Supporting Information

Control of higher-order structures of zinc chlorophyll coordination polymers

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Contents

1. Materials and Methods

All reactions were conducted under Ar. All reagents and solvents purchased for syntheses were used without further purification. $CDCl_3$ was purchased from Sigma-Aldrich.

^{1}H NMR spectra were recorded with a 400 MHz JEOL ECX 400 spectrometer, and chemical shifts were reported in ppm relative to internal tetramethylsilane (TMS). The peaks were assigned with the help of COSY, NOESY, HMQC, HMBC, and DEPT. Gel permeation chromatography was performed with Japan Analytical Industry LC-9201 equipped with Jaigel-1H and Jaigel-2H columns. High-resolution mass spectrometry analyses were performed with an Agilent G1969A mass spectrometer using positive atmospheric chemical ionization (APCI). The fluorescence spectra were recorded with a JASCO FP-8600 fluorometer. The single crystal diffraction analysis data were collected at 93 K with a Rigaku VariMax Dual with Saturn diffractometer using Mo Kα radiation (0.71075 Å). The structures were solved by direct method using SIR2004[1] for Zn3Py or SIR2011[2] for Zn4Py, and refined by the full-matrix least-squares method using SHELXL-97.[3] Contributions of disordered solvents on the reflection data were removed by the SQUEEZE command in the program PLATON.[4]

1. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Cryst.* **2005**, *38*, 381-388.
2. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, *J. Appl. Cryst.* **2007**, *40*, 609-613.
3. G. M. Sheldrick, *Acta Cryst.* **2008,** *A64*, 112-122.
4. A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148-155.

2. Syntheses and Characterization Data
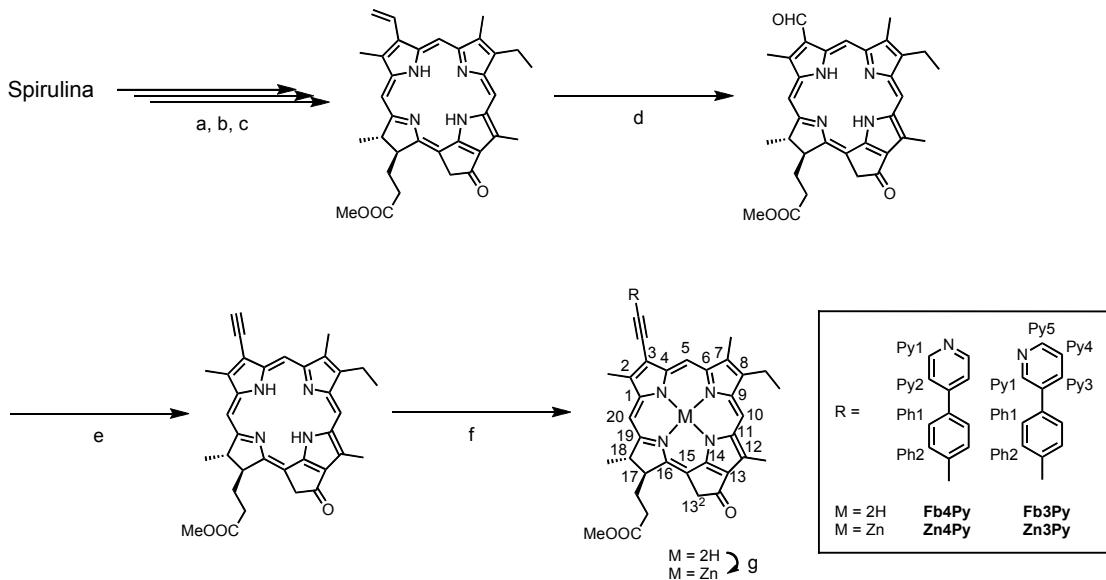
Scheme S1. Synthetic procedures of the zinc chlorophyll derivatives with phenylpyridine. (a) acetone, reflux with Soxlet apparatus, 10 days. (b) MeOH, H_2SO_4, overnight. (c) 2,4,6-trimethylpyridine, reflux, 3 h. (d) OsO_4, $NaIO_4$, AcOH, H_2O, THF, overnight. (e) Bestmann-Ohira reagent, $CsCO_3$, MeOH, THF, 3 h. (f) bromophenylpyridine, $Pd_2(dba)_3$, P(o-tolyl)$_3$, Et$_3$N, toluene, reflux, 24 h. (g) Zn(OAc)$_2$•2H$_2$O, MeOH, CHCl$_3$, 3 h.

Sonogashira Coupling. To a degassed solution of ethynylchlorophyll (100 mg, 0.186 mmol) and bromophenylpyridine (89 mg, 0.38 mmol) in toluene (60 mL) and Et$_3$N (12 mL) were added P(o-tolyl)$_3$ (66 mg, 0.22 mmol), Pd$_2$(dba)$_3$ (26 mg, 0.028 mmol). The mixture was then refluxed for 24 h. After cooling to r.t., the solvent was eliminated in *vacuo* to give a black solid. The crude mixture was purified by column chromatography to afford the product as a brown solid.

Fb3Py: Yield: 41%. ^{1}H-NMR (CDCl$_3$): δ / ppm = 9.60 (s, 1H, meso), 9.54 (s, 1H, meso), 9.00 (d, J = 1.4 Hz, 1H, Py), 8.68 (dd, J = 1.4, 5.5 Hz, 1H, Py), 8.61 (s, 1H, meso), 8.03 (d, J = 8.3 Hz, 2H, Ph), 8.01 (dd, J =1.4, 5.5 Hz, 1H, Py), 7.79 (d, J = 8.3 Hz, 2H, Ph), 7.46 (m, 1H, Py), 5.30 (d, J = 20.2 Hz, 1H, 13^2), 5.14 (d, J = 20.2 Hz, 1H, 13^2), 4.52 (m ,1H, 18-H), 4.22 (m, 1H, 17-H), 3.71 (quartet, J = 7.8 Hz, 2H, 8-C<u>H$_2$</u>CH$_3$), 3.69, 3.62, 3.55, 3.30 (each s, each 3H, ring CH$_3$×3, COOMe), 2.76–2.68, 2.62–2.54, 2.35–2.26 (each m, 1H, 1H, 2H, 17^1, 17^2), 1.84 (d, J = 7.3 Hz, 3H, 18-CH$_3$), 1.71 (t, J = 7.8 Hz, 3H, 8-CH$_2$<u>CH$_3$</u>), 0.30 (bs, 1H, NH), and -1.84 (bs, 1H, NH); APCI-HRMS: calcd for C$_{45}$H$_{41}$N$_5$O$_3$, MH$^+$, 700.3288, found 700.3291; GPC: V_R = 163.4 mL (100%).

Fb4Py : Yield: 75%. ^{1}H-NMR (CDCl$_3$): δ / ppm = 9.60 (s, 1H, meso), 9.52 (s, 1H, meso), 8.75 (d, J = 6.0 Hz, 2H, Py), 8.61 (s, 1H, meso), 8.02 (d, J = 8.5 Hz, 2H, Ph), 7.83 (d, J = 8.5 Hz, 2H, Ph), 7.63 (d, J = 6.0 Hz, 2H, Py), 5.29 (d, J = 19.7 Hz, 1H, 13^2), 5.14 (d, J = 19.7 Hz, 1H, 13^2), 4.52 (m, 1H, 18-H), 4.33 (m, 1H, 17-H), 3.70 (quartet, J = 7.8 Hz, 2H, 8-C<u>H$_2$</u>CH$_3$), 3.68, 3.62, 3.54, 3.28 (each s, each 3H, CH$_3$×3, COOMe), 2.76–2.67, 2.63–2.55, 2.36–2.26 (each m, 1H, 1H, 2H, 17^1, 17^2), 1.84 (d, J = 7.3 Hz, 3H, 18-CH$_3$), 1.71 (t, J = 7.8 Hz, 3H, 8-CH$_2$<u>CH$_3$</u>), 0.26 (bs, 1H, NH), and

-1.87 (bs, 1H, NH); APCI-HRMS: calcd for $C_{45}H_{41}N_5O_3$, MH^+, 700.3288, found 700.3273; GPC : V_R = 167.6 mL (100%).

Zinc Insertion. To a solution of the free-base compounds (50 mg, 0.07 mmol) in $CHCl_3$ (56 mL) was added sat. $Zn(OAc)_2 \cdot 2H_2O$ in MeOH (5 mL). After stirring for 3 h, 4% $NaHCO_3$ was added. The organic layer was separated, and was washed with H_2O. The solvent was eliminated in *vacuo* to quantitatively give the product as a green solid.

Zn3Py: ^{1}H-NMR (CDCl$_3$): δ/ppm = 9.61 (s, 1H, meso), 9.56 (s, 1H, meso), 8.40 (s, 1H, meso), 7.82 (d, J = 7.3 Hz, 2H, Ph), 6.92 (d, J = 5.5 Hz, 1H, Py), 6.68 (d, J = 7.3 Hz, 2H, Ph), 5.97 (bt, J = 6.0 Hz, 1H, Py), 5.34 (d, J = 19.2 Hz, 1H, 13^2), 5.19 (d, J = 19.2 Hz, 1H, 13^2), 4.43 (m, 1H, 18-H), 4.30 (m, 1H, 17-H), 3.74 (m, 2H, Py, 3-CH$_2$CH$_3$), 3.74, 3.63, 3.51, 3.30 (each s, each 3H, ring CH$_3$×3, COOMe), 3.30 (bs, 1H, Py), 2.72–2.64, 2.54–2.46, 2.38–2.29, 2.24–2.16 (each m, each 1H, 17^1, 17^2), and 1.76–1.69 (m, 6H, 8-CH$_2$CH$_3$, 18-CH$_3$); APCI-HRMS: calcd for $C_{45}H_{40}N_5O_3Zn$, MH^+, 762.2423, found 762.2414.

Zn4Py: ^{1}H-NMR (CDCl$_3$): δ/ppm = 9.59 (s, 1H, meso), 9.36 (s, 1H, meso), 8.39 (s, 1H, meso), 7.60 (d, J = 8.0 Hz, 2H, Ph), 6.97 (d, J = 8.0 Hz, 2H, Ph), 6.17 (bs, 2H, Py), 5.19 (d, J = 19.7 Hz, 1H, 13^2), 5.07 (d, J = 19.7 Hz, 1H, 13^2), 4.44 (m ,1H, 18-H), 4.25 (m, 1H, 17-H), 3.85 (bs, 2H, Py), 3.74 (quartet, J = 7.3 Hz, 2H, 8-CH$_2$CH$_3$), 3.70, 3.53, 3.38, 3.19 (each s, each 3H, ring CH$_3$×3, COOMe), 2.63–2.58, 2.43–2.38, 2.36–2.26, 2.08–2.00 (each m, each 1H, 17^1, 17^2), 7.3 (d, J = 7.3 Hz, 3H, 18-CH$_3$), and 1.70 (t, J = 7.3 Hz, 3H, 8-CH$_2$CH$_3$); APCI-HRMS: calcd for $C_{45}H_{40}N_5O_3Zn$, MH^+, 762.2423, found 762.2400.
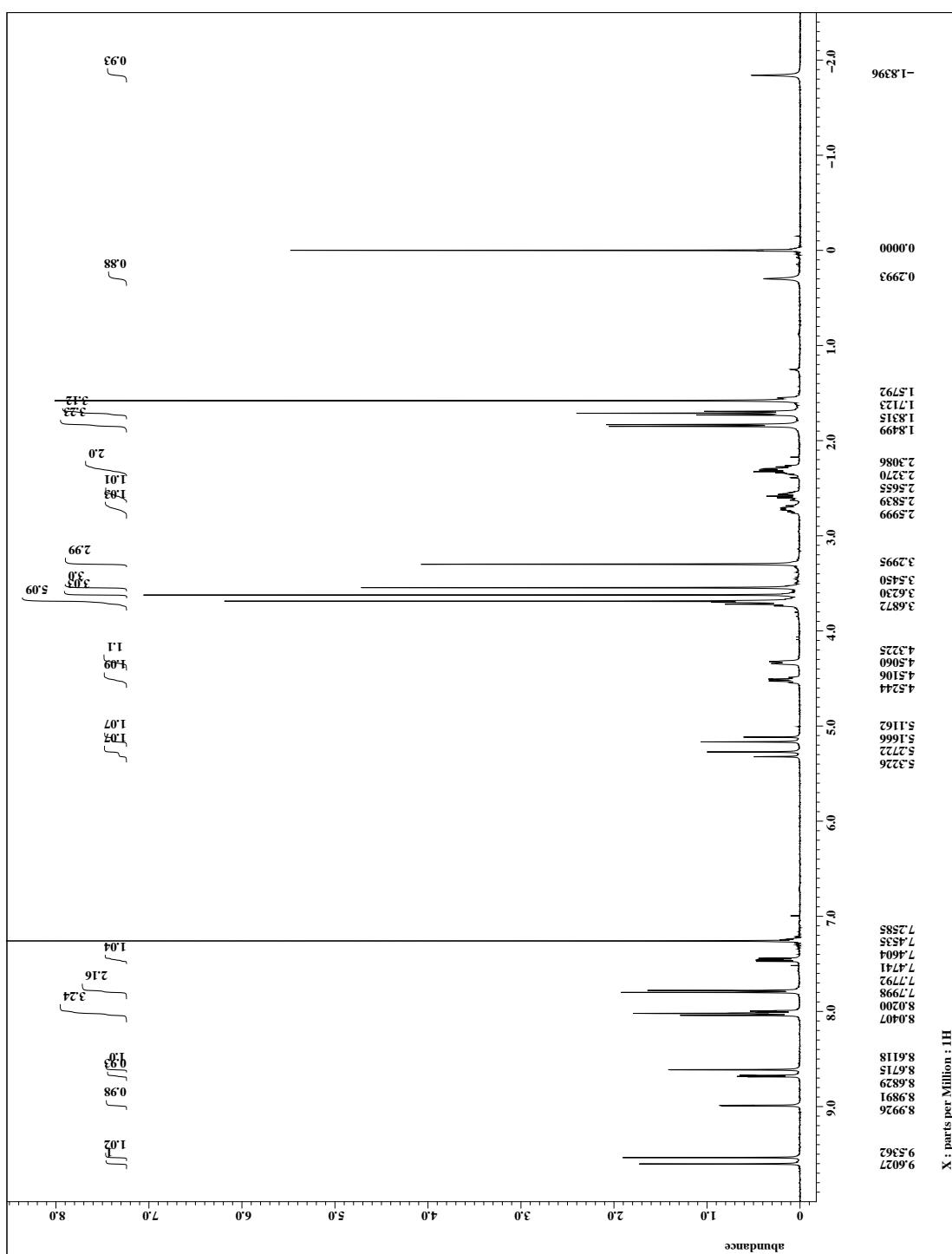
Figure S1. ^{1}H-NMR spectrum of **Fb3Py**.
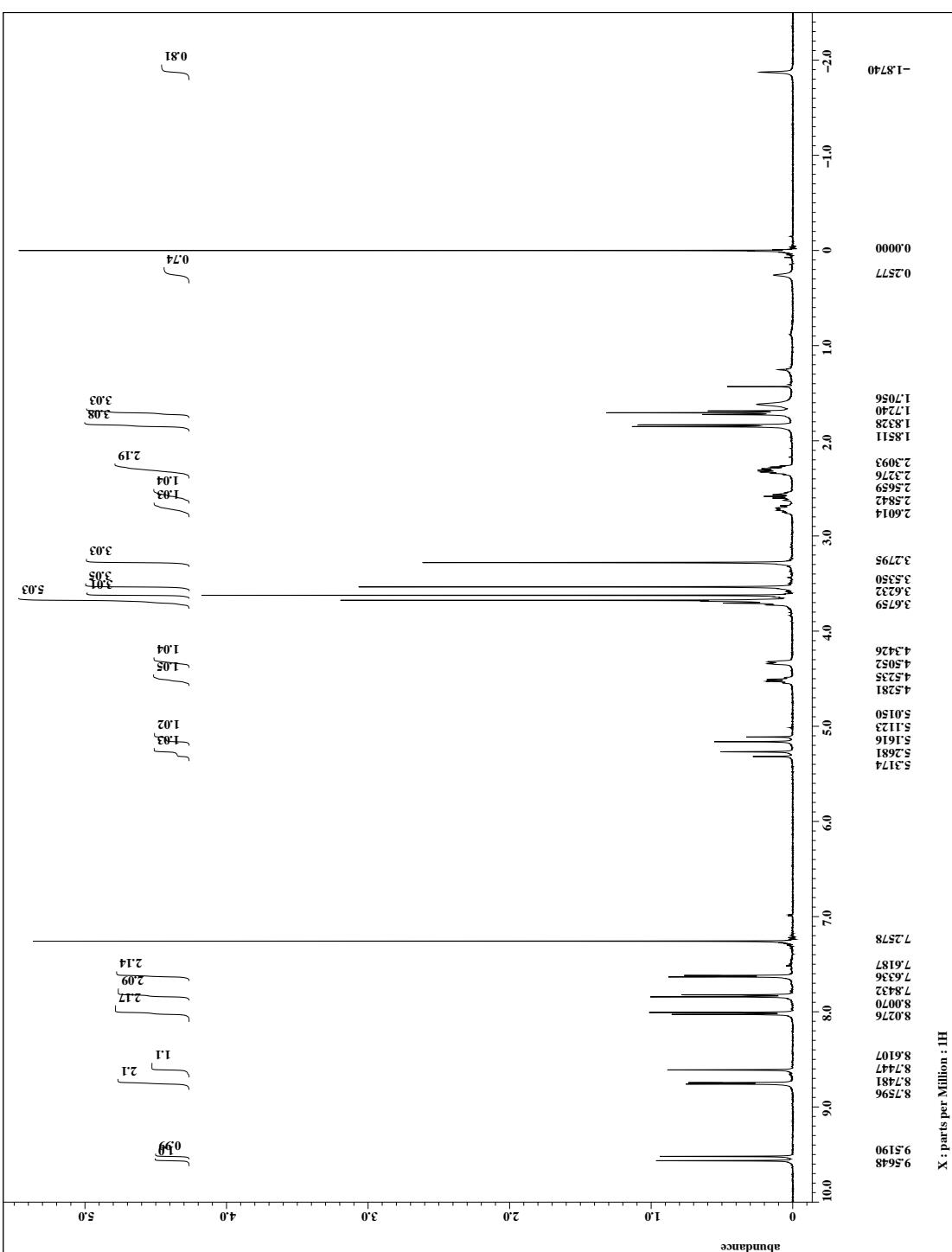
Figure S2. ^{1}H-NMR spectrum of **Fb4Py**.

*Figure 3.* ¹H-NMR spectrum of **Zn3Py**.
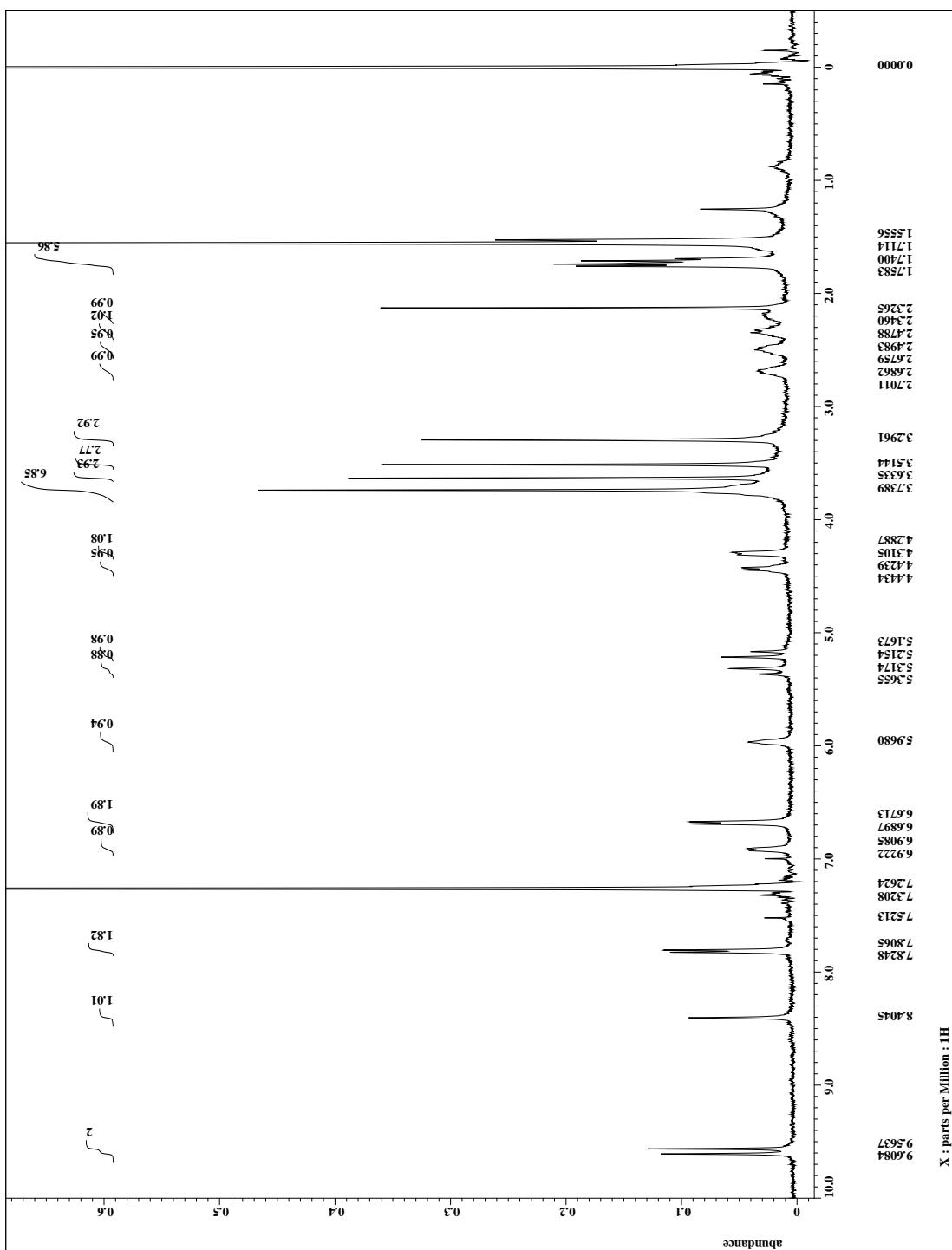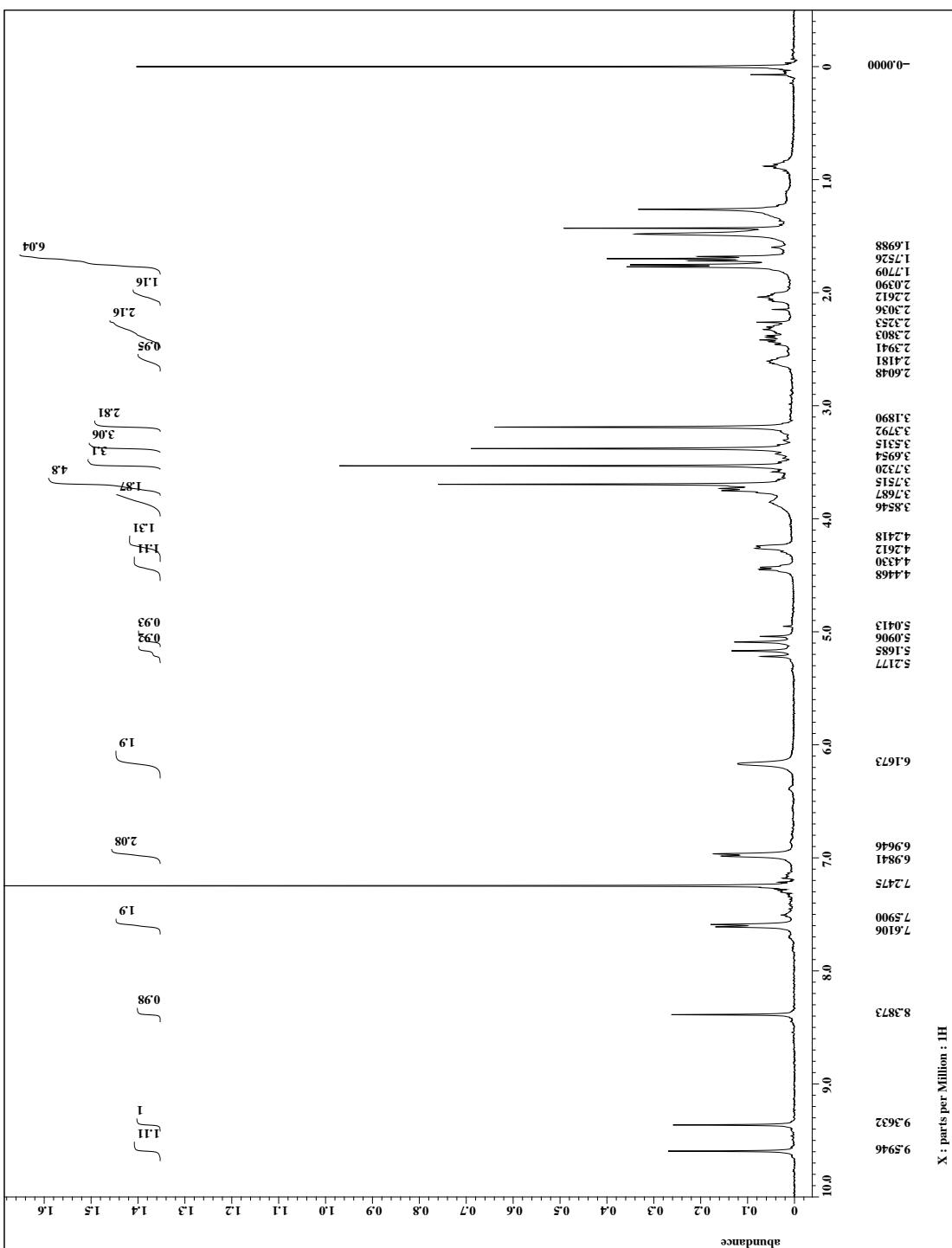
***Figure S4.*** ¹H-NMR spectrum of **Zn4Py**.
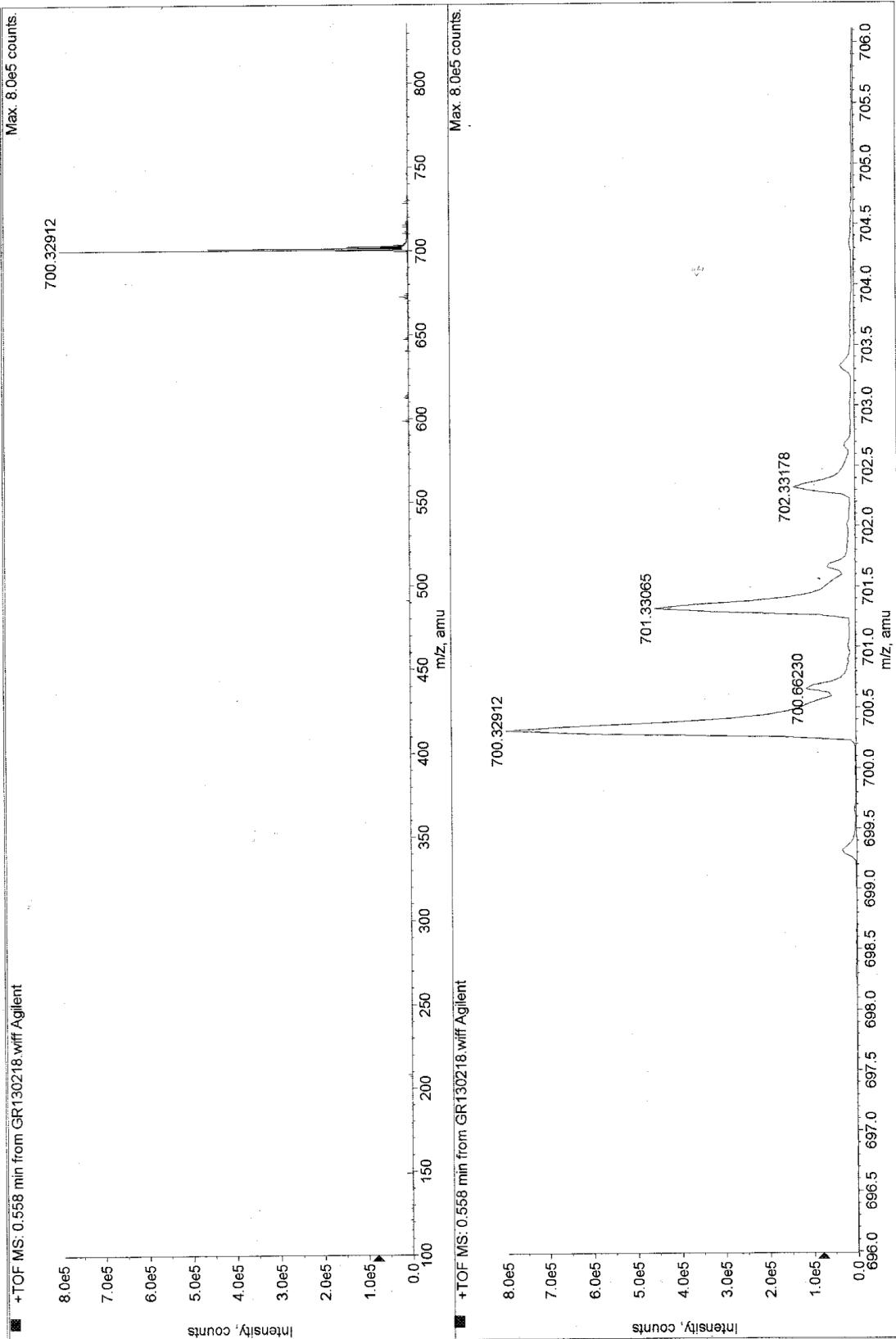
Figure S5. APCI-HRMS spectrum of **Fb3Py**.
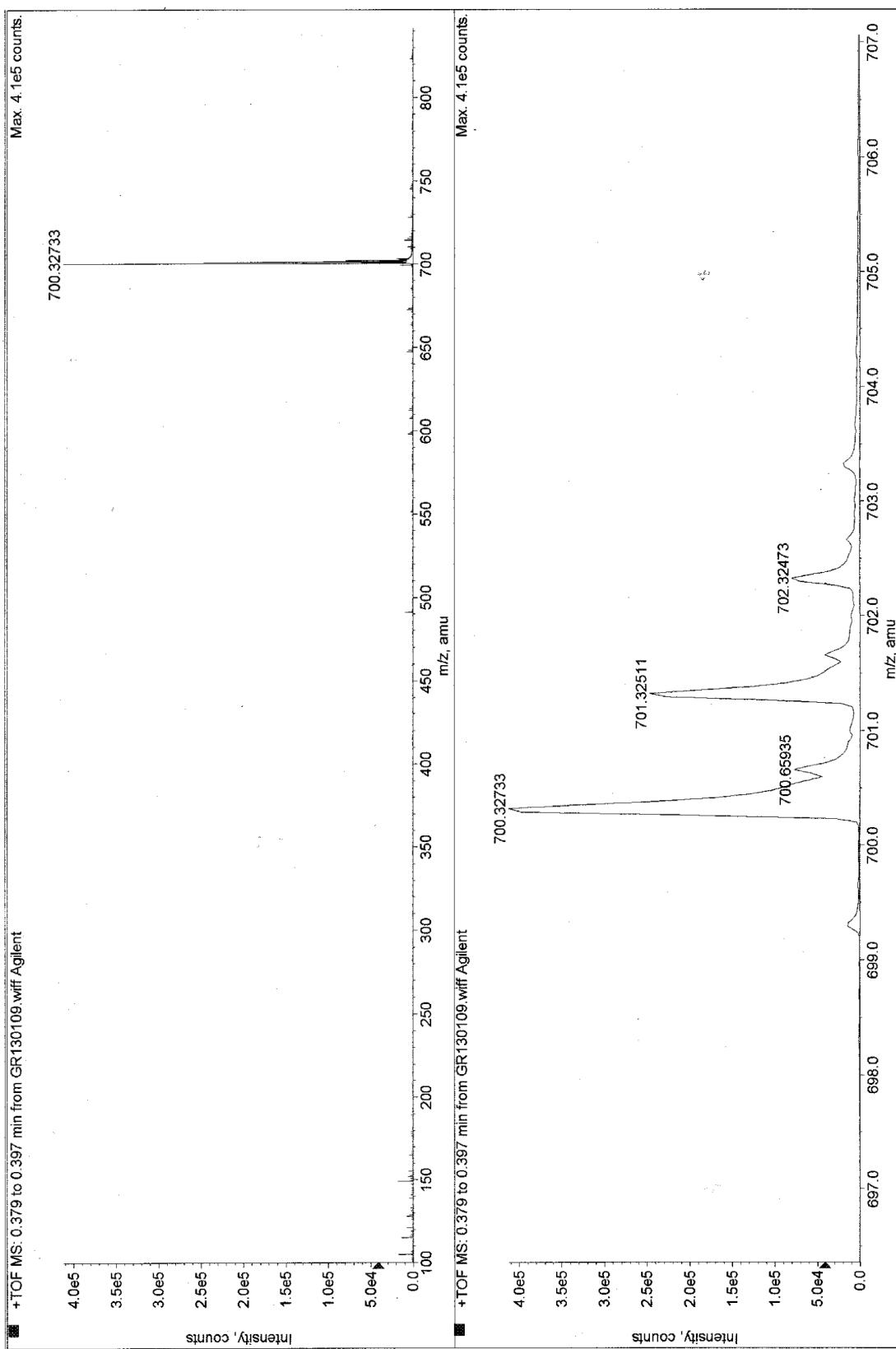
*Figure S6.* APCI-HRMS spectrum of **Fb4Py**.
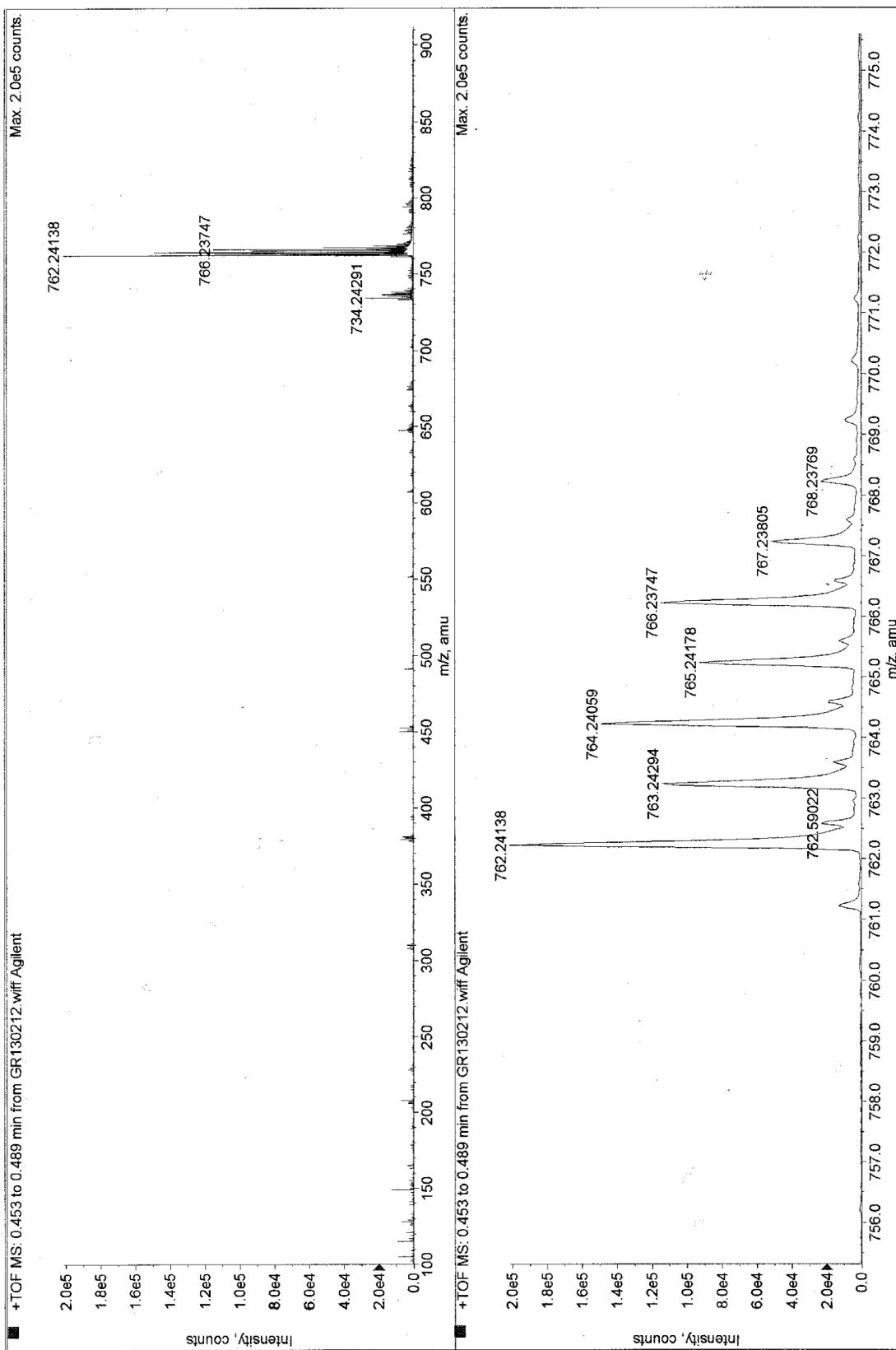
*Figure S7.* APCI-HRMS spectrum of **Zn3Py**.
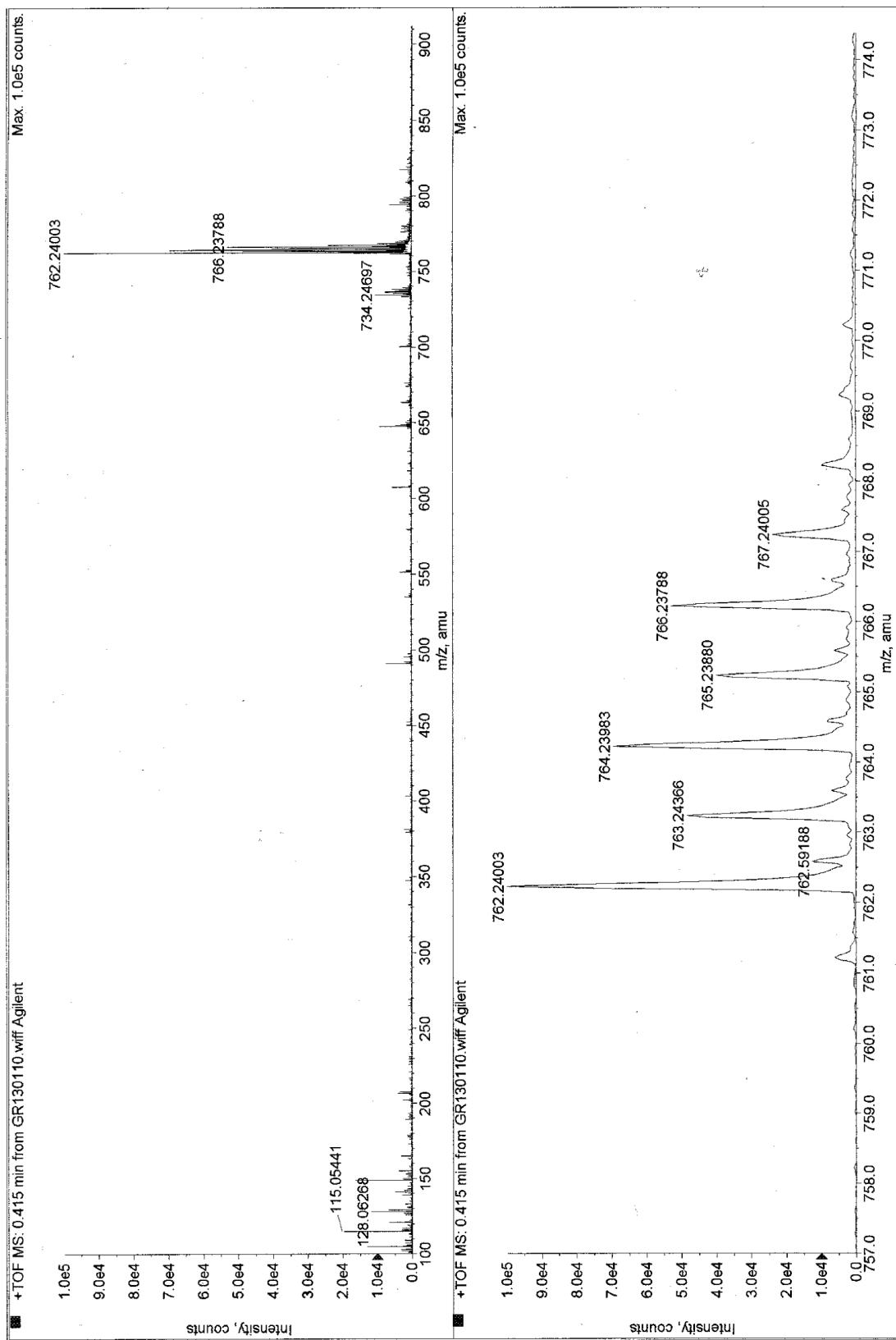
*Figure S8.* APCI-HRMS spectrum of **Zn4Py**.
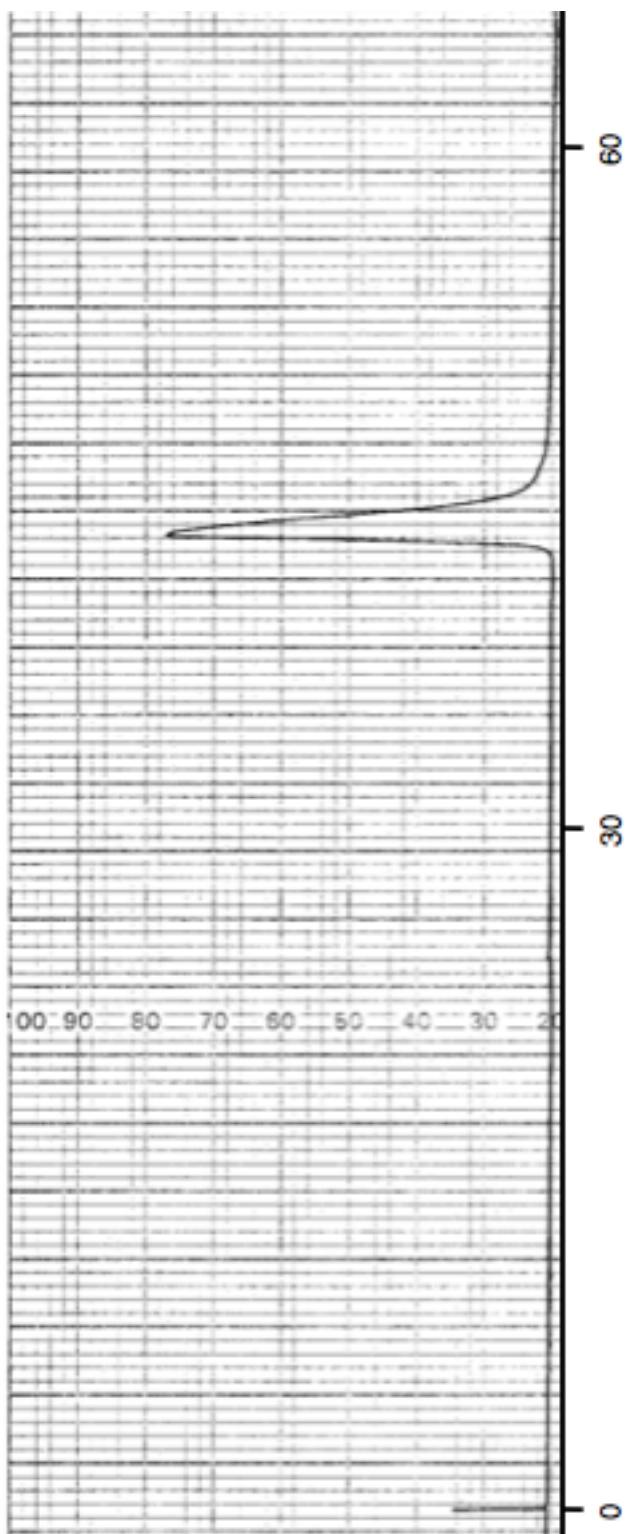
Figure S9. GPC chromatogram of **Fb3Py**.
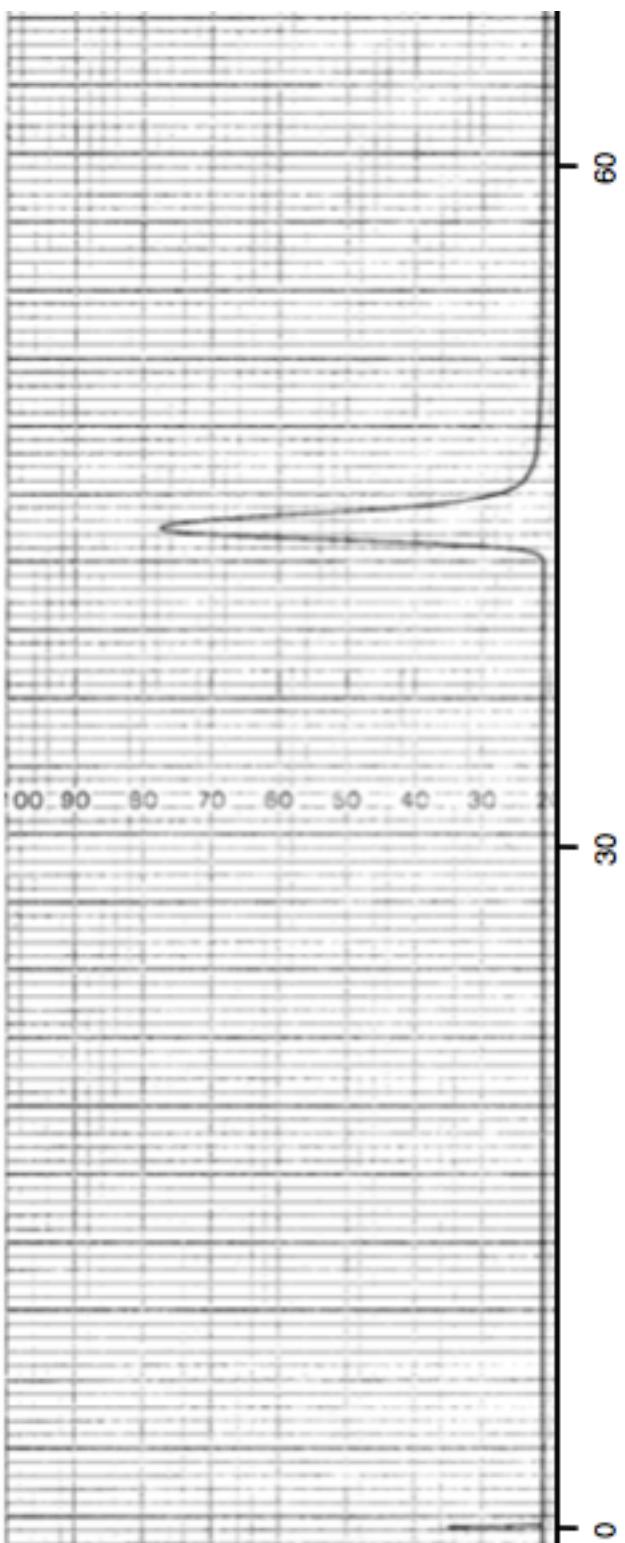
Figure S10. GPC chromatogram of **Fb4Py**.

3. Comparison of ^{1}H-NMR Spectra for the Free-Base Derivatives and Their Zinc Complexes
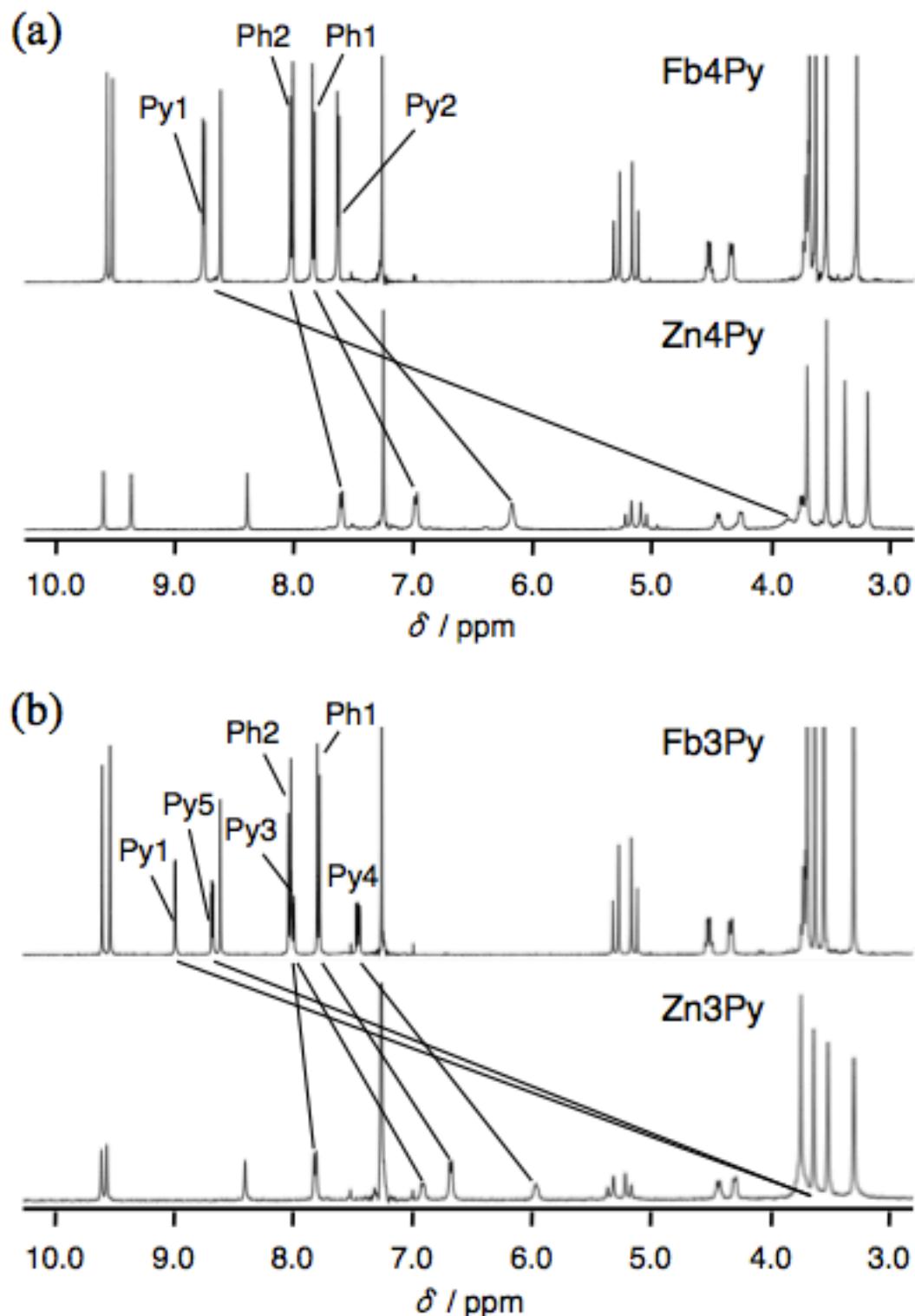
*Figure S11.* ^{1}H-NMR spectra of (a) **Fb4Py** and **Zn4Py**, (b) **Fb3Py** and **Zn3Py** in CDCl$_3$ at 298 K (ca 10 mM for free-base compounds, saturated solution for zinc complexes due to poor solubility). The solid lines indicate the upfield shift upon zinc insertion. See Chart1 for proton labels.

4. Crystallographic Data

Table S1. Crystallographic Data for **Zn3Py**.

Compound	**Zn3Py**
Empirical formula	$C_{102}H_{106}N_{10}O_9Zn_2$
Formula weight	1746.70
Color, Habit	Black, Rhombic
Temperature / K	93
Wavelength / Å	0.71075
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions / Å	$a = 14.904(4)$ $b = 14.159(3)$ $c = 21.949(5)$
Volume / Å^3	4563.1(19)
Z	2
Absorption coefficient / mm^{-1}	0.589
F(000)	1840
Crystal size / mm^3	0.25×0.16×0.13
θ for data collection	3.0 to 27.5
Index ranges	$-17 \leq h \leq 19, -18 \leq k \leq 18, -24 \leq l \leq 27$
Reflections collected	37583
Independent reflections	19583
Completeness	97.5% ($\theta = 27.48°$)
Absorption correction	Numerical
Max. and min. transmission	0.926 and 0.888
Refinement method	Full-matrix least-squares on F^2
Flack parameter	0.061(11)
Data/restraints/parameters	19583/341/999
Goodness-of-fit on F^2	1.021
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0787$
R indices (all data)	$wR_2 = 0.2032$
Largest diff. peak and hole / e Å^{-3}	1.066 and −0.811

Table S2. Crystallographic Data for **Zn4Py**.

Compound	**Zn4Py**
Empirical formula	$C_{45}H_{39}N_5O_3Zn$
Formula weight	763.18
Color, Habit	Black, Needle
Temperature / K	93
Wavelength / Å	0.71075
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions / Å	$a = 10.372(7)$ $b = 22.684(14)$ $c = 18.375(11)$
Volume / $Å^3$	4187.(5)
Z	4
Absorption coefficient / mm^{-1}	0.630
F(000)	1592
Crystal size / mm^3	0.34×0.050×0.020
θ for data collection	2.10 to 25.30
Index ranges	$-12 \leq h \leq 12, -27 \leq k \leq 27, -22 \leq l \leq 21$
Reflections collected	29029
Independent reflections	14538
Completeness	92.4% ($\theta = 25.26°$)
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Flack parameter	0.10(2)
Data/restraints/parameters	14538/333/968
Goodness-of-fit on F^2	1.046
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.1136$
R indices (all data)	$wR_2 = 0.2384$
Largest diff. peak and hole / e $Å^{-3}$	0.803 and -0.528

Table S3. Selected Structural Parameters for **Zn3Py** Molecules

	Red	Blue
	Angle / °	
$\angle N_1-Zn-N_2$	91.3(3)	91.6(3)
$\angle N_2-Zn-N_3$	88.0(3)	87.1(3)
$\angle N_3-Zn-N_4$	87.9(3)	89.4(3)
$\angle N_4-Zn-N_1$	88.9(3)	88.4(3)
	Distance / Å	
N_1-Zn	2.033(6)	1.995(6)
N_2-Zn	2.072(8)	2.056(9)
N_3-Zn	2.012(6)	1.992(6)
N_4-Zn	2.186(9)	2.210(7)
$N_{Py}-Zn$	2.179(7)	2.161(7)
$N_1N_2N_3N_4-Zn$	0.272	0.258
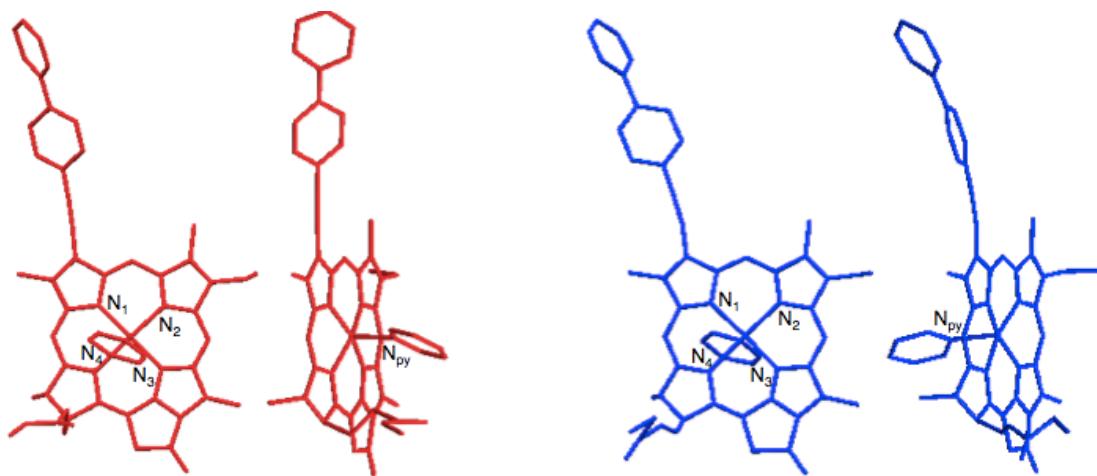
Table S4. Selected Structural Parameters for **Zn4Py** Molecules

	Red	Blue
	Angle / °	
$\angle N_1-Zn-N_2$	90.5(6)	91.2(6)
$\angle N_2-Zn-N_3$	87.6(7)	86.7(6)
$\angle N_3-Zn-N_4$	88.3(7)	89.3(6)
$\angle N_4-Zn-N_1$	89.5(6)	88.6(6)
	Distance / Å	
N_1-Zn	2.04(1)	2.00(1)
N_2-Zn	2.10(2)	2.05(1)
N_3-Zn	2.02(2)	2.02(2)
N_4-Zn	2.16(2)	2.19(1)
$N_{Py}-Zn$	2.13(2)	2.15(2)
$N_1N_2N_3N_4-Zn$	0.279	0.277
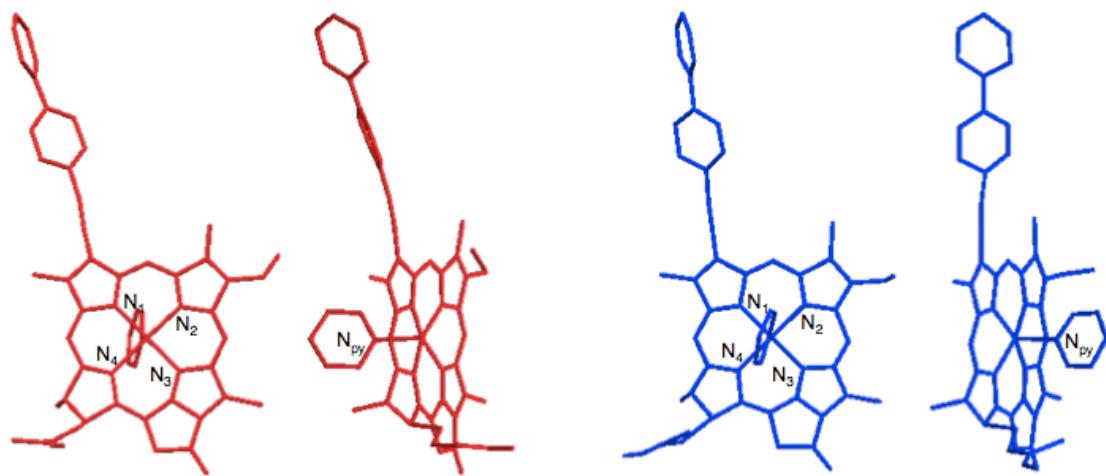
## 5. Relative Efficiency of Förster-type Energy Transfer
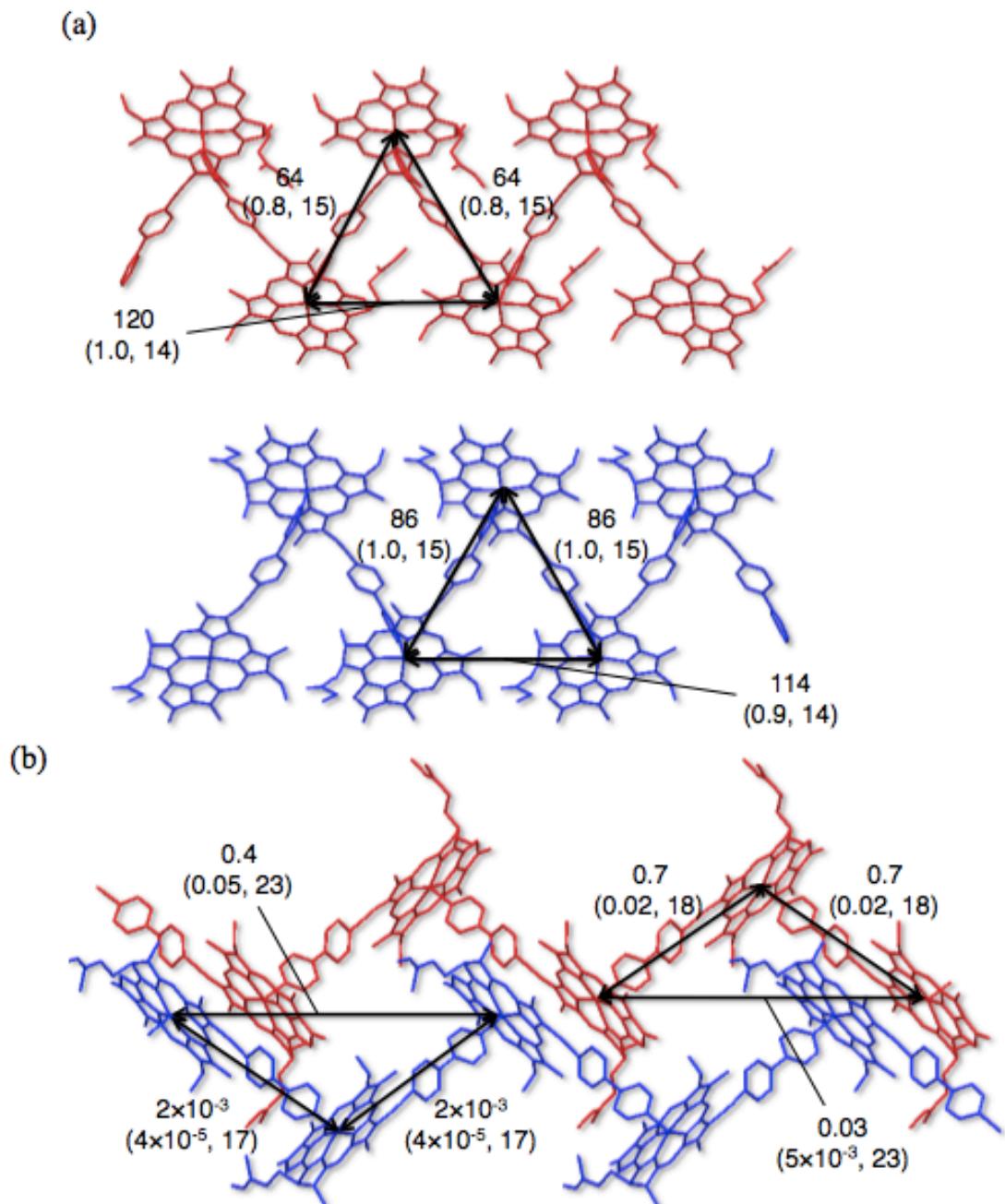
Figure S12. Values of ($k^2/r^6 \times 10^9$) (in Å^{-6}) as a measure of relative efficiencies of Förster-type energy transfer in the coordination polymers of (a) **Zn3Py** and (b) **Zn4Py**. The arrows represent the pair of donor and acceptor molecules. The orientation factor κ^2 and the distance r (in Å) are shown in parenthesis.

6. Fluorescence Spectra

(a)

(b)
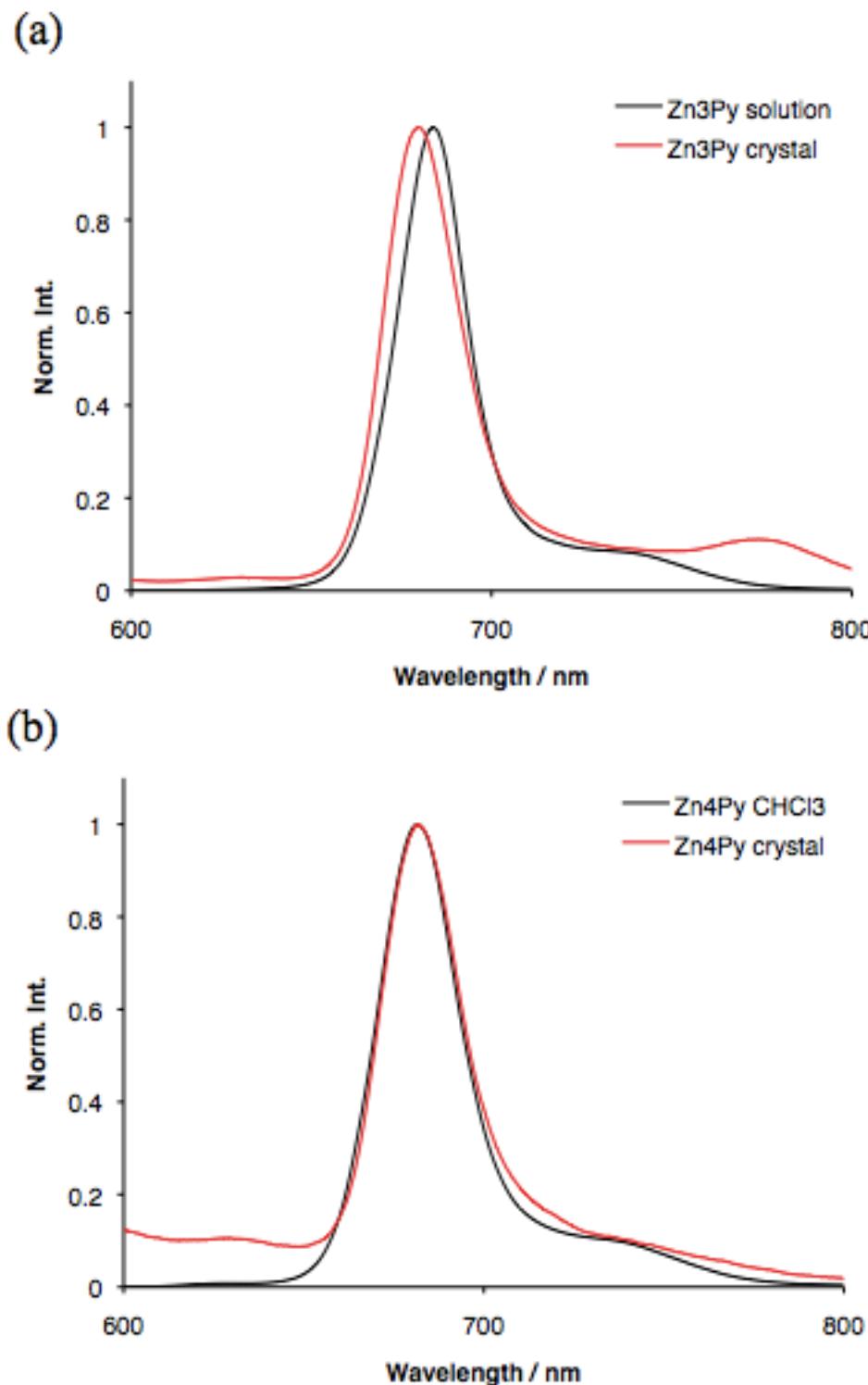
Figure S13. Fluorescence spectra of (a) **Zn3Py** (λ_{ex} = 439 nm) and (b) **Zn4Py** ((λ_{ex} = 432 nm) in CHCl$_3$ (ca. 10 µM) and their crystals. The spectra of the crystals were measured in liquid paraffin by a reflection geometry.