy-driven 379 change enables effective recognition in the presence of highly polar water. Furthermore, the cyclic binuclear zinc 380 complex 3 can be used as for colorimetric "naked eye" recognition of acetate or fluoride anions in acetonitrile aqueous 381 solution.

382 We think that such cyclic dinuclear positively charged square coordination cages with appropriate direction NH or

- 383 OH groups will provide highly efficient anion recognition in pure water, and we are now investigating the preparation
- $384 \qquad \text{of more robust similar complexes for anion recognition in water}.$

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388 Appendix A. Supplementary material

389 Supplementary data associated with this article can be found, in the online version, at 390 http://doi.org/10.1016/j.ica. xxxxx.

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506	Scheme, Table, and Figure Captions
507	Scheme 1. Syntheses of ligands and complexes 1–3.
508	Table 1. Crystallographic data for complexes 1–3.
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515	Figure 1. Molecular square of complexes 1 (left), 2(middle) and 3(right) (Part hydrogen bonding and solvent
516	molecules are shown). Color scheme: C gray, O red, N blue, Cl green, Co violet red, Ni sea green and Zn
517	cyan
518	Figure 2. Changes in UV-vis absorption spectrum of H_2L (1.0 × 10 ⁻⁵ mol/L) on addition of 10 equiv of different anions
519	in acetonitrile solution. Inset shows changes in absorbance at 422 nm on addition of 10 equiv of different
520	anions.
521	Figure 3. Changes in UV-vis absorption spectrum of complex 3 (1.0×10^{-5} mol/L) on addition of 10 equiv of different
522	anions in acetonitrile solution. Inset shows changes in absorbance at 332 nm on addition of 10 equiv of
523	different anions.
524	Figure 4. Changes in UV-vis absorption spectrum of complex 3 (1.0×10^{-5} mol/L) on addition of 10 equiv of different
525	anions in acetonitrile solution containing 40% water. Inset shows changes in absorbance at 381 nm on
526	addition of 10 equiv of different anions.
527	Figure 5. Changes in UV-vis absorption spectrum of complex 3 (1.0×10^{-5} mol/L) on addition of different
528	concentrations of acetate in acetonitrile solution containing 40% water.
529	Figure 6. Color changes of H_2L (a and b) and complex 3 (c and d) in presence of various anions: (a) and (c) in pure
530	acetonitrile solution; (c) and (d) in acetonitrile solution containing 50% water.
531	Figure 7. ¹ H NMR spectra of H ₂ L in presence of 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 equiv of
532	$CH_3COO [nBu_4N]$ in 9:1 acetonitrile- $d_3/DMSO-d_6$ solvent.
533	Figure 8. ¹ H NMR spectra of complex 3 in presence of 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 equiv
534	of $CH_3COO[nBu_4N]$ in 9:1 acetonitrile-DMSO- d_6 solvent.
535	Figure 9. UV-vis spectra of the possible structures calculated by TD-DFT and the experimental spectra of complex 3
536	on addition of fluoride or acetate anions.
537	



able 1.			
Crystal data	1	2	3
CCDC number	1831733	1831731	1831732
Empirical formula	$C_{168}H_{156}CI_8Co_6N_{52}O_{70}$	C ₁₆₄ H ₁₄₄ Cl ₈ Ni ₆ N ₅₂ O ₇₄	$C_{164}H_{144}Cl_8Zn_6N_{52}O_{70}$
Moiety formula	3(C ₅₂ H ₄₄ N ₁₆ Co ₂ O ₄),	3(C ₅₂ H ₄₄ N ₁₆ Ni ₂ O ₄),	3(C ₅₂ H ₄₄ N ₁₆ O ₄ Zn ₂),
	8(ClO ₄), 2(C ₂ H ₆ O),	8(ClO ₄), 4(C ₂ H ₃ N),	8(ClO ₄), 4(C ₂ H ₃ N),
	4(C ₂ H ₃ N), 24(O)	30(O) [+ solvent]	26(O) [+ solvent]
Formula weight	4660.62	4663.05	4639.12
Wavelength(Å)	0.71073	1.54184	0.71073
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	C222	C222	C222
<i>a</i> (Å)	24.345(3)	24.320(2)	24.232(4)
b (Å)	28.593(4)	28.857(2)	28.447(5)
c (Å)	21.598(3)	21.392(8)	21.400(4)
α (°)	90	90	90
β(°)	90	90	90
(°)	90	90	90
V (ų)	15034(3)	15013(1)	14751(5)
z	2	2	2
Cal density (Mg m ⁻³)	1.030	1.029	1.044
Abs coefficient (mm ⁻¹)	0.463	1.663	0.622
ϑ range	1.424 to 28.401	3.063 to 61.999	1.457 to 28.532
Reflections collected	66582	15329	65256
Data/restraints/para	17951/0/701	10398/0/695	17663/6/680
Goodness of fit on F ²	0.810	0.981	0.835
Final <i>R</i> indexes [I>=2σ(I)]	$R_1 = 0.0623$	$R_1 = 0.0732$	$R_1 = 0.0579$
	$WR_2 = 0.1513$	$WR_2 = 0.1958$	$WR_2 = 0.1460$
R indices [all data]	$R_1 = 0.1028$	$R_1 = 0.0881$	$R_1 = 0.0972$
	$WR_2 = 0.1593$	<i>WR</i> ₂ = 0.2126	$WR_2 = 0.1541$

- Table 2

Compounds	CH₃COO ⁻	F-	CI⁻	H ₂ PO ₄	Br-	
H ₂ L (0%)	7.93	8.38	_	_	_	
1 (0%)	9.83	10.22	8.34	7.32	- (
1 (40%)	9.46	9.23	_	-	-	
1 (60%)	9.36	9.16	_	-	-	,
2 (0%)	9.37	10.11	-	7.74	9.63	
2 (40%)	9.15	9.37			_	
2 (60%)	7.95	7.04	- 5	-	-	
3 (0%)	9.46	9.79	9.01	9.31	9.60	
3 (40%)	9.32	9.22	-	_	-	
3 (60%)	9.07	8.68	-	_	-	

(The relative uncertainty was less than 10%.)

 $\begin{array}{c} 608\\ 609\\ 610\\ 611\\ 612\\ 613\\ 614\\ 615\\ 616\\ 617\\ 618\\ 619\\ 620\\ 621\\ 622\\ 623\\ 624\\ 625\\ 626\\ 627\\ 628\\ 629\\ 630\\ 631\\ 632\\ 633\\ 634\\ 635\\ 636 \end{array}$

- 638 639 640 641 642 643 644

Table 3

Anion		F-			CH₃COO [_]		
Compounds	т (°С)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol·K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol·K)
	25.0	-47.8					
H ₂ L	30.0	-49.4	60.9	0.36	- 5	-	_
(acetonitrile)	35.0	-51.4	1				
3 (acetonitrile)	25.0	-55.8			-53.9		
	30.0	-60.4	160.7	0.72	-57.6	117.4	0.57
	35.0	-63.1	1		-59.7	1	
-	25.0	-52.6			-53.2	-497.4	
3	30.0	-50.2	-271.2	-0.73	-42.0		-1.50
(40% water)	35.0	-45.3			-38.2		
	Ŗ						

647

Table 4

o1B

14R

$ \begin{array}{c} \hline Complexes/No. Wavelength (nm) & Osc. Strength Symmetry Major contribs \\ \hline [Zn_2(H_2)_1] (ClO_3)_A/ \\ \hline I & 409 & 1.1883 & singlet-A & H-1->LUMO (61%), HOMO->L+1 (10%), HOMO->L+2 (19%) \\ \hline 3 & 386 & 0.2703 & Singlet-A & H-3->L+1 (30%), H-2->LUMO (56%) \\ \hline 4 & 383 & 0.1788 & Singlet-A & H-3->L+1 (30%), H-2->LUMO (56%) \\ \hline 4 & 383 & 0.1788 & Singlet-A & H-3->L+1 (30%), H-2->LUMO (56%) \\ \hline 5 & 321 & 0.1483 & Singlet-A & H-5->L+1 (42%), H-4->L+3 (37%) \\ \hline 6 & 318 & 0.2770 & Singlet-A & H-5->L+2 (40%), H-4->L+3 (37%) \\ \hline 7 & 311 & 1.2244 & Singlet-A & H-7->LUMO (38%), H-6->L+1 (26% \\ \hline 8 & 309 & 0.5227 & Singlet-A & H-7->LUMO (36%), H-6->L+1 (26% \\ \hline 7 & 311 & 0.223 & Singlet-A & H-7->LUMO (26%), H-9->L+3 (11%), H-6->L+2 (32%) \\ \hline 2 & 404 & 1.0223 & Singlet-A & H-2->LUMO (76%) \\ \hline 3 & 399 & 0.3442 & Singlet-A & H-2->LUMO (76%) \\ \hline 3 & 399 & 0.3442 & Singlet-A & H-2->LUMO (76%) \\ \hline 5 & 386 & 0.2218 & Singlet-A & H-2->LUMO (76%) \\ \hline 6 & 383 & 0.1555 & Singlet-A & H-2->LUMO (76%) \\ \hline 7 & 379 & 0.1111 & Singlet-A & H-1->L+2 (31%), H-1->L+3 (63\%) \\ \hline 7 & 379 & 0.1111 & Singlet-A & H-2->LUMO (14%), H-3->L+3 (24%), HOMO->L+2 (11%) \\ \hline 6 & 383 & 0.1565 & Singlet-A & H-1->L+2 (31%), H-1->L+3 (63\%) \\ \hline 10 & 313 & 0.2126 & Singlet-A & H-3->L+2 (22%), H-4-1+2 (57%) \\ \hline 11 & 312 & 0.5705 & Singlet-A & H-1->L+2 (13\%), H-1->L+3 (63\%) \\ \hline 11 & 312 & 0.5705 & Singlet-A & H-1-3-L+2 (13\%), H-1-2L+3 (57\%) \\ \hline 12 & 310 & 0.3014 & Singlet-A & H-1-3-L+2 (13\%), H-1-2L+3 (17\%) \\ \hline 12 & 310 & 0.3014 & Singlet-A & H-1-3-L+2 (13\%), H-1-2L+1 (17\%) \\ \hline 13 & 0.2266 & Singlet-A & H-1-3-L+2 (19\%), HOMO-3L+3 (11\%) \\ \hline 2 & 407 & 0.5297 & Singlet-A & H-1-3-L+2 (19\%), HOMO-3L+3 (11\%) \\ \hline 2 & 407 & 0.5297 & Singlet-A & H-1-3-L+2 (69\%), HOMO-3L+3 (11\%) \\ \hline 3 & 401 & 0.8009 & Singlet-A & H-1-3-L+2 (75\%), H-2-3-L+1 (15\%), HOMO-3L+3 (10\%) \\ \hline 3 & 380 & 0.3679 & Singlet-A & H-1-3-L+2 (75\%), H-2-3-L+1 (15\%), HOMO-3L+3 (10\%) \\ \hline 3 & 381 & 0.3579 & Singlet-A & H-1-3-L+2 (75\%), H-2-3-L+1 (19\%) \\ \hline 3 & 300 & 0.2816 & Singlet-A & H-1-3-L+2 (17\%), H-3-L+1 $	3					
$ \begin{bmatrix} 2n_2(H_2L)_2 \\ Clo_4)_A / \\ 1 & 409 & 1.1883 & Singlet-A & H-1->L+3 (72%), HOMO->L+1 (10%), HOMO->L+2 (19%) \\ 2 & 399 & 0.3167 & Singlet-A & H-3->L+1 (30%), H-2->LUMO (56%) \\ 4 & 383 & 0.1788 & Singlet-A & H-3->L+1 (19%), H-3->L+2 (14%), H-2->LUMO (30%), H-2->L+3 (30%) \\ 5 & 321 & 0.1483 & Singlet-A & H-3->L+1 (19%), H-3->L+2 (14%), H-2->LUMO (30%), H-2->L+3 (30%) \\ 6 & 318 & 0.2770 & Singlet-A & H-5->L+2 (20%), H-4->L+3 (14%), H-2->L+3 (25%) \\ 7 & 311 & 1.2244 & Singlet-A & H-7->L42 (40%), H-6->L+1 (26% \\ 8 & 309 & 0.5227 & Singlet-A & H-7->L+3 (40%), H-6->L+1 (14%), H-6->L+2 (32%) \\ 9 & 298 & 0.1202 & Singlet-A & H-9->LUMO (26%), H-9->L+3 (11%), H-8->L+2 (28%) \\ \hline [Zn_2(H_1L)_2] F_2 (COL_0)_7 / \\ 1 & 415 & 0.6329 & Singlet-A & H-0MO->L+2 (70%), H-1->L+3 (11%) \\ 2 & 404 & 1.0223 & Singlet-A & H-2->LUMO (76%) \\ 3 & 399 & 0.3442 & Singlet-A & H-2->LUMO (76%) \\ 3 & 399 & 0.3442 & Singlet-A & H-2->LH (88\%) \\ 5 & 386 & 0.2218 & Singlet-A & H-2->LH (88\%) \\ 5 & 386 & 0.2218 & Singlet-A & H-2->LH (63\%), H-1->L+3 (24\%), HOMO->L+2 (11%) \\ 6 & 383 & 0.1455 & Singlet-A & H-1->L+2 (31%), H-1->L+3 (63%) \\ 7 & 379 & 0.1111 & Singlet-A & H-3->L+2 (22%), H-4->L+3 (25\%), H-3->L+1 (23\%) \\ 8 & 337 & 0.1561 & Singlet-A & H-5->L+2 (22\%), H-4->L+3 (25\%), H-4->L+3 (51\%) \\ 9 & 336 & 0.104 & Singlet-A & H-5->L+2 (22\%), H-4->L+3 (25\%), H-4->L+3 (41\%), H-7->LUMO (13%) \\ 10 & 313 & 0.2126 & Singlet-A & H-13->L+2 (11\%), H-12->L+3 (10\%), H-12->L+3 (14\%), H-7->LUMO (13\%) \\ 11 & 312 & 0.5705 & Singlet-A & H-13->L+2 (11\%), H-12->L+3 (10\%), H-12->L+3 (14\%), H-7->LUMO (13\%) \\ 12 & 100 & 0.3014 & Singlet-A & H-13->L+2 (11\%), H-12->L+3 (10\%), H-4->L+1 (15\%) \\ 12 & 110 & 0.3014 & Singlet-A & H-13->L+2 (11\%), H-12->L+3 (10\%), H-6->L+1 (15\%) \\ 12 & 110 & 0.3014 & Singlet-A & H-13->L+2 (10\%), H-12->L+3 (10\%), H-6->L+1 (15\%) \\ 12 & 110 & 0.2561 & Singlet-A & H-13->LUMO (25\%), H-0->L+1 (15\%), HOMO->L+2 (10\%) \\ 3 & 401 & 0.8009 & Singlet-A & H-13->LUMO (25\%), H-0->L+1 (15\%), HOMO->L+2 (10\%) \\ 3 & 401 & 0.8009 & Singlet-A & H-13->LUMO (25\%), H-2->L+1$		Com	nplexes,	/No. Wavel	ength (nm)	Osc. Strength Symmetry Major contribs
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		[Zn ₂	$(H_2L)_2$	(ClO ₄) ₄ /		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		1	409	1.1883	Singlet-A	H-1->LUMO (61%), HOMO->L+1 (10%), HOMO->L+2 (19%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		2	399	0.3167	Singlet-A	H-1->L+3 (72%), HOMO->L+1 (16%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		3	386	0.2703	Singlet-A	H-3->L+1 (30%), H-2->LUMO (56%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		4	383	0.1788	Singlet-A	H-3->L+1 (19%), H-3->L+2 (14%), H-2->LUMO (30%), H-2->L+3 (30%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		5	321	0.1483	Singlet-A	H-5->L+1 (42%), H-4->LUMO (43%)
73111.2244Singlet-AH-7->LUMO (38%), H-6->L+1 (26%83090.5227Singlet-AH-7->L+3 (40%), H-6->L+1 (14%), H-6->L+2 (32%)92980.1202Singlet-AH-9->LUMO (26%), H-9->L+3 (11%), H-8->L+2 (28%) $[Zn_2(H_2L)_2] F_2 (Clo_4)_2/$ 14150.6329Singlet-A14150.6329Singlet-AHOMO->L+2 (70%), H-1->L+3 (11%)24041.0223Singlet-AH-2->LUMO (76%)33990.3442Singlet-AH-2->L+1 (88%)53860.2218Singlet-AH-2->L+1 (88%)53860.2118Singlet-AH-1->L+2 (64%), H-1->L+3 (24%), HOMO->L+2 (11%)63830.1456Singlet-AH-1->L+2 (64%), H-1->L+3 (63%)73790.1111Singlet-AH-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%)93360.104Singlet-AH-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%)93360.104Singlet-AH-12->L+3 (13%), H-7->LUMO (25%), H-6->L+1 (17%)113120.5705Singlet-AH-12->L+3 (13%), H-7->LUMO (25%), H-6->L+1 (34%)133000.2969Singlet-AH-1->L+7 (18%), HOMO->L+2 (10%), H-6->L+1 (15%)[Zn2(H_3L)_2] (CH_3COD)_2 (ClO_4)_7IH150.256114150.2561Singlet-AH-1->L+2 (10%), HOMO->L+3 (15%)[Zn2(H_3L)_2] (CH_3COD)_2 (ClO_4)_7IH150.259714150.2597Singlet-AH-1->L+2 (15%), HOMO->L+3 (15%), HOMO->L+2 (10%) </td <td></td> <td>6</td> <td>318</td> <td>0.2770</td> <td>Singlet-A</td> <td>H-5->L+2 (40%), H-4->L+3 (37%)</td>		6	318	0.2770	Singlet-A	H-5->L+2 (40%), H-4->L+3 (37%)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		7	311	1.2244	Singlet-A	H-7->LUMO (38%), H-6->L+1 (26%
92980.1202Singlet-AH-9->LUMO (26%), H-9->L+3 (11%), H-8->L+2 (28%) $[Zn_2(H_2L)_2]$ F2 (ClO4)2/14150.6329Singlet-AHOMO->L+2 (70%), H-1->L+3 (11%)24041.0223Singlet-AH-2->LUMO (76%)33990.3442Singlet-AH-2->LUMO (76%)43930.1555Singlet-AH-2->L+1 (88%)53860.2218Singlet-AH-1->L+2 (10%), HOMO->L+2 (17%)68830.1456Singlet-AH-1->L+2 (64%), H-1->L+3 (63%)73790.1111Singlet-AH-1->L+2 (23%), H-3->L+3 (63%)73790.1111Singlet-AH-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%)93360.104Singlet-AH-5->L+2 (29%), H-4->L+3 (57%) H-5->L+3 (9%)103130.2126Singlet-AH-13->L+2 (11%), H-12->L+2 (10%), H-12->L+3 (41%), H-7->LUMO (13%)113120.5705Singlet-AH-13->L+2 (11%), H-7->LUMO (25%), H-6->L+1 (17%)123100.3014Singlet-AH-12->L+3 (13%), H-7->LUMO (25%), H-6->L+1 (34%)133000.2969Singlet-AH-10->L+2 (69%), HOMO->L+3 (11%)24070.5297Singlet-AH-2->LUMO (26%), H-2->L+1 (15%), HOMO->L+2 (10%)34010.8009Singlet-AH-2->LUMO (26%), H-2->L+1 (15%), HOMO->L+2 (10%)43930.2555Singlet-AH-2->LUMO (26%), H-2->L+1 (15%)53880.3579Singlet-AH-2->LUMO (26%), H-2->L+1 (15%)4393 <t< td=""><td></td><td>8</td><td>309</td><td>0.5227</td><td>Singlet-A</td><td>H-7->L+3 (40%), H-6->L+1 (14%), H-6->L+2 (32%)</td></t<>		8	309	0.5227	Singlet-A	H-7->L+3 (40%), H-6->L+1 (14%), H-6->L+2 (32%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		9	298	0.1202	Singlet-A	H-9->LUMO (26%), H-9->L+3 (11%), H-8->L+2 (28%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		[Zn ₂	$(H_2L)_2$	$F_2 (ClO_4)_2 /$		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	415	0.6329	Singlet-A	HOMO->L+2 (70%), H-1->L+3 (11%)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2	404	1.0223	Singlet-A	H-2->LUMO (76%)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3	399	0.3442	Singlet-A	HOMO->L+2 (10%), HOMO->L+3 (87%)
53860.2218Singlet-AH-1->L+2 (64%), H-1->L+3 (24%), HOMO->L+2 (11%)63830.1456Singlet-AH-1->L+2 (31%), H-1->L+3 (63%)73790.1111Singlet-AH-4->LUMO (10%), H-3->LUMO (48%), H-3->L+1 (23%)83370.1561Singlet-AH-4->LUMO (10%), H-3->LUMO (48%), H-3->L+1 (23%)93360.104Singlet-AH-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%)93360.104Singlet-AH-5->L+2 (29%), H-4->L+3 (57%)H-5->L+3 (9%)103130.2126Singlet-AH-13->L+2 (11%), H-12->L+2 (10%), H-12->L+3 (41%), H-7->LUMO (13%)113120.5705Singlet-AH-13->L+2 (11%), H-12->L+2 (10%), H-6->L+1 (17%)123100.3014Singlet-AH-7->LUMO (28%), H-6->LUMO (14%), H-6->L+1 (34%)133000.2969Singlet-AH-1->L+2 (69%), HOMO->L+6 (58%), HOMO->L+7 (15%)[Zn2(H ₂ L) ₂] (CH ₃ COO) ₂ (ClO ₄) ₂ /I4150.256114150.2561Singlet-AHOMO->L+2 (69%), HOMO->L+3 (11%)24070.5297Singlet-AH-2->LUMO (20%), H-2->L+1 (15%), HOMO->L+2 (10%)34010.8009Singlet-AH-1->L+2 (78%), HOMO->L+3 (16%)43930.2555Singlet-AH-1->L+2 (77%), H-7->L+2 (11%)53880.3579Singlet-AH-4->LUMO (86%)73170.3021Singlet-AH-1+>LUMO (27%), H-9->L+1 (49%)93100.2816Singlet-AH-11->LUMO (52%), H-9->L+1 (31%) <td></td> <td>4</td> <td>393</td> <td>0.1555</td> <td>Singlet-A</td> <td>H-2->L+1 (88%)</td>		4	393	0.1555	Singlet-A	H-2->L+1 (88%)
6 383 0.1456 Singlet-A H-1->L+2 (31%), H-1->L+3 (63%) 7 379 0.1111 Singlet-A H-4->LUMO (10%), H-3->LUMO (48%), H-3->L+1 (23%) 8 337 0.1561 Singlet-A H-4->LUMO (10%), H-3->LUMO (48%), H-3->L+1 (23%) 9 336 0.104 Singlet-A H-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%) 9 336 0.104 Singlet-A H-5->L+2 (29%), H-4->L+3 (57%) H-5->L+3 (9%) 10 313 0.2126 Singlet-A H-13->L+2 (11%), H-12->L+2 (10%), H-12->L+3 (41%), H-7->LUMO (13%) 11 312 0.5705 Singlet-A H-12->L+3 (13%), H-7->LUMO (25%), H-6->L+1 (17%) 12 310 0.3014 Singlet-A H-7->LUMO (28%), H-6->LUMO (14%), H-6->L+1 (34%) 13 300 0.2969 Singlet-A H-1->L+7 (18%), HOMO->L+6 (58%), HOMO->L+7 (15%) [Zn ₂ (H ₂ L) ₂] (CH ₃ COO) ₂ (ClO ₄) ₂ / 1 415 0.2561 Singlet-A HOMO->L+2 (69%), HOMO->L+3 (11%) 2 407 0.5297 Singlet-A H-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%) 3 401 0.8009 Singlet-A HOMO->L+2 (15%), HOMO->L+3 (67%) 4 393 0.2555 Singlet-A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-4->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		5	386	0.2218	Singlet-A	H-1->I+2 (64%), H-1->I+3 (24%), HOMO->I+2 (11%)
73790.1111Singlet-AH-4->LUMO (10%), H-3->LUMO (48%), H-3->L+1 (23%)83370.1561Singlet-AH-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%)93360.104Singlet-AH-5->L+2 (29%), H-4->L+3 (57%) H-5->L+3 (9%)103130.2126Singlet-AH-13->L+2 (11%), H-12->L+2 (10%), H-12->L+3 (41%), H-7->LUMO (13%)113120.5705Singlet-AH-12->L+3 (13%), H-7->LUMO (25%), H-6->L+1 (17%)123100.3014Singlet-AH-1->L+7 (18%), HOMO->L+6 (58%), HOMO->L+1 (34%)133000.2969Singlet-AH-1->L+7 (18%), HOMO->L+3 (11%)[Zn2(H2L)2] (CH3COO)2 (CIO4)2 /II4150.256114150.2561Singlet-AH-0MO->L+2 (69%), HOMO->L+3 (11%)24070.5297Singlet-AH-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%)34010.8009Singlet-AH-0MO->L+2 (15%), HOMO->L+3 (67%)43930.2555Singlet-AH-2->LUMO (20%), H-2->L+1 (17%)53880.3579Singlet-AH-1->L+2 (77%), H-7->L+2 (11%)63840.1465Singlet-AH-4->LUMO (86%)73170.3021Singlet-AH-8->L+2 (77%), H-7->L+2 (11%)83120.7559Singlet-AH-1-1-LUMO (27%), H-9->L+1 (49%)93100.2816Singlet-AH-11->LUMO (52%), H-9->L+1 (31%)		6	383	0.1456	Singlet-A	H-1->L+2 (31%), H-1->L+3 (63%)
83370.1561Singlet-AH-5->L+2 (22%), H-5->L+3 (22%), H-4->L+2 (51%)93360.104Singlet-AH-5->L+2 (29%), H-4->L+3 (57%) H-5->L+3 (9%)103130.2126Singlet-AH-13->L+2 (11%), H-12->L+2 (10%), H-12->L+3 (41%), H-7->LUMO (13%)113120.5705Singlet-AH-12->L+2 (11%), H-12->L+2 (10%), H-6->L+1 (17%)123100.3014Singlet-AH-7->LUMO (28%), H-6->LUMO (14%), H-6->L+1 (34%)13300.2969Singlet-AH-1->L+7 (18%), HOMO->L+6 (58%), HOMO->L+7 (15%) $[Zn_2(H_2L)_2]$ $[CH_3COO)_2$ $(ClO_4)_2/$ 14150.2561Singlet-AHOMO->L+2 (69%), HOMO->L+3 (11%)24070.5297Singlet-AH-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%)34010.8009Singlet-AHOMO->L+2 (15%), HOMO->L+3 (67%)43930.2555Singlet-AH-1->L+2 (78%), HOMO->L+3 (16%)63840.1465Singlet-AH-4->LUMO (86%)73170.3021Singlet-AH-4->LUMO (27%), H-9->L+1 (49%)83120.7559Singlet-AH-11->LUMO (27%), H-9->L+1 (31%)		7	379	0.1111	Singlet-A	H-4->LUMO (10%), H-3->LUMO (48%), H-3->L+1 (23%)
9 336 0.104 Singlet A H-5->L+2 (22%), H-4->L+3 (57%) H-5->L+3 (9%) 10 313 0.2126 Singlet A H-13->L+2 (11%), H-12->L+3 (17%), H-7->LUMO (13%) 11 312 0.5705 Singlet A H-13->L+2 (11%), H-12->L+2 (10%), H-12->L+3 (41%), H-7->LUMO (13%) 12 310 0.3014 Singlet A H-12->L+3 (13%), H-7->LUMO (25%), H-6->L+1 (17%) 13 300 0.2969 Singlet A H-1->L+7 (18%), HOMO->L+6 (58%), HOMO->L+7 (15%) [$Zn_2(H_2L)_2$] (CH_3COO) ₂ (CIO_4) ₂ / 1 415 0.2561 Singlet A H-1->L+7 (18%), HOMO->L+3 (11%) 2 407 0.5297 Singlet A H-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%) 3 401 0.8009 Singlet A H-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%) 4 393 0.2555 Singlet A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet A H-4->LUMO (86%) 7 317 0.3021 Singlet A H-8->L+2 (77%), H-7->L+2 (11%) 8 312 0.7559 Singlet A H-11->LUMO (27%), H-9->L+1 (31%)		8	337	0 1561	Singlet-A	H-5->I+2 (22%), $H-5->I+3$ (22%), $H-4->I+2$ (51%)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		9	336	0 104	Singlet-A	H-5 - > I + 2 (29%), H-5 - > I + 3 (57%) H-5 - > I + 3 (9%)
103130.2120Singlet AH 13 × L/2 (11/3), H 12 × L/2 (10/3), H 12 × L/3 (11/3), H 12 × L/3 (11/3) H 12 × L/3 (11/3), H 12 × L/3 (11/3), H 12 × L/3 (11/3)		10	313	0 2126	Singlet-A	$H_{-13->1+2}(11\%)$ $H_{-12->1+2}(10\%)$ $H_{-12->1+3}(41\%)$ $H_{-7->11}MO(13\%)$
11312 0.5705 Singlet-A $H-12->L+3$ (13%), $H-7->LUMO$ (25%), $H-6->L+1$ (17%)12310 0.3014 Singlet-A $H-7->LUMO$ (28%), $H-6->LUMO$ (14%), $H-6->L+1$ (34%)13300 0.2969 Singlet-A $H-1->L+7$ (18%), $HOMO->L+6$ (58%), $HOMO->L+7$ (15%) $[Zn_2(H_2L)_2]$ ($CH_3COO)_2$ ($CIO_4)_2/$ I 415 0.2561 Singlet-A1415 0.2561 Singlet-A $HOMO->L+2$ (69%), $HOMO->L+3$ (11%)2407 0.5297 Singlet-A $H-2->LUMO$ (62%), $H-2->L+1$ (15%), $HOMO->L+2$ (10%)3401 0.8009 Singlet-A $H-2->LUMO$ (20%), $H-2->L+1$ (15%), $HOMO->L+2$ (10%)4393 0.2555 Singlet-A $H-2->LUMO$ (20%), $H-2->L+1$ (70%)5388 0.3579 Singlet-A $H-1->L+2$ (78%), $HOMO->L+3$ (16%)6384 0.1465 Singlet-A $H-4->LUMO$ (86%)7317 0.3021 Singlet-A $H-8->L+2$ (77%), $H-7->L+2$ (11%)8312 0.7559 Singlet-A $H-11->LUMO$ (27%), $H-9->L+1$ (49%)9310 0.2816 Singlet-A $H-11->LUMO$ (52%), $H-9->L+1$ (31%)		10	515	0.2120	Singlet A	
113120.5/03Singlet AIn 12 2 kto (15/k), In 7 2 kto (125/k), In 6 2 kto (17/k)123100.3014Singlet-AH-7->LUMO (28%), H-6->LUMO (14%), H-6->L+1 (34%)133000.2969Singlet-AH-1->L+7 (18%), HOMO->L+6 (58%), HOMO->L+7 (15%) $[Zn_2(H_2L)_2]$ (CH ₃ COO) ₂ (ClO ₄) ₂ /14150.2561Singlet-A14150.2561Singlet-AHOMO->L+2 (69%), HOMO->L+3 (11%)24070.5297Singlet-AH-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%)34010.8009Singlet-AHOMO->L+2 (15%), HOMO->L+3 (67%)43930.2555Singlet-AH-2->LUMO (20%), H-2->L+1 (70%)53880.3579Singlet-AH-1->L+2 (78%), HOMO->L+3 (16%)63840.1465Singlet-AH-4->LUMO (86%)73170.3021Singlet-AH-8->L+2 (77%), H-7->L+2 (11%)83120.7559Singlet-AH-11->LUMO (27%), H-9->L+1 (49%)93100.2816Singlet-AH-11->LUMO (52%), H-9->L+1 (31%)		11	312	0 5705	Singlet_A	H-12->I+3 (13%) H-7->I IIMO (25%) H-6->I+1 (17%)
123100.3014Singlet AH172LONIO (28%), H072LONIO (14%), H		12	312	0.3703	Singlet-A	$H_{12} \to UIMO(28\%)$ $H_{-6} \to UIMO(11\%)$ $H_{-6} \to U1(17\%)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		12	300	0.3014	Singlet_A	$H_1 > L_7 (18\%) HOMO > L_6 (58\%) HOMO > L_7 (15\%)$
1 415 0.2561 Singlet-A HOMO->L+2 (69%), HOMO->L+3 (11%) 2 407 0.5297 Singlet-A H-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%) 3 401 0.8009 Singlet-A HOMO->L+2 (15%), HOMO->L+3 (67%) 4 393 0.2555 Singlet-A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-4->LUMO (27%), H-7->L+2 (11%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		 [7n	<u> </u>			
1 413 0.2301 Singlet-A HOMO->L+2 (03%), HOMO->L+3 (11%) 2 407 0.5297 Singlet-A H-2->LUMO (62%), H-2->L+1 (15%), HOMO->L+2 (10%) 3 401 0.8009 Singlet-A HOMO->L+2 (15%), HOMO->L+3 (67%) 4 393 0.2555 Singlet-A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-8->L+2 (77%), H-7->L+2 (11%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		1	/125	0.2561	Singlet A	
2 407 0.3257 Singlet-A HP2+2L0HO (02.%), HP2+2L11 (15.%), HOMO+2L12 (10.%) 3 401 0.8009 Singlet-A HOMO+2L+2 (15%), HOMO+2L+3 (67%) 4 393 0.2555 Singlet-A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-4->LUMO (27%), H-7->L+2 (11%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		2	415	0.2301	Singlet-A	$H_{2} = 1000 - 2000, H_{2} = 1000 - 2000, H_{2} = 1000 - 2000, H_{2} = 1000, H_{2} =$
3 401 0.8009 Singlet-A HOMO-2L+2 (13%), HOMO-2L+3 (07%) 4 393 0.2555 Singlet-A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-4->LUMO (86%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		2	407	0.3237	Singlet A	$H_{2} > 1000 (02.0), H_{2} > 11 (13.0), HOMO > 12 (10.0)$
4 393 0.2333 Singlet-A H-2->LUMO (20%), H-2->L+1 (70%) 5 388 0.3579 Singlet-A H-1->L+2 (78%), HOMO->L+3 (16%) 6 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-8->L+2 (77%), H-7->L+2 (11%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		3	202	0.0005	Singlet A	$H = 2 \times H MO (2000) + 2 \times H = 1 (7000)$
3 388 0.3373 Singlet-A H=1=2L+2 (78%), HORIO=2L+3 (10%) 6 384 0.1465 Singlet-A H=4=>LUMO (86%) 7 317 0.3021 Singlet-A H=8=>L+2 (77%), H=7=>L+2 (11%) 8 312 0.7559 Singlet-A H=11=>LUMO (27%), H=9=>L+1 (49%) 9 310 0.2816 Singlet-A H=11=>LUMO (52%), H=9=>L+1 (31%)		4 5	292	0.2555	Singlet A	$H = 1 \times 1 \times 2 \times$
0 384 0.1465 Singlet-A H-4->LUMO (86%) 7 317 0.3021 Singlet-A H-8->L+2 (77%), H-7->L+2 (11%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		5	200	0.3375	Singlet A	11-1-2L+2(7876), 1101010-2L+3(1076)
7 317 0.3021 Singlet-A H-8->L+2 (77%), H-7->L+2 (11%) 8 312 0.7559 Singlet-A H-11->LUMO (27%), H-9->L+1 (49%) 9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		0	384	0.1405	Singlet-A	Π -4->LUIVIU (80%)
9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (49%)		/	317	0.3021	Singlet-A	H-8->L+2 (//%), H-/->L+2 (11%)
9 310 0.2816 Singlet-A H-11->LUMO (52%), H-9->L+1 (31%)		8	312	0.7559	Singlet-A	H-11->LUNIO(27%), H-9->L+1(49%)
		9	310	0.2816	Singlet-A	H-11->LUMO (52%), H-9->L+1 (31%)
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818 Research Highlights

819	•	Three new macrocyclic dinuclear complexes, containing amide and hydrazine groups were synthesized and characterized.
820	•	The macrocyclic dinuclear molecule is a square cage with edges of length around 8.4 Å.
821	•	The complexes can recognize acetate and fluoride anions in an acetonitrile solution containing 60% volume water.
822	•	The anion recognition is through exothermic and entropy-reducing reactions.
823	•	The dinuclear zinc(II) complex can be used for colorimetric "naked eye" recognition of acetate or fluoride anions.
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