Blue Transition Metal Complexes of a Natural Bilin-Type Chlorophyll Catabolite

Supporting Information

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Experimental Part.

General. Solvents (CH_2Cl_2, DMF, pyridine and toluene) were regent-grade commercials and distilled before use. HPLC grade methanol (MeOH) and acetonitrile (MeCN) was from VMR (Leuven, Belgium). Potassium dihydrogen phosphate puriss p.a. and Potassium phosphate dibasic-anhydrous puriss p.a. were from Fluka (Buchs, Switzerland). Samples of PiCC (**1**)[1] and YCC (**2**, earlier named *Cj*-YCC-2 [2]) were prepared as described.[1] Transition metal acetates and acetylacetonates were from Acros Organics (Geel, Belgium) and Fluka (Buchs, Switzerland). Sep-Pak-C18 Cartridges were obtained from Waters Associates (Milford, USA). pH values were measured with a WTW Sentix 21 electrode connected to a WTW pH535 digital pH meter.

Spectroscopy. UV/Vis: HITACHI U-3000 spectrophotometer; λ_{max} in nm (log ε).- CD-spectra: JASCO J-715 spectropolarimeter; λ_{max} and λ_{min} in nm (relative $\Delta\varepsilon$).- Fluorescence. Varian Cary Eclipse Fluorescence Spectrophotometer; ^{1}H-NMR: Varian UNITYplus 500; δ in ppm with $\delta(CHD_2CN) = 1.94$ ppm, $\delta(CD_2HSOCD_3) = 2.50$ and $\delta(CD_2HOD) = 3.31$; J_{HH}(Hz), spectra were recorded at 25 °C. ESI-MS: ESI source, flow rate 2 mL min^{-1}, spray voltage 1.4 kV, solvent water/methanol 1:1 (v/v).

Analytical HPLC: *Phenomenex*, *ODS-Hypersil* 5µ, 250 × 4.6 mm i.d., *Gynkotek* 'high precision pump' *480G* with vacuum on-line degasser, *Gynkotek* diode array detector *DA340*, UV-Vis detection between 190 and 600 nm, all chromatograms were taken at r.t.

Synthesis of the PiCC 1 from 2. To a solution of 5.07 mg of **2** (7.89 µmol) [2] in 3 mL distilled DMF, 7.45 mg anhydrous $Zn(OAc)_2$ (40.6 µmol, 5.1 eq) and pyridine (0.3 mL) were added. The resulting (still yellow) solution was stirred at r.t. under air and in the dark. After 24 hours, the conversion of **2** to **Zn-1** was complete according to TLC analysis (on silica gel). The dark blue reaction mixture was diluted with 30 mL of water and extracted three times with 20 mL each of dichloromethane. The combined organic phases were filtered through a plug of dry cotton-wool. The solvent was evaporated in vacuo to give a dark blue residue of raw **Zn-1**. The dark blue residue was dissolved in 0.1 mL of DMF and diluted with 10 mL of CH_3CN. To this mixture, 10 mL of 100 mM potassium dihydrogen phosphate (pH 4.7) was added. After 1 hour, a red reaction mixture was obtained. On the basis of TLC analysis (on silica gel), the conversion of **Zn-1** to **1** was complete. The obtained red solution was extracted three times with 20 mL each of dichloromethane. The combined organic phases were washed twice with 25 mL eash of 20 mM potassium dihydrogen phosphate (pH 4.7) and filtered through a plug of dry cotton-wool. The solvent was evaporated in vacuo and the dark red residue of the raw product was dissolved in 2 mL of MeOH and diluted with 3 mL of 50 mM potassium phosphate buffer (pH 7.0). The obtained deep red solution was applied to a Sep-Pak-C18 cartridge (5 g). After washing with 40 mL H_2O, the red pigment was eluted with 20 mL of MeOH. The solvent was evaporated to give a dark red residue. The residue was dissolved in 2 mL of MeOH and diluted with 3 mL of toluene. The solution was concentrated under reduced pressure (150 mbar, 30 °C), furnishing **1** as a dark red precipitate. The precipitate was separated off by centrifugation and washed with toluene (3 × 0.7 mL) and pentane (4 × 0.5 mL). The sample of **1** was dried under high vacuum and obtained as 4.60 mg dark red powder (91.0 % yield), identified as the PiCC **1** [1] by UV/Vis- and ^{1}H-NMR spectra.

For crystallization, a solution of 3.28 mg of the PiCC **1** in 5 mL 2/3 (v/v) MeOH / 50 mM potassium phosphate buffer (pH = 7) was applied to a Sep-Pak-C18 cartridge (5 g) and the red fraction was washed down with about 30 mL 5/3 (v/v) MeOH / 50 mM potassium phosphate buffer (pH = 7). The collected eluate was concentrated to 80 % of the original volume and loaded on another Sep-Pak-C18 cartridge (5 g) washed with about 100 mL of H_2O. Then, pure **1** was eluted with about 40 mL of MeOH / H_2O (3/4, v/v). The obtained red fraction was dried under reduced pressure. The residue (ca. 3 mg) was dissolved in MeOH (2 mL) and the solution was filtered through a tight plug of cotton wool. The filtrate was collected in a vial, which was put into a jar that contained CH_2Cl_2. Clear rhombus-shaped single crystals formed on the wall of the vial. PiCC (**1**) crystallized as the potassium complex **K-1**.

Data were measured on a Nonius Kappa CCD with Mo K_α-radiation at 233 K (see Table S1 for crystal structure data).

The small crystal gave low diffraction giving a high R-value. Intensity data were measured only to a diffraction angle in 2 θ of 45° (visible reflections at diffraction frames were only seen below 40°, for refinement reflections down to 43° were used). The crystal quality allowed isotropic refinement of H-atoms at N and O-atoms with bond restraints (d(N) = 0.88 Å and d(O) = 0.83 Å). Hydrogens at C-atoms were calculated, using a riding model. Around the K-cation all solvent molecules, H_2O and MeOH, are occupationally disordered with an occupation factor of 0.5 for C22-O1, C23-O2, O3, O4, O5, O6 and O7. The disorder is caused by an inversion centre, which bridge two potassium cations over the oxygen atoms O1 and O3. The position of water O4 and O5 was excluded by the position of MeOH C23-O2 at the same place in crystal lattice just as O6 and O7 by C22-O1, respectively. Due to this disorder H-atoms of solvent molecules could not been localized and were omitted in the refinement.

Table S1. Crystal data and structure refinement for **K-1**.

Empirical formula	$C_{35} H_{35} KN_4O_8$ x CH_3OH x 2.5 H_2O	
Formula weight	755.85	
Temperature	233(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1 (no. 2)	
Unit cell dimensions	a = 11.7592(8) Å	α = 98.948(4)°.
	b = 12.7470(9) Å	β = 100.210(4)°.
	c = 13.3933(9) Å	γ = 97.418(3)°.
Volume	1926.2(2) $Å^3$	
Z	2	
Density (calculated)	1.303 g/cm^3	
Absorption coefficient	0.202 mm^{-1}	
F(000)	798	
Crystal size	0.2 × 0.1 × 0.04 mm^3	
Theta range for data collection	1.57 to 21.49°	
Index ranges	-12<=h<=12, -13<=k<=13, -13<=l<=13	
Reflections collected	8392	
Independent reflections	4396 [R(int) = 0.0509]	
Reflections [I>2sigma(I)]	3127	
Completeness to theta = 21.49°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4396 / 4 / 534	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R1 = 0.0769, wR2 = 0.1824	
R indices (all data)	R1 = 0.1111, wR2 = 0.1968	
Largest diff. peak and hole	0.413 and -0.227 e.$Å^{-3}$	

Table S2. Hydrogen bonds observed in the crystal structure of **K-1**.

D-H...A	d(D-H) / Å	d(H...A) / Å	d(D...A) / Å	<(DHA) / °
N(21)-H(21N)...O(125)	0.88(2)	2.06(3)	2.818(6)	144(3)
N(22)-H(22N)...O(125)	0.89(2)	1.90(3)	2.753(5)	158(5)
N(24)-H(24N)...N(23)	0.88(2)	2.16(4)	2.750(6)	124(4)
N(24)-H(24N)...O(84B)	0.88(2)	2.49(4)	3.224(6)	142(4)
O(33)-H(33O)...O(82)#5	0.84(2)	2.05(4)	2.839(6)	156(9)

Symmetry transformations used to generate equivalent atoms:

#5 -x,-y,-z

Synthesis of metal complexes of the PiCC 1.

Synthesis of Zn-1 from 2. To a solution of 5.07 mg of **2** (7.89 µmol) [2] in 3 mL distilled DMF, 7.45 mg anhydrous $Zn(OAc)_2$ (40.6 µmol, 5.1 eq) and pyridine (0.3 mL) were added. The resulting (still yellow) solution was stirred at r.t. under air and in the dark. After 24 hours, the conversion of **2** to **Zn-1** was complete according to analysis by TLC (on silica gel). The dark blue reaction mixture was diluted with 30 mL of water and extracted three times with 20 mL each of dichloromethane. The combined organic phases were filtered through a plug of dry cotton-wool. The solvent was evaporated in vacuo to give a dark blue residue of raw **Zn-1**. The raw product was dissolved in 2 mL of MeOH and diluted with 3 mL of toluene. The solution was concentrated under reduced pressure (150 mbar, 30 °C), furnishing **Zn-1** as a blue precipitate. The precipitate was separated off by centrifugation and the obtained blue powder was washed with toluene (3 × 0.7 mL) and pentane (4 × 0.5 mL). The sample of **Zn-1** was dried under high vacuum and obtained as 5.22 mg dark blue powder (93.9 % yield), identified as **Zn-1** by ^{1}H-NMR and UV-Vis spectra.

Synthesis of metal complexes from the PiCC 1.

Zn-1. To a sample of 4.50 mg of PiCC **1** (7.03 µmol), dissolved in 4.5 mL MeOH, 2.80 mg of $Zn(acac)_2$ (10.6 µmol, 1.5 eq) were added. The suspension was purged with Ar for 10 min. After 2 hours reaction at r.t. under Ar, the conversion of **1** to **Zn-1** was complete according to TLC analysis (on silica gel), and a deep blue mixture was obtained which was filtered through a tight plug of cotton wool. The filtrate was concentrated to 1 mL under reduced pressure. Toluene (4.0 mL) was added and the solution was concentrated (150 mbar, 30 °C) to remove MeOH, furnishing **Zn-1** as a blue precipitate. The precipitate was separated off by centrifugation and the obtained blue powder was washed with toluene (3 × 1.0 mL) and pentane (5 × 0.5 mL). The sample of **Zn-1** was dried under high vacuum and obtained as 4.67 mg dark blue powder (94.5 % yield), which was characterized as **Zn-1**, as described below

Cd-1. To a sample of 3.10 mg of PiCC **1** (4.84 µmol), dissolved in 3 mL MeOH, 2.25 mg of $Cd(acac)_2$ (7.24 µmol, 1.5 eq) were added. The suspension was purged with Ar for 10 min. After 2 hours reaction at r.t. under Ar, the conversion of **1** to **Cd-1** was complete according to TLC analysis (on silica gel), and a deep blue mixture was obtained which was filtered through a tight plug of cotton wool. The filtrate was concentrated to 1.5 mL under reduced pressure. Toluene (4.0 mL) was added and the solution was concentrated (150 mbar, 30 °C) to remove MeOH, furnishing **Cd-1** as a blue precipitate. The precipitate was separated off by centrifugation and the obtained blue powder was washed by toluene (3 × 0.9 mL) and pentane

(5 × 0.4 mL). The complex **Cd-1** was dried under high vacuum and obtained as 3.48 mg (95.6 % yield) of dark blue powder, which was characterized as **Cd-1**, as described below.

Cu-1. To a sample of 4.02 mg of PiCC **1** (6.28 µmol), dissolved in 5 mL MeOH, 2.44 mg of $Cu(acac)_2$ (9.32 µmol, 1.5 eq) were added. The suspension was purged with Ar for 10 min. After 2 hours reaction at r.t. under Ar, the conversion of **1** to **Cu-1** was complete according to TLC analysis (on silica gel), and a deep blue mixture was obtained which was filtered through a tight plug of cotton wool. The filtrate was concentrated to 1.5 mL under reduced pressure. Toluene (2.0 mL) was added and the solution was concentrated (150 mbar, 30 °C) to remove MeOH, furnishing **Cu-1** as a blue precipitate, which was separated off by centrifugation. The obtained blue powder was washed with toluene (3 × 0.5 mL) and pentane (3 × 0.5 mL). A sample of 3.97 mg of **Cu-1** was dried under high vacuum and obtained (90 % yield) as dark blue powder, identified as **Cu-1** as described below.

Ni-1. To a solution of 3.83 mg of PiCC **1** (5.98 µmol) in 4 mL MeOH, 10.8 mg of $Ni(acac)_2$ (42.0 µmol, 7 eq) were added. The suspension was purged with Ar for 10 min. After 20 hours reaction at r.t. under Ar, the conversion of **1** to **Ni-1** was complete according to TLC analysis (on silica gel), and a deep blue mixture was obtained which was filtered through a tight plug of cotton wool. The filtrate was diluted with 8 mL H_2O. The blue solution was loaded on the Sep-Pak-C18 (5 g) for purification. A blue fraction was washed down by using MeOH / H_2O = 3 / 5 (v / v). The solvent was evaporated under reduced pressure. A sample of 3.64 mg (88 % yield) of **Ni-1** was dried under high vacuum and obtained as residue, characterized as **Ni-1**, as described below.

Spectroscopic data

PiCC 1: UV/Vis (λ_{max}, log ε, MeOH): 523 (4.56), 495sh (4.49), 313 (4.40). Fluorescence (exc. at 520 nm, rel. int.): 712sh (0.44), 620 (1.00). Fluorescence excitation (obs. at 620 nm, rel.int.): 526 (1.00), 496sh (0.77), 315 (0.44)**.** CD: insignificant absorptions ($\Delta\varepsilon < 0.40$). ESI-MS: m/z (%) = 687.3 (18), 686.2 (42), 685.2 (100, $[M+2Na-H]^+$); 665.3 (2), 664.3 (13), 663.3 (25, $[M+Na]^+$)**.**

Zn-1: UV/Vis (λ_{max}, log ε, MeOH): 620 (4.43), 578 (4.23), 349 (4.31), 318 (4.35). Fluorescence (excitation at 620 nm, rel. int.): 704 (0.32), 650 (1.00). Excitation spectrum (emission at 651 nm, rel.int.): 621 (1.00), 576 (0.60), 348 (0.42)**.** ^{1}H-NMR: (500 MHz, CD_3CN / DMSO-d^6): δ[ppm] = 1.67 (s, H_3C13^1), 2.05 (s, H_3C7^1), 2.11 (m, H_2C12^2), 2.20 (s, H_3C17^1), 2.26 (s, H_3C2^1), 2.29 (m, H_AC12^1), 2.65 (m, H_2C3^1), 2.79 (m, H_BC12^1), 3.37 (m, H_AC3^2), 3.46 (m, H_BC3^2), 3.55 (s, H_3C8^5), 4.00 (br. s, $HO3^3$), 4.09 / 4.30 (AB-system, J =

14.3 Hz, H_2C5), 4.80 (s, $HC8^2$), 5.40 (dd, *J* = 11.4 Hz, H_AC18^2), 5.68 (s, HC15), 6.37 (dd, *J* = 2.3/17.6 Hz, H_BC18^2), 6.67 (dd, *J* = 11.4/17.6 Hz, $HC18^1$), 9.56 (s, $HC1^1$), 11.90 (br. s, HN21). ^{1}H NMR: (500 MHz, CD_3OD): δ [ppm] = 2.07 (s, H_3C13^1), 2.19 (br. s, H_3C17^1, superimposed by m, H_2C12^2), 2.23 (s, H_3C7^1), 2.29 (s, H_3C2^1), 2.68 (t, *J* = 6.9 Hz, H_2C3^1, superimposed by m, H_AC12^1), 2.79 (m, H_BC12^1), 3.48 (t, *J* = 6.9 Hz, H_2C3^2), 3.67(s, H_3C8^5), 4.19 / 4.21 (AB-system, *J* = 16.1 Hz, H_2C5), 5.48 (dd, *J* = 1.5, 11.6 Hz, H_AC18^2), 6.02 (s, HC15), 6.31 (d, *J* = 17.6 Hz, H_BC18^2), 6.68 (dd, *J* = 11.6, 17.6 Hz, $HC18^1$), 9.46 (s, $HC1^1$). ESI-MS: m/z (%) = 1473.2 (15, $[2M+3Na{-}2H]^+$); 1451.3 (18, $[2M+2Na{-}H]^+$); 1444.9 (15, $[2M+K]^+$); 1428.9 (36, $[2M+Na]^+$); 728.1 (16), 727.1 (36), 726.1 (66), 725.1 (100, $[M+Na]^+$); 707.1 (9), 706.0 (7), 705.1 (10), 704.1 (9), 703.1 (18, $[M+H]^+$).

Cd-1: UV/Vis (λ_{max}, log ε, MeOH): 613 (4.52), 570sh (4.35), 347 (4.29), 317 (4.33). Fluorescence (exc. at 621 nm, rel. int.): 706 (0.34), 648 (1.00). Fluorescence excitation (obs. at 648 nm, rel. int.): 616 (1.00), 571sh (0.66), 348 (0.38). ^{1}H NMR (500 MHz, CD_3OD): δ [ppm] = 2.00 (s, H_3C7^1), 2.13 (br. s, H_3C13^1), 2.23 (s, H_3C17^1), 2.30 (s, H_3C2^1, superimposed by m, H_2C12^2), 2.73 (m, H_2C3^1), 2.80 (m, H_AC12^1), 2.90 (m, H_BC12^1), 3.65 (m, H_2C3^2), 3.73 (s, H_3C8^5), 4.31 / 4.35 (AB-system, *J* = 16.5 Hz, H_2C5), 5.42 (d, *J* = 11.6 Hz, H_AC18^2), 6.06 (s, HC15), 6.14 (d, *J* = 17.9 Hz, H_BC18^2), 6.64 (dd, *J* = 11.6, 17.9 Hz, $HC18^1$), 9.37 (s, $HC1^1$). ESI-MS: m/z (%) = 1600.8 (39, $[2M+2K+Na{-}2H]^+$), 1585.1 (66, $[2M+K+2Na{-}2H]^+$), 1571.3 (53, $[2M+3Na{-}2H]^+$), 1547.0 (37, $[2M+2Na{-}H]^+$), 799.5 (25), 798.1 (36), 797.2 (49), 796.1 (49), 795.1 (59), 794.1 (50), 793.2 (24, $[M+2Na{-}H]^+$), 778.3 (21), 777.1 (35), 776.1 (61), 775.1 (100), 774.1 (66), 773.1 (72), 772.1 (40), 771.1 (28, $[M+Na]^+$); 753.2 (21, $[M+H]^+$).

Cu-1: UV/Vis (λ_{max}, log ε, MeOH): 635 (4.38), 589 (4.16), 360 (4.26), 323 (4.33). ESI-MS: m/z (%) = 1462.8 (30, $[2M+K+Na{-}H]^+$), 1447.1 (17, $[2M+2Na{-}H]^+$), 1441.0 (50, $[2M+K]^+$), 1425.3 (22, $[2M+Na]^+$), 781.1 (8), 780.1 (22), 779.1 (12), 778.1 (24, $[M+2K{-}H]^+$), 765.3 (7), 764.3 (20), 762.9 (10), 762.1 (28, $[M+Na+K{-}H]^+$), 749.1 (9), 748.2 (8), 747.2 (10), 746.1 (16, $[M+2Na{-}H]^+$), 743.2 (18), 742.0 (52), 741.1 (30), 740.1 (100, $[M+K]^+$), 727.4 (10), 726.3 (26), 725.1 (23), 724.3 (60, $[M+Na]^+$), 702.2 (10, $[M+H]^+$).

Ni-1: UV/Vis (λ_{max}, log ε, MeOH): 626 (4.41), 585 (4.20), 356 (4.17), 326 (4.23). ^{1}H-NMR: (500 MHz, d_6-DMSO): δ[ppm] = 2.00 (m, H_2C12^2), 2.08, 2.09 (2 s, rel. int. 0.6/1, H_3C2^1), 2.11 (s, H_3C17^1), 2.13, 2.15 (2 s, rel. int. 1/0.6, H_3C13^1), 2.15, 2.16 (2 s, rel. int. 0.6/1, H_3C7^1), 2.43 (m, H_AC3^1), 2.56 (m, H_BC3^1), 2.62 (m, H_2C12^1), 3.21 (m, H_2C3^2), 3.586, 3.591 (2 s, rel. int. 0.6/1, H_3C8^5), 3.98, 3.99 (2 s, rel. int. 0.6/1, H_2C5), 4.468, 4.471 (t, *J* = 5.2 Hz, $HO3^3$), 4.84, 4.87 (2 s, rel. int. 1/0.6, $HC8^2$), 5.25, 5.26 (2 d, rel. int. 0.6 / 1, *J* = 11.5 Hz,

H_AC18^2), 5.93, 5.94 (2 d, rel. int. 1/0.6, *J* = 2.6 / 17.6 Hz, H_BC18^2), 6.01, 6.02 (2 s, rel. int. 1/0.6, HC15), 6.348, 6.353 (2 dd, rel. int. 1/0.6, *J* = 11.5 / 17.6 Hz, $HC18^1$), 9.71, 9.78 (2 s, rel. int. 0.6/1, $HC1^1$)**.** ESI-MS: m/z (%) = 1452.9 (40, $[2M+Na+K–H]^+$); 1431.0 (66, $[2M+K]^+$); 1415.0 (46, $[2M+Na]^+$); 1392.9 (26, $[2M+H]^+$); 773.3 (15, $[M+2K–H]^+$); 760.1 (13), 759.2 (20), 758.1 (14),757.2 (32, $[M+Na+K–H]^+$); 743.2 (10), 742.1 (10), 741.3 (26, $[M+2Na–H]^+$); 738.0 (20), 737.1 (56), 736.1 (40), 735.1 (88, $[M+K]^+$); 722.1 (20), 721.1 (48), 720.1 (40), 719.1 (90, $[M+Na]^+$); 700.1 (18), 699.1 (45), 698.1 (38), 697.1 (100, $[M+H]^+$)**.**

Measurement of complexation rates

At 22 °C and in a 1 cm UV/Vis cell, to 3.0 mL the methanolic solution of PiCC (**1**), about 80 μL of a methanolic solution of $M(OAc)_2$ were injected (see **Table 1** for specification of calculated concentrations). The cell was immediately placed in the spectrophotometer and the absorption intensity at 620 nm was recorded in a time scan model. Kinetic analysis of the experimental absorption values of 620 nm by pseudo first order kinetic ($y = y_0 + Ae^{-kt}$) gave the *k* values (see **Table 1** and **Figure S5**).

Assay for Zn(II)-ions by detection of the red fluorescence of Zn-1

Preparation of stock solutions:

Two stock solutions (A: 3 μM, B: 150 μM) of $Zn(OAc)_2·2H_2O$ in 2 mL of freshly distilled MeOH were prepared

Crystallized PiCC (**1**) was dissolved in 3 mL of freshly distilled MeOH to furnish the stock solution with 7.0 μM **1** (calculated from the UV/Vis spectrum)

Procedure:

First, the luminescence spectrum of PiCC (**1**) in 3.0 mL MeOH was measured at 22 °C (excited at 620 nm, PMT voltage: 650 V) in the absence of $Zn(OAc)_2$. To the solution of **1**, 1 μL of $Zn(OAc)_2$ solution (A) was injected to obtained a sample with 1 nM Zn^{2+}. After 50 minutes, the emission spectrum of this sample was recorded at the same measurement condition as that for **1**. Subsequently, 1 μL of $Zn(OAc)_2$ solution (A) was again injected into the aforementioned solution to get a new sample with 2 nM Zn^{2+}. The emission spectrum of this sample ($[Zn^{2+}]$ = 2 nM) was measured after 50 min. In the same way, additional volumes of $Zn(OAc)_2$ solution (A) or $Zn(OAc)_2$ solution (B) were injected to the previous mixture to form new samples with higher concentration of Zn^{2+} and the corresponding emission spectra were detected. In the emission spectra, values of intensities at 650 nm were chosen to view the linear log/log plots of the fluorescence intensity and the concentration of Zn^{2+} after correction.

Assay for Cd(II)-ions by detection of the red fluorescence of Cd-1

Preparation of stock solutions:

Two stock solutions (A: 3 μM, B: 150 μM) of $Cd(OAc)_2 \cdot 2H_2O$ in 2 mL of freshly distilled MeOH were prepared.

Crystallized PiCC (**1**) was dissolved in 3 mL of freshly distilled MeOH to furnish the stock solution with 13.0 μM **1** (calculated from the UV/Vis spectrum)

Procedure:

First, the luminescence spectrum of PiCC (**1**) in 3.0 mL MeOH was measured at 22 °C (excited at 620 nm, PMT voltage: 650 V) in the absence of $Cd(OAc)_2$. To the solution of **1**, 1 μL of $Cd(OAc)_2$ solution (A) was injected to obtained a sample with 1 nM Cd^{2+}. After 50 minutes, the emission spectrum of this sample was recorded at the same measurement condition as that for **1**. Subsequently, 1 μL of $Cd(OAc)_2$ solution (A) was again injected into the aforementioned solution to get a new sample with 2 nM Cd^{2+}. The emission spectrum of this sample ($[Cd^{2+}]$ = 2 nM) was measured after 50 min. In the same way, additional volumes of $Cd(OAc)_2$ solution (A) or $Cd(OAc)_2$ solution (B) were injected to the previous mixture to form new samples with higher concentration of Cd^{2+} and the corresponding emission spectra were detected. In the emission spectra, values of intensities at 648 nm were chosen to view the linear log/log plots of the fluorescence intensity and the concentration of Cd^{2+} after correction.

Table S3. ^{1}H-NMR data (500MHz) and ^{13}C-NMR data (125MHz) of PiCC and Zn-PiCC

	PiCC (^{1}H NMR) in d_6-DMSO	PiCC (^{13}C NMR) in d_6-DMSO	Zn-PiCC (^{1}H NMR) in CD_3CN / d_6-DMSO (10 : 1)	Zn-PiCC (^{1}H NMR) in CD_3OD	Zn-PiCC(^{13}C NMR) in CD_3OD
C1		127.9			129.9
C-1^1	9.51		9.56	9.46	
C-2					136.2
C-2^1	2.19	9.0	2.26	2.29	9.5
C-3		119.5			121.3
C-3^1	2.55	27.1	2.65	2.68	27.8
C-3^2	3.33	61.3	3.37 / 3.46	3.48	62.7
O-3^3			4.00		
C-4		134.9			137.4
C-5	4.10 / 4.12	22.6	4.09 / 4.30	4.19 / 4.21	27.5
C-6		146.1			154.3
C-7		114.1			117.9
C-7^1	2.13	8.7	2.05	2.23	9.7
C-8		135.9			
C-8^1		187.0			
C-8^2	5.04	65.2	4.80		
C-8^3		169.7			170.6
C-8^5	3.62	52.0		3.67	53.2
C-9		146.0			
C-10		129.5			
C-11		144.6			
C-12		141.1			143.7
C-12^1	3.02	23.7	2.29 / 2.79	2.79	22.4
C-12^2	2.13	39.2	2.11	2.19	36.0
C-12^3		175.1			178.2
C-13		135.4			136.5
C-13^1	2.09	9.5	1.67	2.07	9.4
C-14		163.9			164.5
C-15	6.15	98.1	5.68	6.02	96.6
C-16		143.6			157.1
C-17		141.3			145.1
C-17^1	2.20	9.0	2.20	2.19	9.7
C-18		126.9			130.7
C-18^1	6.65	126.3	6.67	6.68	127.5
C-18^2	5.49 / 6.33	120.3	5.40 / 6.37	5.48 / 6.31	120.8
C19		169.8			182.3
N21	12.04		11.90		
N22					
N23					
N24	10.00				

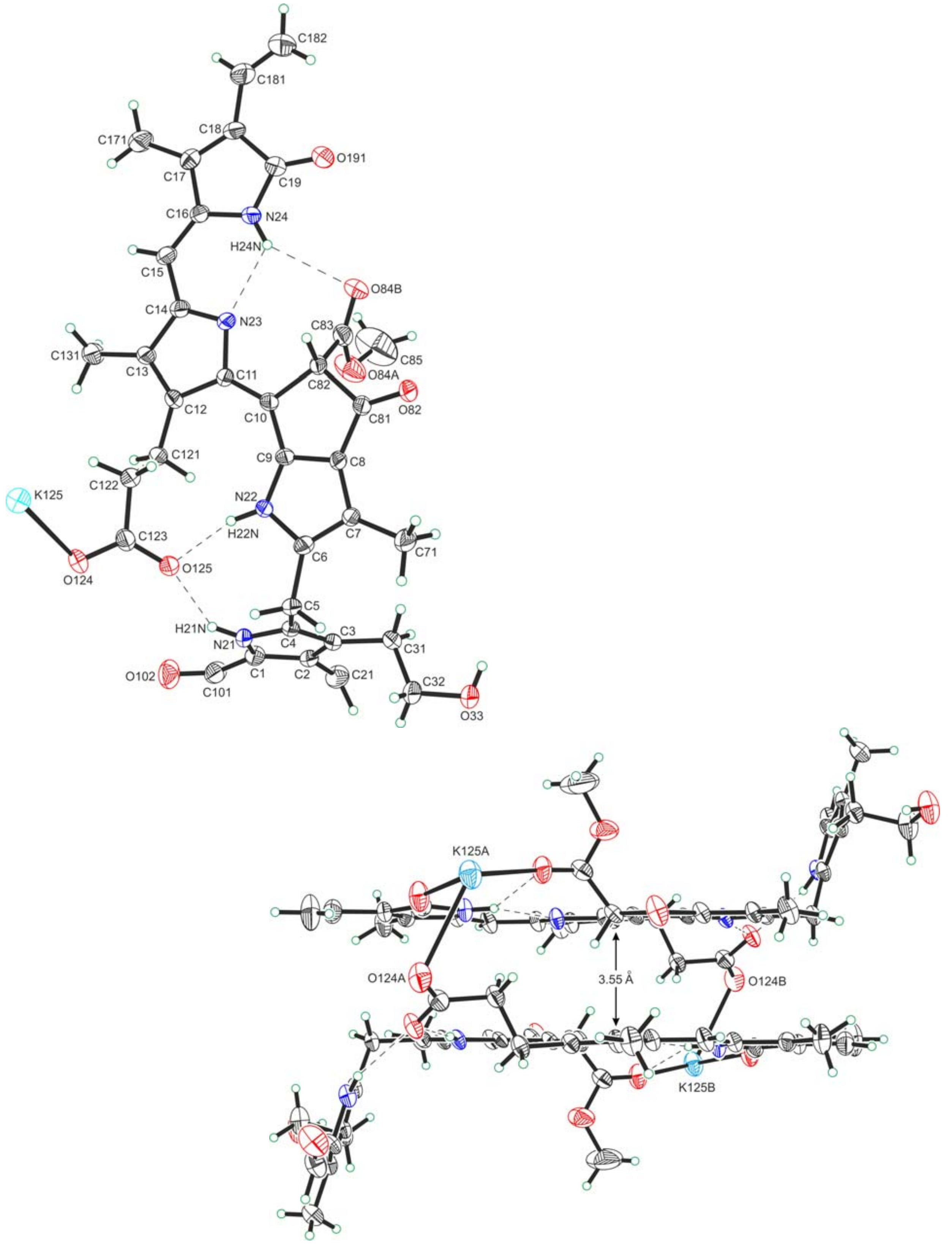


Figure S1. Crystal structure of the potassium salt **K-1** of PiCC (**1**) (top: single molecule, bottom: side view of K-bridged pair of enantiomers; atoms are coloured black (C), red (O), blue (N), green (H) and cyan (K)).

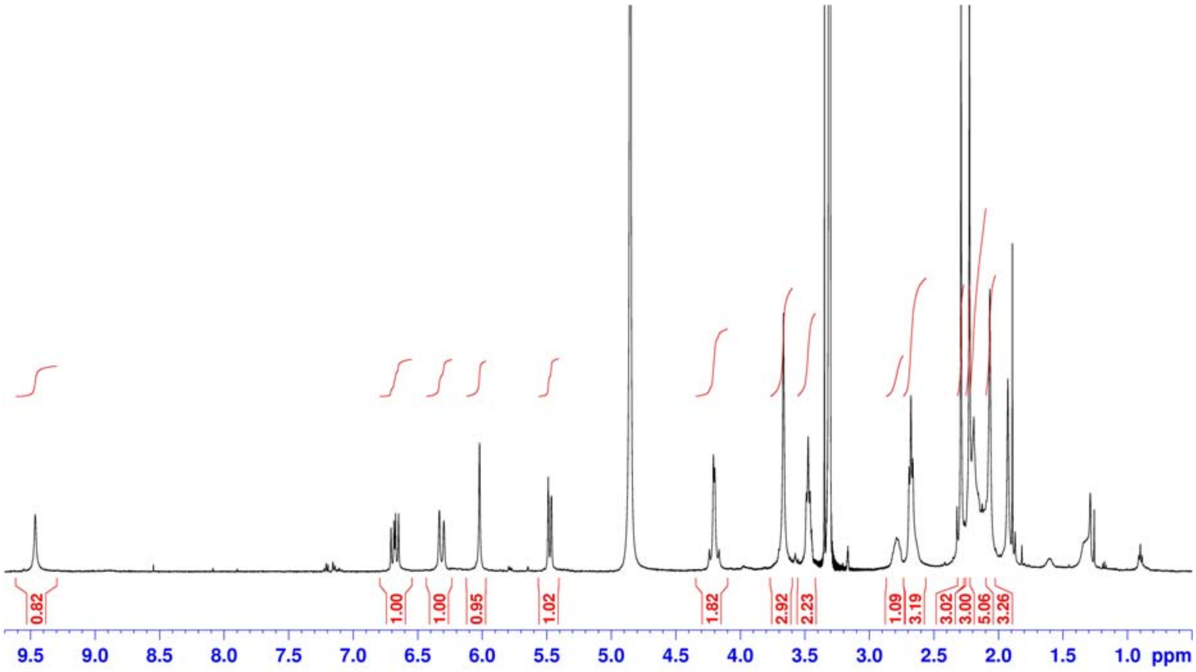


Figure S2. ^{1}H-NMR spectrum of **Zn-1** in CD_3OD (500MHz, 25 °C).

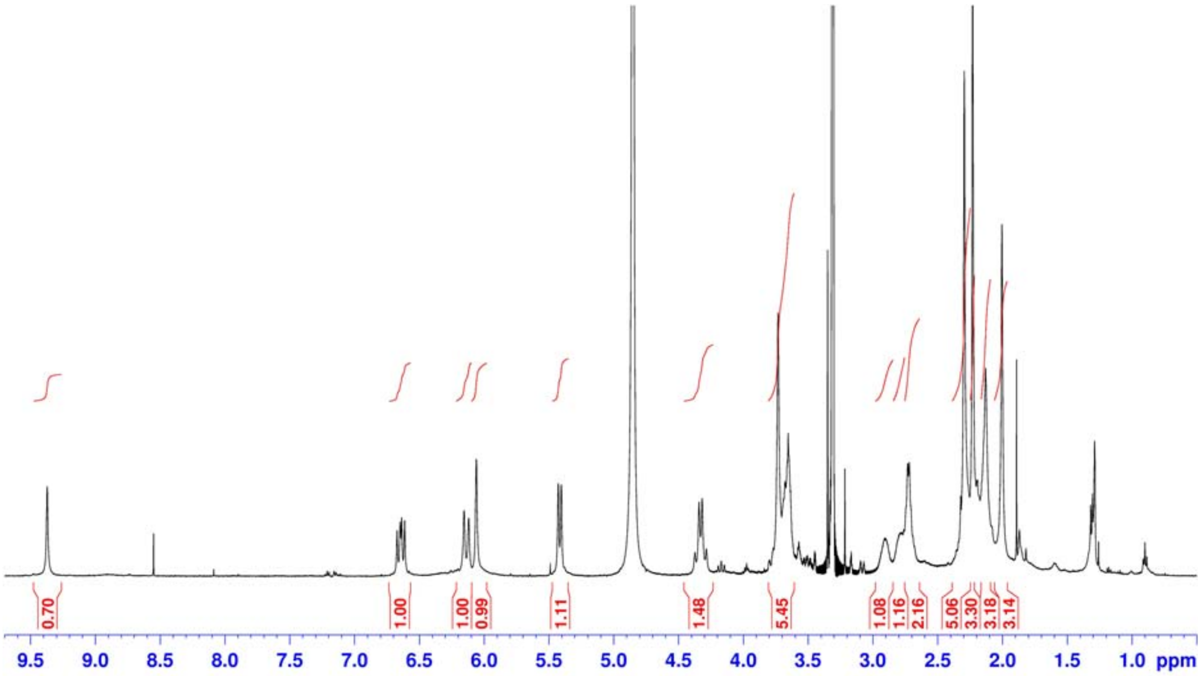


Figure S3. ^{1}H-NMR spectrum of **Cd-1** in CD_3OD (500MHz, 25 °C).

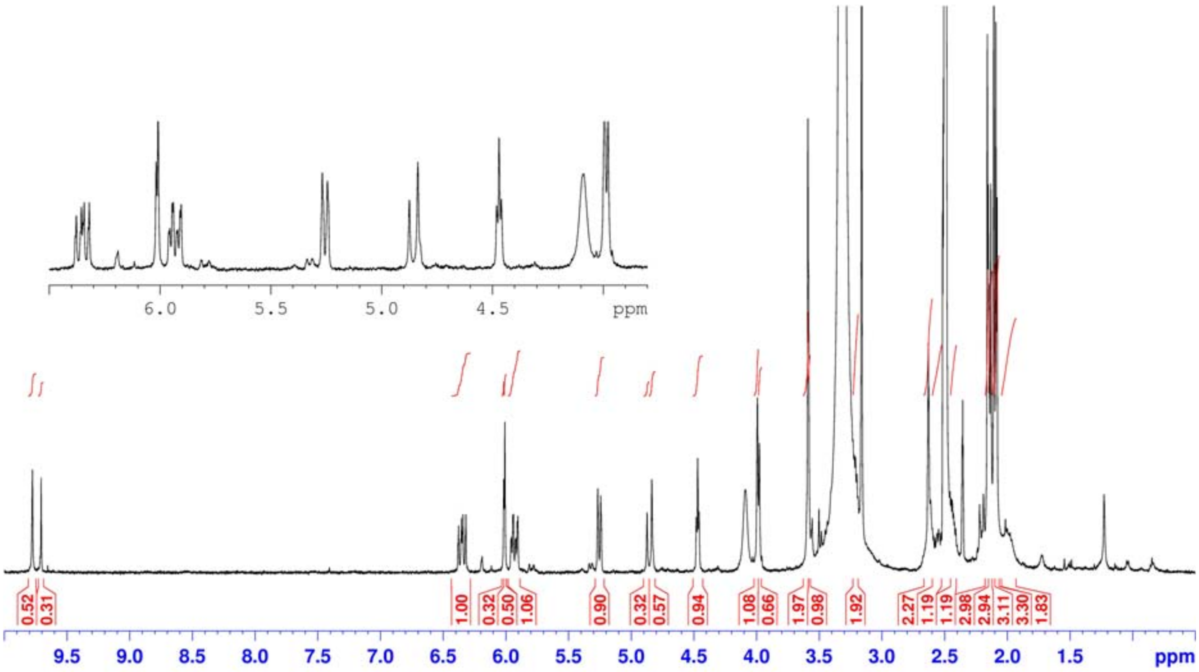


Figure S4. ^{1}H-NMR spectrum of **Ni-1** in d^6-DMSO (500MHz, 25 °C).

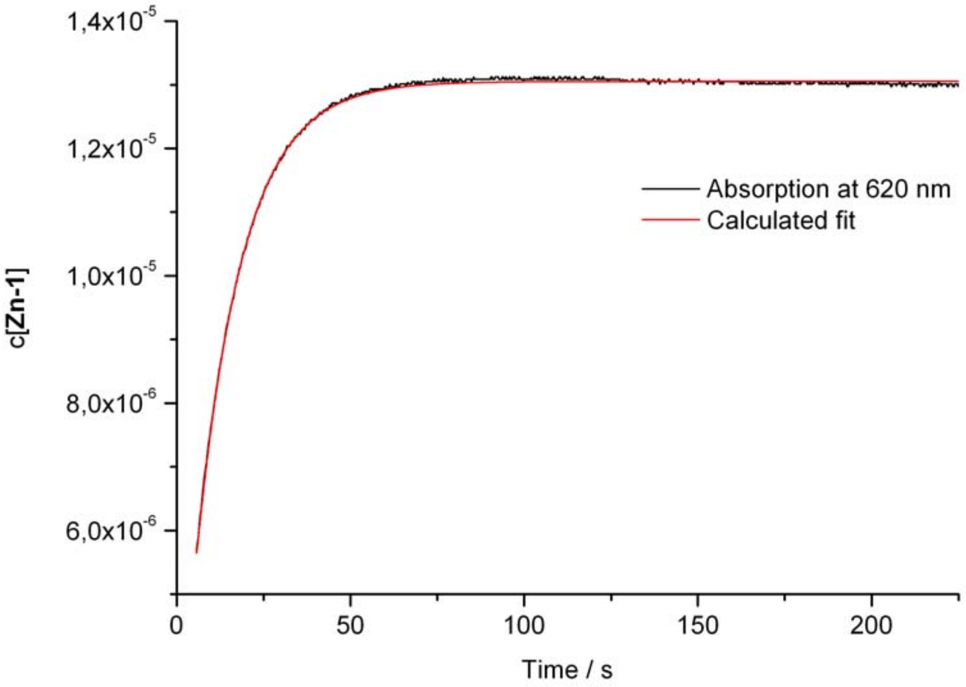
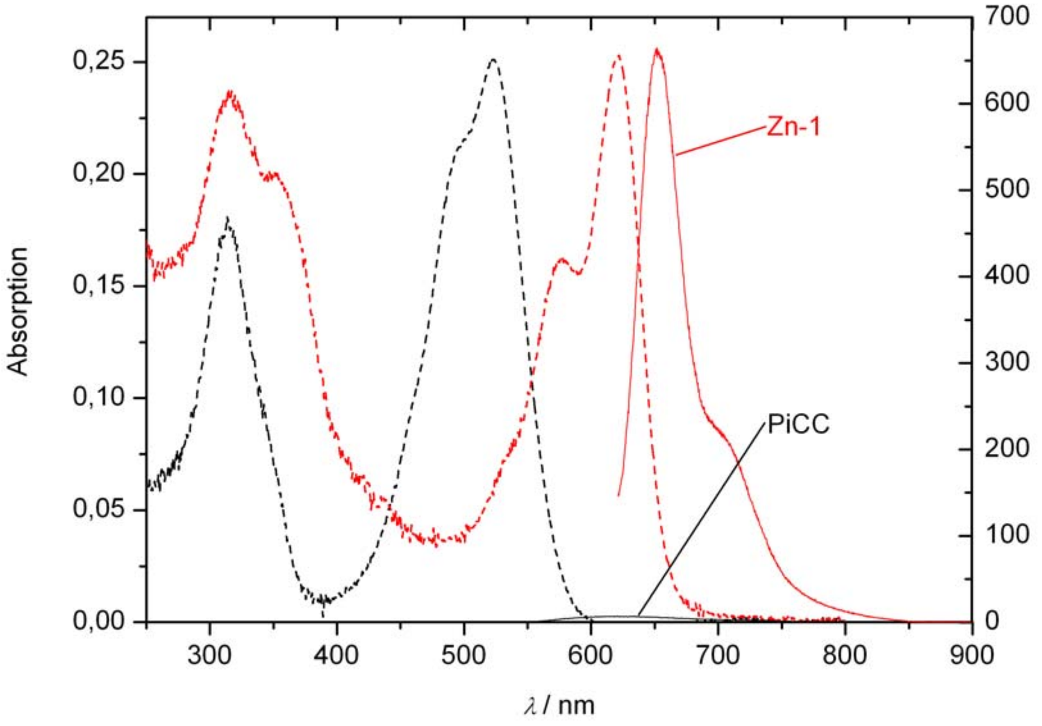


Figure S5. Kinetics of the formation of **Zn-1** from PiCC (**1**), in a solution of **1** (13.1 μM) and of $Zn(OAc)_2$ (123 μM) in MeOH at 22 °C. Kinetic analysis from a fit of the experimental absorption values of 620 nm (black line) by pseudo first order kinetics ($y = y_0 + Ae^{-kt}$), gives $k = 0.075\ s^{-1}$ and $t_{1/2} = 9.2$ s.



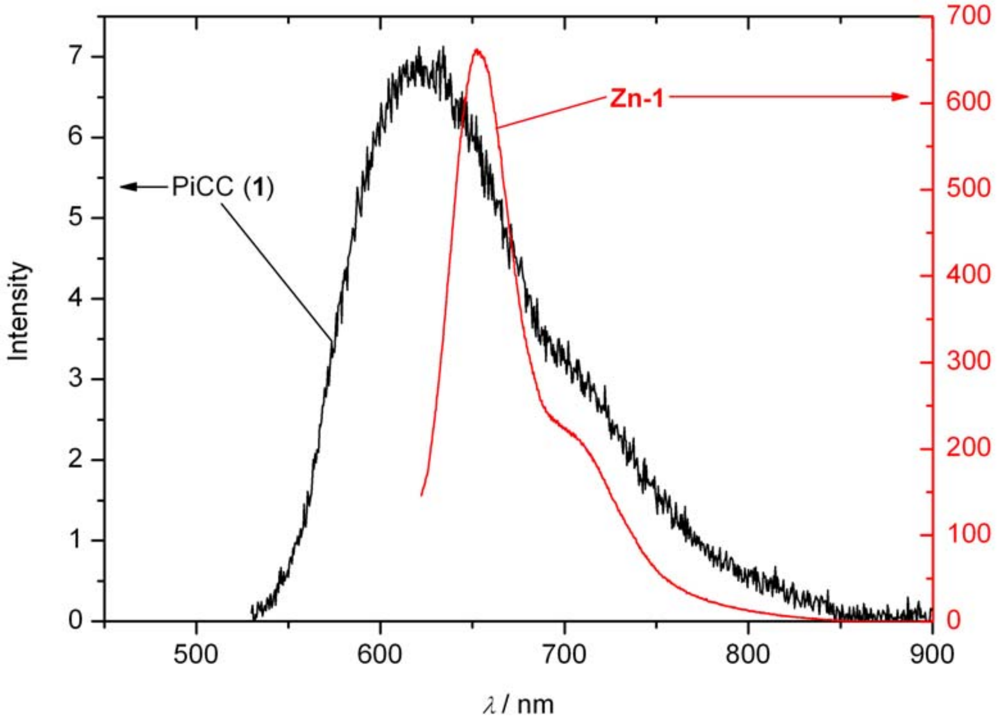
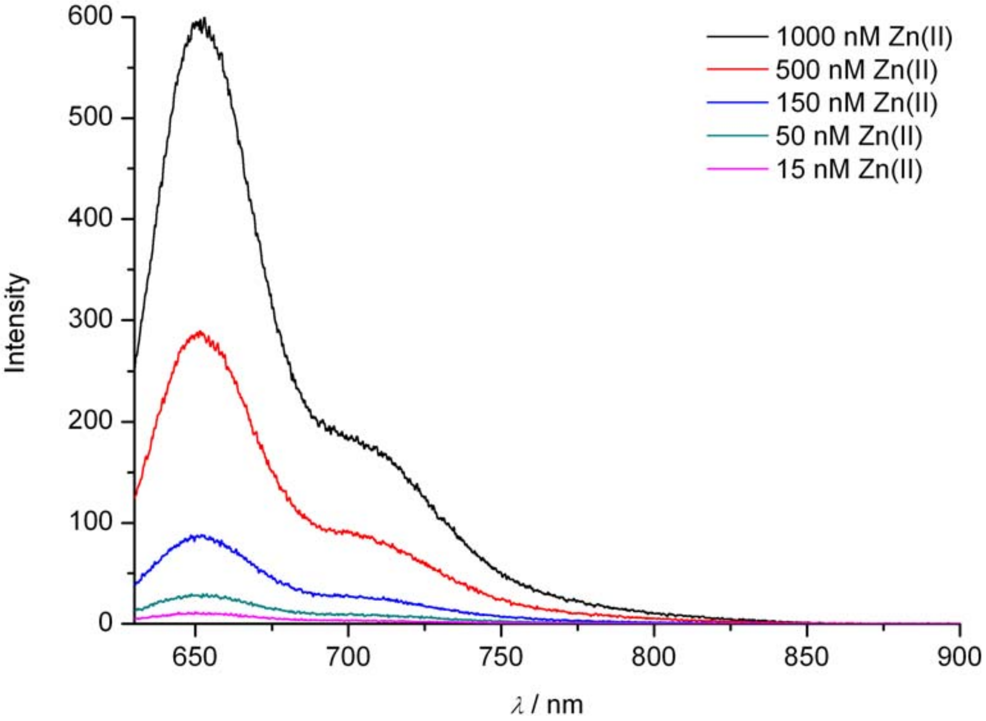


Figure S6. Fluorescence emission spectra (full lines) and absorption spectra (dashed lines) of solutions of PiCC (**1**, black lines) and of **Zn-1** (red lines) in MeOH. Note: concentration of **1** and of **Zn-1** were set to give solutions with identical absorption intensity at the wavelengths of the excitation, i.e. at 520 nm and at 620 nm, resp. (see top).



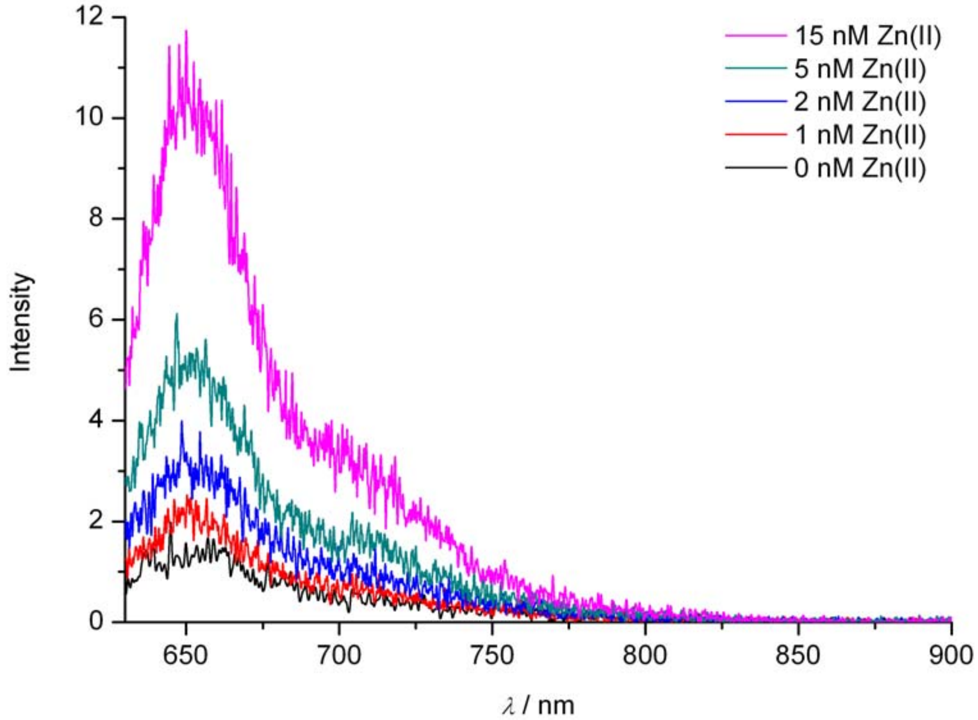
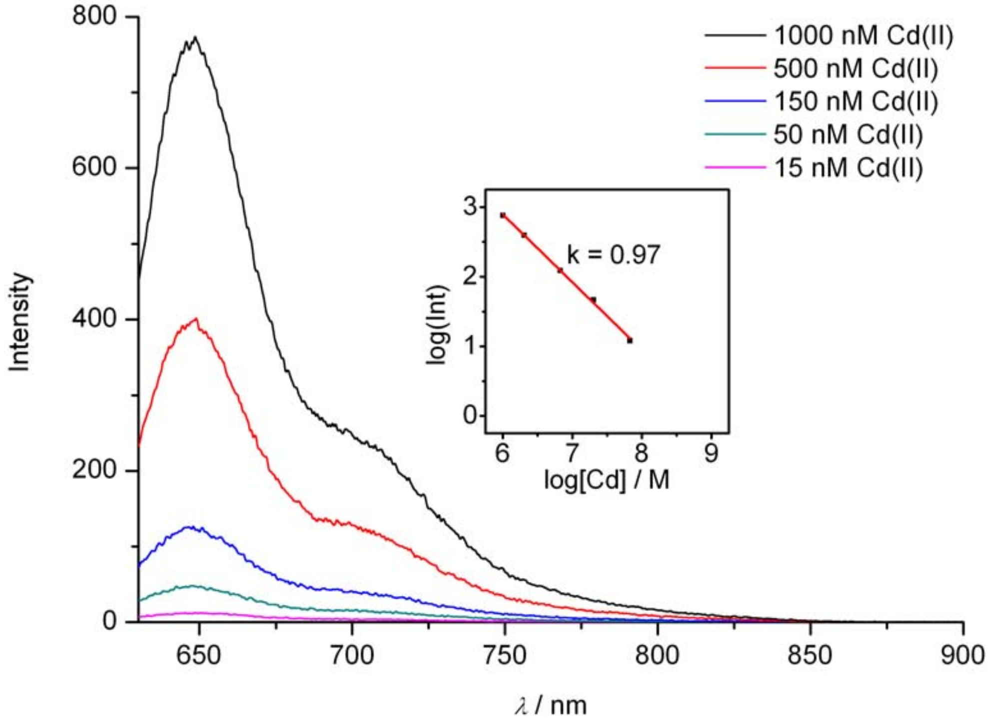


Figure S7. Assay for Zn(II)-ions in solution by detection of the red fluorescence of the zinc complex **Zn-1**. Top: Original (uncorrected) fluorescence spectra for methanolic solutions of PiCC (**1**, 7.0 μM) and concentrations of Zn(II)-ions (total) from 1000 nM down to 15 nM. Bottom: Fluorescence spectra for methanolic solutions of PiCC (**1**, 7.0 μM) and concentrations of Zn(II)-ions (total) from 15 nM down to 0 nM.



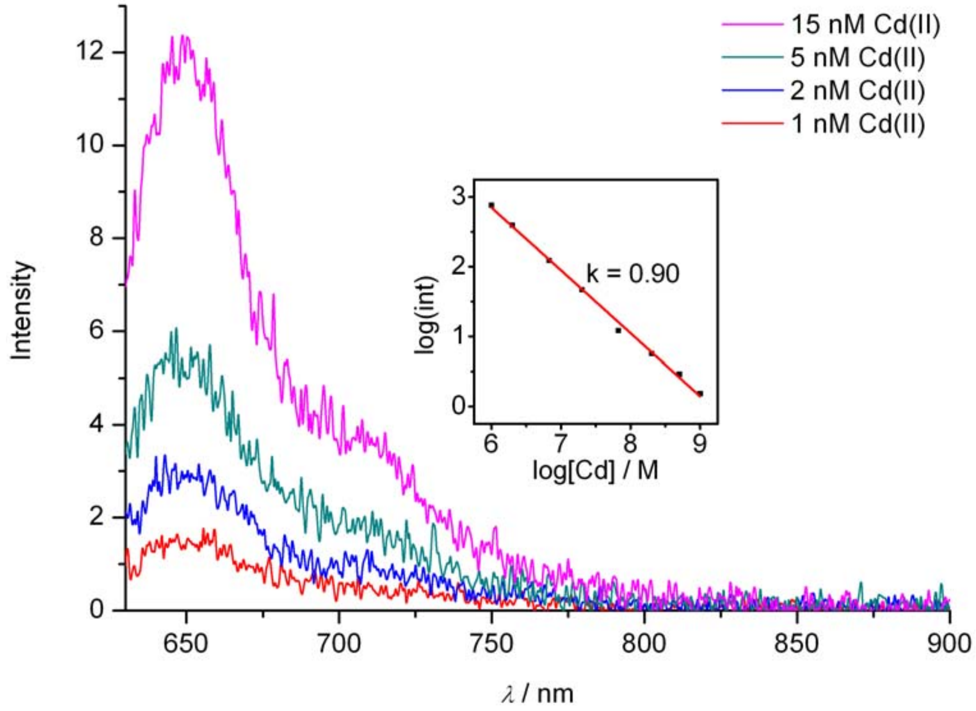


Figure S8. Assay of Cd(II)-ions in solution by detection of the red fluorescence of the cadmium complex **Cd-1**. Top: Corrected fluorescence spectra for methanolic solutions of PiCC (**1**, 13.0 μM) and concentrations of Cd(II)-ions (total) from 1000 nM down to 15 nM. Inset is the log/log plot on the basis of the corrected data from 1000 nM to 15 nM. Bottom: Corrected fluorescence spectra for methanolic solutions of PiCC (**1**, 13.0 μM) and concentrations of Cd(II)-ions (total) from 15 nM down to 1 nM. Inset is the log/log plot on the basis of the corrected data from 15 nM down to 1 nM.

References

[1] M. Ulrich, S. Moser, T. Müller, and B. Kräutler, *Chem. Europ. J.*, 2011, **17**, 2330.

[2] S. Moser, M. Ulrich, T. Müller, and B. Kräutler, *Photochem. Photobiol. Sci.*, 2008, **7**, 1577.