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A Selective Metal–Ligand Fluorescent Chemosensor for Dihydrogen Phosphate via Intermolecular Excimer Formation in Water

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Two new anthrylpolyamine ligands and their zinc complexes **1**·2Zn and **2**·Zn have been synthesized. The recognition ability of **1**·2Zn and **2**·Zn towards inorganic anions was studied by fluorescence spectroscopy in water at physiological pH values. The receptor **1**·2Zn displays an excellent selective fluorescent enhancement of the excimer emissive peak with $H_2PO_4^-$ that is absent with other inorganic anions such as SO_4^{2-}, NO_3^-, HCO_3^-, AcO^-, F^-, Cl^-, Br^- and I^-. The obvious excimer formation can be explained by 2+2-type binding between **1**·2Zn and $H_2PO_4^-$, which was confirmed by electrospray ionization data. The sensitive fluorescent response and excellent selectivity show that receptor **1**·2Zn can be used as a fluorescent chemosensor for the $H_2PO_4^-$ anion under physiological pH conditions.

Introduction

Anions play a huge number of key roles in biological processes, and the design of a chemosensor for selective recognition and sensing of a particular anion has received considerable attention.[1] Many anion receptors containing amide, urea and thiourea subunits, which can form hydrogen-bonded complexes with some anions, have been extensively investigated.[2] The main drawback of such receptors is that they cannot show sensing properties in aqueous solvents because the aqueous solvent competes strongly for the hydrogen-bonding sites. Therefore, their application as chemosensors is very limited. Sensors that can detect and sense biologically important anions in aqueous environments and at physiological pH are of special significance owing to their potential applications as biological markers.[3]

Sensors based on anion-induced changes in fluorescence appear to be particularly attractive due to the simplicity and high detection limit of the fluorescence.[4] A fluorescent anion sensor for use in aqueous solution must meet two requirements. One is a sufficiently strong affinity for anions in water and the other is the ability to convert anion recognition into a fluorescence signal. The metal–ligand interaction can be highly energetic as a result of strong ligand-field stabilization energy effects induced by coordination; the energy of the metal–ligand interaction is much higher than the energy associated with electrostatic interactions.[5] Therefore metal–ligand receptors have a stronger affinity for anions in the competitive water.[6]

Czarnik reported his pioneering work on anthrylpolyamine fluorescent chemosensors for anion recognition.[7] In recent decades, anthrylpolyamines have been widely researched in pH switching and in the recognition of various anions.[8]

Phosphate ions and their derivatives play important roles in signal transduction and energy storage in biological systems.[9] Although many fluorescent chemosensors for $H_2PO_4^-$ have been reported,[10] sensors that can selectively recognize and sense $H_2PO_4^-$ in water under physiological pH conditions are still rare.[11]

In this paper we report two metal–ligand receptors **1**·2Zn and **2**·Zn that contain anthrylpolyamines. Both exhibit selective recognition and a fluorescent response with $H_2PO_4^-$ that is absent with other inorganic anions such as $CH_3CO_2^-$, F^-, Cl^-, Br^- and I^-. Upon the addition of $H_2PO_4^-$, the sensor **1**·2Zn shows a significant fluorescence increase of the excimer emissive peak. To the best of our knowledge, a fluorescent chemosensor that can display unique excimer formation with $H_2PO_4^-$ in water has not been reported.

Results and Discussion

Synthesis

Polyamine ligands **1** and **2** bearing the same fluorophore were obtained easily by the same process from 9,10-bis(aminomethyl)- and 9-aminomethylanthracene, respectively.[12] The metal complexes **1**·2Zn and **2**·Zn were obtained by the

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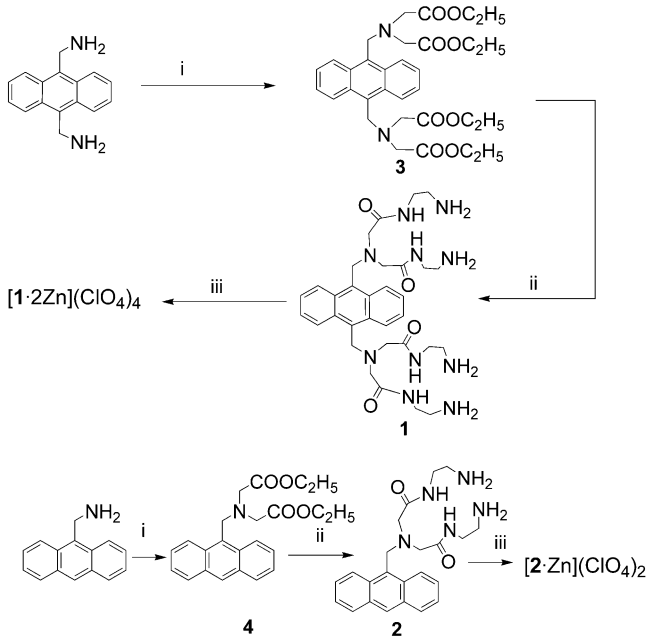
reaction of ligands **1** and **2** with $Zn(ClO_4)_2 \cdot 6H_2O$ in methanol. The synthetic route to the receptors is shown in Scheme 1.



Scheme 1. Synthetic route to the receptors **1**·2Zn and **2**·Zn. Reagents and conditions: i) $BrCH_2COOC_2H_5$, K_2HPO_4, KI, CH_3CN, reflux; ii) ethylenediamine, $CHCl_3$, C_2H_5OH; iii) $Zn(ClO_4)_2 \cdot 6H_2O$, CH_3OH.

Fluorescence and UV/Vis Study

The binding properties of **1**·2Zn towards $H_2PO_4^-$, SO_4^{2-}, NO_3^-, HCO_3^-, AcO^-, F^-, Cl^-, Br^- and I^- were investigated in water (0.01 HEPES buffer, pH = 7.4) in the presence of 0.15 M KCl to maintain a constant ionic strength.

Figure 1 shows the change in the fluorescence emission spectra of **1**·2Zn at different concentrations of $H_2PO_4^-$ (λ_{ex} = 370 nm). In the absence of anions, the fluorescence emission spectra of **1**·2Zn showed three well-defined bands (411, 432 and 457 nm) of anthracene centred at 432 nm.[3b,13] On gradually increasing the concentration of $H_2PO_4^-$, the monomer emission bonds at 411 and 432 nm were slightly quenched, the band at 457 nm was remarkably enhanced with a clear bathochromic shift from 457 to 490 nm and a noticeable isoemissive point at 438 nm was observed. It was particular noteworthy that the band at 490 nm reached a maximum after adding 23 equiv. of $H_2PO_4^-$. The fluorescent quenching effect of the monomer emission at 411 and 432 nm could be due to a photoinduced electron-transfer (PET) mechanism, as explained in the preceding reports.[2a,14] On the other hand, the peak at 490 nm corresponds to the excimer emission of anthracenes.[15]

The anion-recognition properties of **1**·2Zn with other anions were also investigated. Under the same conditions, NO_3^-, HCO_3^-, AcO^-, F^-, Cl^-, Br^- and I^- cause only a minor fluctuation in monomer fluorescence intensity. Addition of a large amount of SO_4^{2-}, however, did also lead to an increase in the band at 490 nm (see the Supporting Information), as shown in Figure 2, which indicates that receptor **1**·2Zn is a highly selective fluorescent probe for $H_2PO_4^-$.

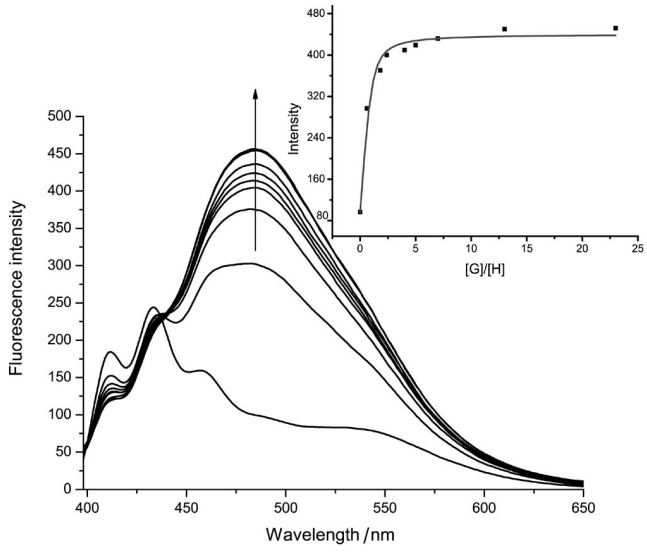


Figure 1. Fluorescence emission spectra of **1**·2Zn (5×10^{-5} mol L^{-1}) with the $H_2PO_4^-$ anion in water (0.01 M HEPES buffer, pH = 7.4, 0.15 M KCl). Equivalents of anion: 0→23.0. λ_{ex} = 370 nm. Inset: changes in fluorescence intensity at 490 nm upon addition of the $H_2PO_4^-$ anion; the line is afitting curve.

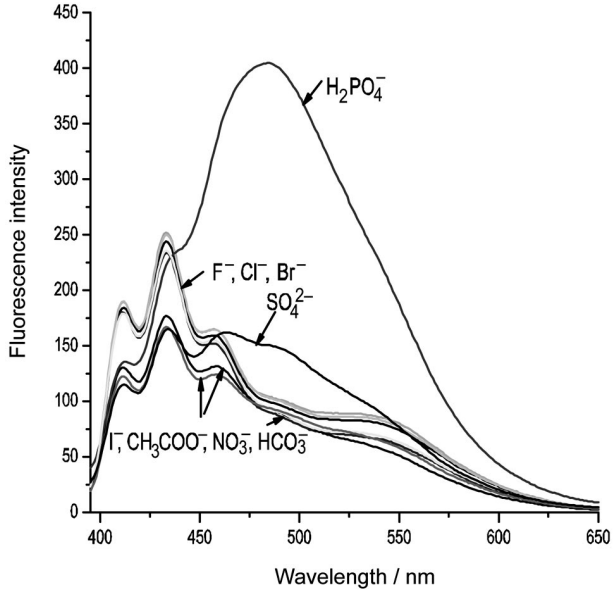


Figure 2. Fluorescence emission spectra of **1**·2Zn (5×10^{-5} mol·L^{-1}) in water (0.01 M HEPES buffer, pH = 7.4, 0.15 M KCl) after addition of $H_2PO_4^-$ (1 equiv.) and other anions (10 equiv.).

The chemosensor **1**·2Zn shows an excimer peak at 490 nm in the presence of $H_2PO_4^-$. A likely reason could be four zinc sites as well as the favourable π–π interaction between two flat anthracene moieties that can induce tight 2+2-type binding between **1**·2Zn and $H_2PO_4^-$.[16]

The electrospray ionization (ESI) mass spectrum of the complex **1**·2Zn was also studied to find further support for

this excimer formation. Two major peaks corresponding to $[(\mathbf{1}\cdot 2Zn)(OH)_4 + H]^+$ and $[(\mathbf{1}\cdot 2Zn)(OH)_4 + 2H_2O + H]^+$ were observed at m/z = 835 ($C_{32}H_{53}N_{10}O_8Zn_2$) and 871 ($C_{32}H_{57}N_{10}O_{10}Zn_2$), respectively. When the sodium salt of dihydrogen phosphate (1.1 equiv.) was added, two major peaks corresponding to $[2(\mathbf{1}\cdot 2Zn) + 2H_2PO_4^- + 4OH^- + 2H_2O]^{2+}$ and $[2(\mathbf{1}\cdot 2Zn) + 2H_2PO_4^- + 5OH^- + 2H_2O + Na^+]^{2+}$ were observed at m/z = 915 ($C_{64}H_{108}N_{20}O_{22}P_2Zn_4/2$) and 935 ($C_{64}H_{109}N_{20}O_{23}P_2Zn_4Na/2$), respectively (see the Supporting Information). The results suggest **1**·2Zn binds to $H_2PO_4^-$ as a 2+2 complex.

Of the various anions studied, the receptor showed excimer emission when interacting with $H_2PO_4^-$ and SO_4^{2-}, which can be ascribed to their tetrahedral structure. No excimer emission was observed with trigonal anions such as AcO^-, NO_3^- and HCO_3^-, and these may form 1:1 complexes with the receptor.

For comparison, mono-armed anthracene polyamine **2** was synthesized and its metal complex **2**·Zn was obtained as a pale-yellow precipitate when treated with 1 equiv. of $Zn(ClO_4)_2{\cdot}6H_2O$ in methanol. The binding properties of **2**·Zn towards $H_2PO_4^-$ were evaluated under the same conditions as those described above. On increasing the concentration of $H_2PO_4^-$, the monomer emission of anthracene was gradually quenched (Figure 3). In contrast to **1**·2Zn, no new excimer peak evolved, even when the concentration of $H_2PO_4^-$ was as high as 100 equiv. This chelation-enhanced fluorescence quenching effect upon addition of $H_2PO_4^-$ can be attributed to the classic photoinduced electron-transfer (PET) mechanism.[17]

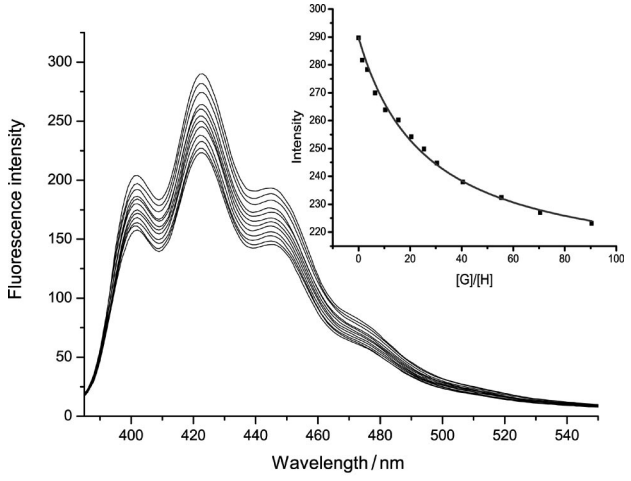


Figure 3. Fluorescence emission spectra of **2**·Zn (5×10^{-5} mol L^{-1}) with the $H_2PO_4^-$ anion in water (0.01 M HEPES buffer, pH = 7.4, 0.15 M KCl) at 25 °C. Equivalents of anion: 0→90.4. λ_{ex} = 370 nm. Inset: changes in fluorescence intensity at 422 nm upon addition of the $H_2PO_4^-$ anion. The line is a fitting curve.

The job-plot analysis indicated that receptor **2**·Zn formed a 1:1 complex with $H_2PO_4^-$ with an association constant of 2.63×10^2 M^{-1}, as determined by a non-linear least-squares fitting method. No clear fluorescent response was induced by other anions, which shows that **2**·Zn exerts a good selectivity for $H_2PO_4^-$.

When the $H_2PO_4^-$ anion interacts with the receptors, the electron density in the supermolecular system is increased, which enhances the ratio of electron transfer from the HOMO orbital of the complex to the excited anthracene unit and in turn leads to a more facile intramolecular PET process.[17] Therefore, anion-induced fluorescence quenching is observed. The UV/Vis study confirmed this explanation (Figure 4). The changes in the absorption spectra of the anthracene moiety were minor for **1**·2Zn (358, 377 and 398 nm) and **2**·Zn (348, 368 and 387 nm) in the presence of $H_2PO_4^-$, which implies that a PET process occurs with anion-binding.[18]

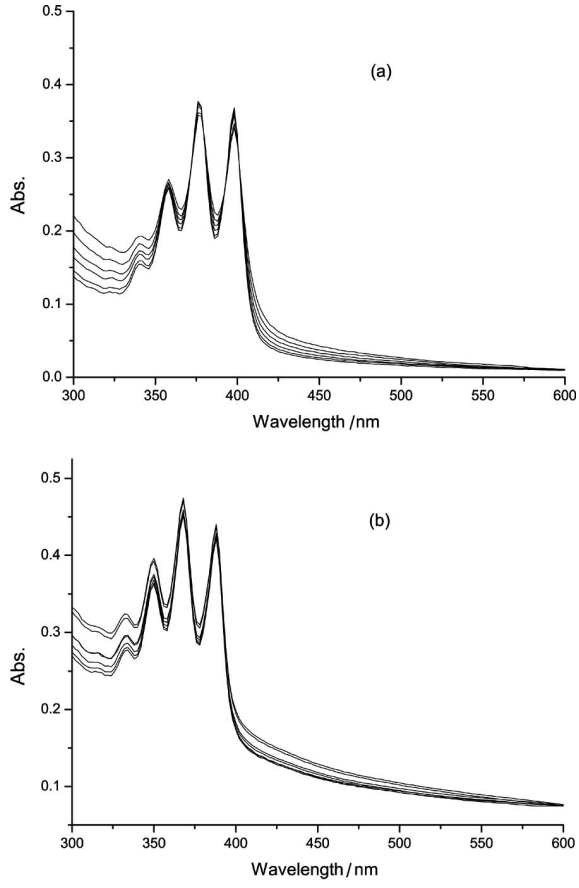


Figure 4. a) UV/Vis absorption spectra of **1**·2Zn (5×10^{-5} mol L^{-1}) with the $H_2PO_4^-$ anion. Equivalents of anion: 0→35.0. b) UV/Vis absorption spectra of **2**·Zn (5×10^{-5} mol L^{-1}) with the $H_2PO_4^-$ anion. Equivalents of anion: 0→85.6.

The dinuclear receptor **1**·2Zn displays an intermolecular excimer peak of anthracene on interaction with $H_2PO_4^-$, whereas such a change is not observed for the mononuclear receptor **2**·Zn. This may be due to the former bearing two metal coordination sites, such that the electrostatic attraction between the receptor and the anions is stronger. The formation of the remarkable excimer emission peak can be attributed to a $H_2PO_4^-$-induced self-assembly of host molecules, which leads to an intermolecular π–π stacking interaction between the hydrophobic aromatic rings, thereby inducing 2+2-type binding.[19]

To understand the specific fluorescence excimer emission peak of $H_2PO_4^-$ with **1**·2Zn we performed a geometry optimization of the interaction between **1**·2Zn and $H_2PO_4^-$. The energy-minimized structure shows that a π–π stacked anthracene dimer is formed upon $H_2PO_4^-$ complexation (Figure 5). This may contribute to a better understanding of the synergistic effect of the $H_2PO_4^-$ anion.

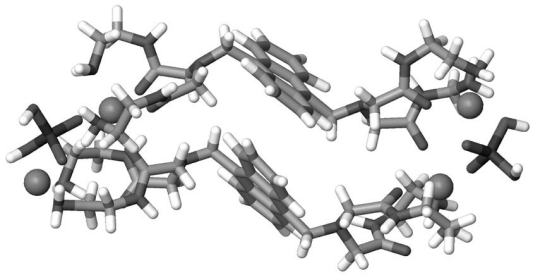


Figure 5. Optimized molecular complexation model for **1**·2Zn and $H_2PO_4^-$ based on PM3 of MOPAC 2007 software.

Assuming the stoichiometry of the complex was 1:1, the association constant (K_{ass}) can be calculated from Equation (1) in the Origin 7.0 software package,[20,21] where I represents the fluorescence intensity and c_H and c_G represent the corresponding concentration of the host and guest, respectively. The non-linear curve-fitting results of the fluorescence intensity of the interaction between **1**·2Zn and **2**·Zn and the anions are shown in Table 1. The association constant (K_{ass}) for **1**·2Zn with $H_2PO_4^-$ and SO_4^{2-} was also calculated from Equation (1) to show the relative selectivity, but it is not accurate.[22] It is too complicated to calculate the association constant for 2+2-type binding systems. The actual values are greater than those reported in Table 1.

$$I = I_0 + (I_{lim} - I_0)/2c_0\{c_H + c_G + 1/K_{ass} - [(c_H + c_G + 1/K_{ass})^2 - 4c_Hc_G]^{1/2}\} \quad (1)$$

Table 1. Association constants K_{ass} for the receptors **1**·2Zn and **2**·Zn with guest anions.

Anions	**1**·2Zn K_{ass}[a]	R[b]	**2**·Zn K_{ass} [M^{-1}][a]	R[b]
$H_2PO_4^-$	4.56×10^5[c]		2.63×10^2	0.9975
SO_4^{2-}	2.18×10^3[c]		1.32×10^2	0.9951
AcO^-	3.37×10^2	0.9954	82	0.9934
HCO_3^-	2.17×10^2	0.9984	32	0.9941
NO_3^-	64	0.9981	–[d]	
F^-	3.84×10^2	0.9912	–[d]	
Cl^-	–[d]		–[d]	
Br^-	–[d]		–[d]	
I^-	1.79×10^2	0.9937	1.13×10^2	0.9987

[a] The data were calculated from the results of fluorescence titrations in water. [b] All error values were obtained from non-linear curve fitting. [c] For 2+2-type binding, K_{ass} was also calculated by Equation (1) and the unit is M^{-3}. [d] The association constants could not be calculated precisely because the signal change was too small to provide reliable data with a tolerable error.

Conclusions

Two novel anthracene-based fluorescent chemosensors **1**·2Zn and **2**·Zn have been synthesized. They exhibit a unique selective binding ability towards the $H_2PO_4^-$ anion in water. The receptor **1**·2Zn shows remarkable 2+2-type binding to $H_2PO_4^-$, and it is the first chemosensor of $H_2PO_4^-$ based on the formation of an excimer that works in a 100% aqueous solution.

Experimental Section

Materials and Methods: CH_2Cl_2 and CH_3CN were dried and distilled from CaH_2. All other commercially available reagents were used without further purification. ^1H NMR spectra were recorded with a Varian Mercury VX 300 MHz spectrometer. Mass spectra were recorded with a Finnigan LCQ Advantage mass spectrometer. Elemental analyses were determined with a Carlo–Erba 1106 instrument. Fluorescence spectra were obtained with a Shimadzu RF-5301 spectrometer. The UV/Vis spectra were recorded with a TU-1901 spectrophotometer.

Synthesis: 9,10-Bis(aminomethyl)- and 9-(aminomethyl)anthracene were prepared following the published procedure.[10]

Compounds 3 and 4: A mixture of 9,10-bis(aminomethyl)anthracene (0.47 g, 2 mmol), K_2HPO_4 (3.48 g, 20 mmol), KI (0.50 g) and ethyl bromoacetate (0.61 mL, 8 mmol) in dry CH_3CN was heated at reflux overnight under N_2. The reaction mixture was evaporated to dryness under reduced pressure and the residue was dissolved in water and extracted with $CHCl_3$. The organic layer was separated and dried with anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by chromatography on silica gel ($CHCl_3/CH_3CH_2OH$ = 100:1, v/v) to give **3** (0.85 g) as an orange viscous oil. Yield 73.3%.^1H NMR ($CDCl_3$): δ = 8.68–8.72 (m, 4 H, AnH), 7.53–7.55 (m, 4 H, AnH), 5.04 (s, 4 H, $AnCH_2$), 4.13 (q, J = 7.2 Hz, 8 H, CH_2O), 3.64 (s, 8 H, CH_2CO), 1.22 (t, J = 7.2 Hz, 12 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 167.0, 126.7, 125.3, 120.9, 56.0, 50.4, 49.3, 44.8, 9.6 ppm. MS (ESI): m/z (%) = 581 (100) $[M + 1]^+$. $C_{32}H_{40}N_2O_8$ (580.67): calcd. C 66.18, H 6.96, N 4.82; found C 66.12, H 7.02, N 4.79.

Compound **4** was synthesized from 9-aminomethylanthracene by the procedure described above. Yield 81.5%. ^1H NMR ($CDCl_3$): δ = 8.66 (d, J = 8.7 Hz, 2 H, AnH), 8.43 (s, 1 H, AnH), 7.99 (d, J = 8.7 Hz, 2 H, AnH), 7.43–7.56 (m, 4 H, AnH), 4.96 (s, 2 H, $AnCH_2$), 4.13 (q, J = 7.2 Hz, 4 H, CH_2O), 3.59 (s, 4 H, CH_2CO), 1.21 (t, J = 7.2 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 167.8, 128.4, 127.3, 123.9, 123.5, 121.3, 56.5, 52.4, 44.8, 10.2 ppm. MS (ESI): m/z (%) = 380 (100) $[M + 1]^+$. $C_{23}H_{25}NO_4$ (379.18): calcd. C 72.80, H 6.65, N 3.69; found C 72.65, H 6.72, N 3.65.

Compounds 1 and 2: Compound **3** (1.16 g, 2 mmol) was dissolved in anhydrous EtOH (20 mL), adding excess ethylenediamine (5 mL) to the solution. Then the mixture was stirred for 6 h at around 50 °C. After evaporation of the solvent and residual ethylenediamine under reduced pressure, the residue was purified by column chromatography (silica, $CHCl_3/CH_3OH/NH_3{\cdot}H_2O$ = 60:25:6, v/v/v) to afford pure **1** (0.81 g) as a mauve oil; yield 63.8%. ^1H NMR ([D_6]DMSO): δ = 8.60–8.64 (m, 4 H, AnH), 8.12 (br., 4 H, NH), 7.54–7.58 (m, 4 H, AnH), 4.75 (s, 4 H, $AnCH_2$), 3.27 (s, 8 H, NCH_2CO), 3.03–3.07 (m, 8 H, CH_2NH), 2.44–2.48 (m, 8 H, CH_2NH_2), 2.58 (br., 8 H, NH_2) ppm. ^{13}C NMR ([D_6]DMSO): δ = 172.0, 141.9, 129.5, 128.8, 124.4, 60.5, 52.5, 47.1, 43.8 ppm. MS (ESI): m/z (%) = 637 (100) $[M + 1]^+$. $C_{32}H_{48}N_{10}O_4$ (636.39): calcd. C 60.34, H 7.61, N 22.00; found C 60.25, H 7.69, N 21.96.

Compound **2** was obtained by following the same procedure; yield 72.4%. ^1H NMR ([D_6]DMSO): δ = 8.68 (d, J = 8.7 Hz, 2 H, AnH),

8.32 (s, 1 H, AnH), 8.18 (d, J = 8.7 Hz, 2 H, AnH), 7.43–7.72 (m, 4 H, AnH), 4.86 (s, 2 H, $AnCH_2$), 3.52 (s, 4 H, NCH_2CO), 3.39–3.43 (m, 4 H, CH_2NH), 3.24–3.28 (m, 4 H, CH_2NH_2), 2.98 (br., 4 H, NH_2) ppm. ^{13}C NMR (D_2O): δ = 177.0, 136.4, 134.3, 131.7, 130.6, 130.2, 62.2, 55.4, 49.1, 41.2 ppm. ESI-MS: m/z (%) = 408 (100) $[M + 1]^+$. $C_{23}H_{29}N_5O_2$ (407.23): calcd. C 67.78, H 7.19, N 17.19; found C 67.73, H 7.30, N 17.08.

Zinc Complexes of Compounds 1 and 2: A methanolic (5 mL) solution of $Zn(ClO_4)_2·6H_2O$ (0.82 g, 2.2 mmol) was added dropwise to a solution of **1** (0.64 g, 1.0 mmol) in methanol (5 mL) and the mixture was stirred for 2 h at room temp. The yellow precipitate was filtered off, washed with cool methanol three times and dried under vacuum to obtain the complex (0.30 g, 31%). ^1H NMR (D_2O): δ = 8.41–8.43 (m, 4 H, AnH), 7.49–7.52 (m, 4 H, AnH), 3.26 (s, 4 H, CH_2An), 2.93 (s, 8 H, NCH_2CO), 2.76–2.78 (m, 8 H, CH_2NH), 2.57 (t, J = 6.6 Hz, 8 H, CH_2NH_2) ppm. ^{13}C NMR (D_2O): δ = 172.3, 135.3, 131.4, 130.7, 126.2, 57.2, 52.5, 43.5, 36.0 ppm. For **1**·2Zn·4ClO_4: MS (ESI): m/z (%) = 1161 (100) $[M +1]^+$. $C_{32}H_{48}N_{10}O_4·2Zn·4ClO_4$ (1160.05): calcd. C 32.99, H 4.12, N 12.03; found C 32.91, H 4.25, N 11.94.

The Zn complex of compound **2** was obtained when treated with 1 equiv. of $Zn(ClO_4)_2·6H_2O$ in methanol by the same procedure; yield 33.5%. ^1H NMR (D_2O): δ = 8.01 (s, 1 H, AnH), 7.92 (d, J = 7.8 Hz, 2 H, AnH), 7.58 (d, J = 7.8 Hz, 2 H, AnH), 7.28 (m, 4 H, AnH), 4.02 (s, 2 H, CH_2An), 3.59 (s, 4 H, NCH_2CO), 3.44–3.49 (m, 4 H, CH_2NH), 3.04–3.09 (m, 4 H, CH_2NH_2) ppm. ^{13}C NMR (D_2O): δ = 173.7, 165.7, 131.0, 129.2, 126.8, 125.4, 124.1, 58.5, 50.8, 37.7, 36.8 ppm. For **2**·Zn·2ClO_4: MS (ESI): m/z (%) = 670 (80) $[M +1]^+$. $C_{23}H_{29}N_5O_2·Zn·2ClO_4$ (669.06): calcd. C 41.07, H 4.32, N 10.42; found C 40.98, H 4.45, N 10.35.

Supporting Information (see also the footnote on the first page of this article): Fluorescence and ESI-MS spectra of **1**·2Zn.

Acknowledgments

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