SUPPORTING INFORMATION FOR

TRLFS Study on the Complexation of novel BTP Type Ligands with Cm(III)

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Table of Contents

title **page**

TRLFS setup 2

Selected emission spectra 2

Fluorescence lifetime measurement 4

Synthesis of Et-BDP (**1**) and ^{n}Pr-tetrazine (**2**)

Instrumentation and Methods 4

Experimental Procedures and Chemicals 5

Synthesis of 2,6-bis(4-ethyl-pyridazin-1-yl)pyridine (Et-BDP, (**1**)) 5

Synthesis of 2,6-bis(4-^{n}propyl-2,3,5,6-tetrazine-1-yl)pyridine (^{n}Pr-tetrazine, (**2**)) 6

References 7

TRLFS setup

TRLFS measurements are performed using a Nd:YAG-pumped dye laser system [Surelite II laser (Continuum), NARROWscan D-R dye laser (Radiant Dyes Laser Accessories)]. For Eu(III) excitation a wavelength of 394.0 nm and for Cm(III) a wavelength of 396.6 nm was used. The emission spectra are recorded at an angle of 90° to the exciting laser beam. A Shamrock 303i spectrograph (ANDOR), equipped with a 300, 900 and 1200 lines/mm grating turret is used for spectral decomposition. The fluorescence emission is detected by an ICCD camera [iStar Gen III, A-DH 720 18F-63 (ANDOR)]. Rayleigh scattering and shortlived fluorescence of organic ligands is discriminated by a delay time of 1.0 µs before the fluorescence light is recorded. The quartz cuvette is temperature controlled at T = 25 °C.

Selected emission spectra

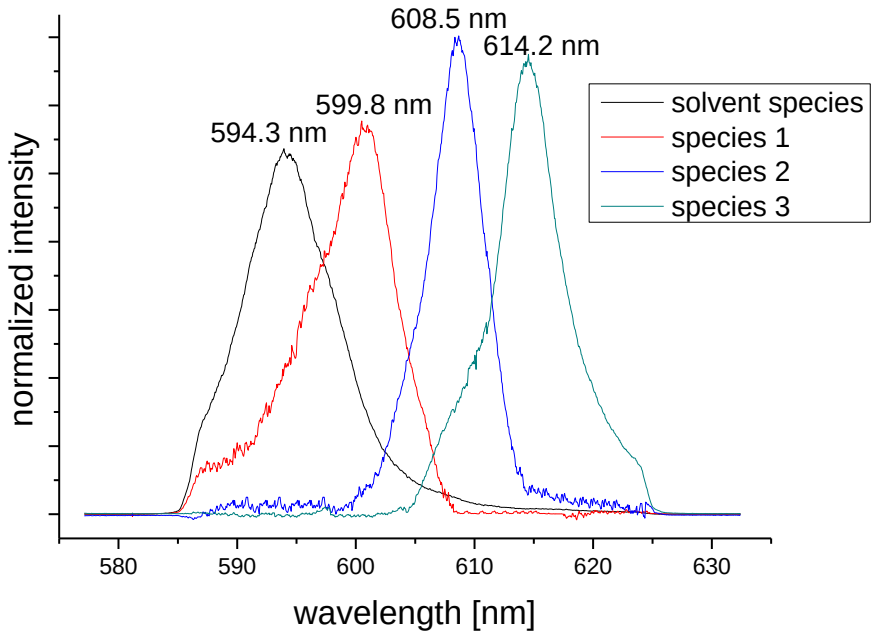


Fig. S1 Emission bands of the solvated Cm(III) ion and the Cm(III)-Et-BDP complex species.

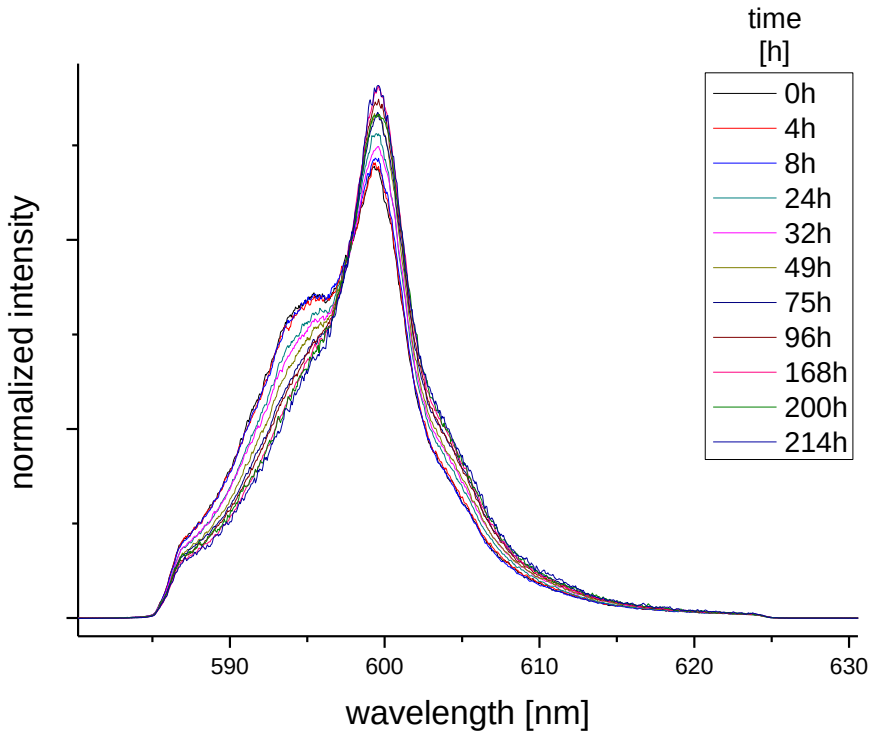


Fig. S2 Normalized fluorescence spectra of Cm(III) in 2-propanol : water 1:1 (vol.) as a function of time. $[Cm(III)]_{ini} = 2.0 \cdot 10^{-7}$ mol/l, [^{n}Pr-Tetrazine] = 52 µmol/l.

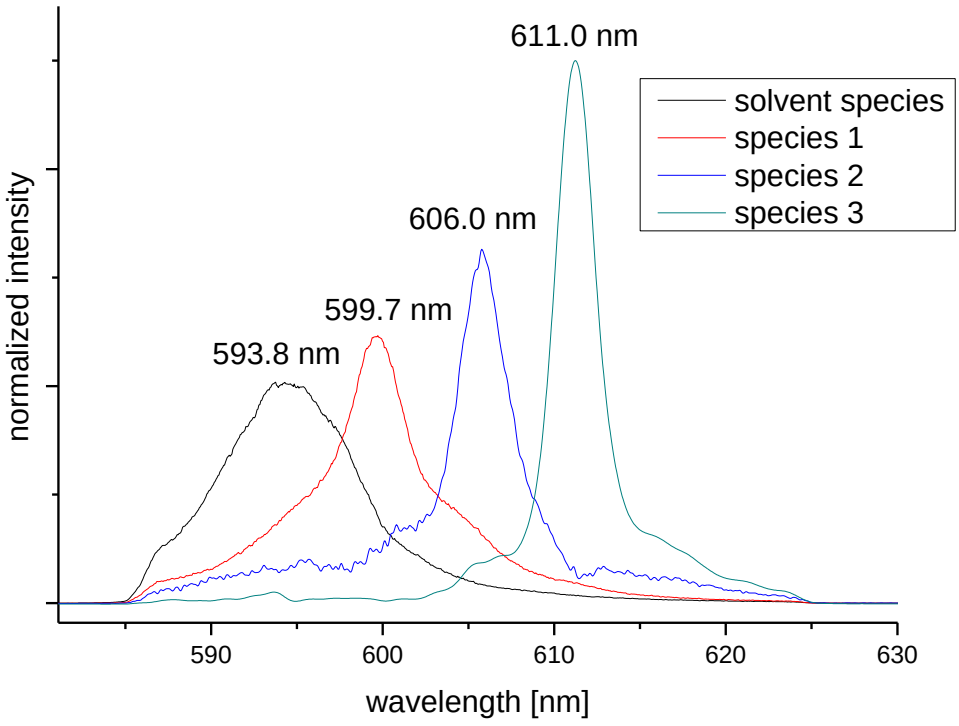


Fig. S3 Emission bands of the solvated Cm(III) ion and the Cm(III)-^{n}Pr-Tetrazine complex species.

Fluorescence lifetime measurement

For lifetime measurements the decay of the emission intensity is scanned with increasing delay time incremented in intervals of 20 µs for ^{n}Pr-BTP complexes, 10 µs for measurements with Et-BDP complexes, and 5 µs for measurements with ^{n}Pr-Tetrazine complexes, respectively. The lifetime τ is obtained by fitting the fluorescence intensity I vs. the delay time t after the laser pulse according to $I(\lambda) = I_0(\lambda) \exp(-\tau/t)$.

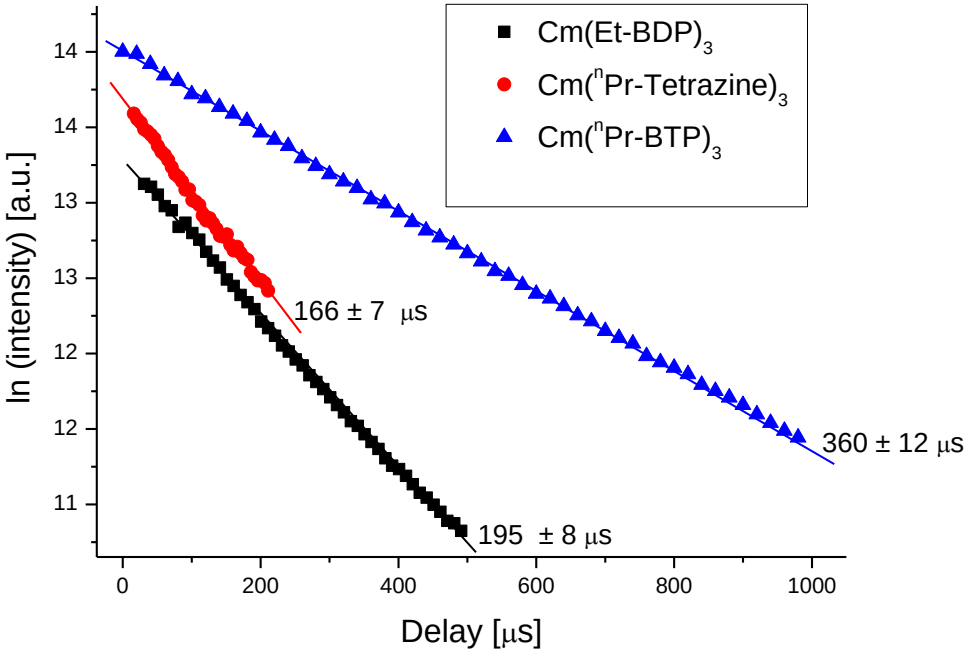


Fig. S4 Decay of the fluorescence intensity of Cm(^{n}Pr-BTP)$_3$, Cm(Et-BDP)$_3$ and Cm(^{n}Pr-Tetrazine)$_3$ in 2-propanol:water, 1:1 (vol.).

Synthesis of Et-BDP (1) and ^{n}Pr-tetrazine (2)

Instrumentation and Methods

NMR spectra are recorded on a Bruker Avance III 400 spectrometer, working at 400.17 MHz for ^{1}H, 100.63 MHz for ^{13}C and 40.56 MHz for ^{15}N, respectively. As solvent $CDCl_3$ is used and spectra are recorded at 27°C if not noted otherwise. $CDCl_3$ is purchased by Euriso-Top GmbH and used as received. Chemical shifts are referenced to internal solvent resonance and reported relative to tetramethylsilane.

^{15}N chemical shifts are referenced to $^{15}NH_4Cl$ with $\delta(NH_4Cl) = 0$. ESI mass spectra are recorded at a Finnigan LCQ spectrometer and HR ESI mass spectra at a Bruker ApexQe FT-ICR instrument at the Mass Spectrometry Facility of the Institute of Organic Chemistry, University of Heidelberg.

Experimental Procedures and Chemicals

Acetic acid, 2,6-pyridinedicarboxylic acid, butyronitrile, and silica for column chromatography (SiO_2 40, particle size 0.063-0.200 mm) are obtained from Merck. All other chemicals and solvents are purchased from Aldrich. The compounds and solvents are used as received.

Synthesis of 2,6-bis(4-ethyl-pyridazin-1-yl)pyridine (Et-BDP, (1))

2,6-Bis(1,4-dioxohex-1-yl)pyridine is obtained in a Stetter reaction from pyridine-2,6-dialdehyde and ethylvinylketone.[S1] 1.50 ml (15.14 mmol) ethylvinylketone are added to a mixture of 1.50 ml dry 1,4-dioxane, 1.25 ml (9.02 mmol) triethylamine and 0.49 g (1.82 mmol) benzyl hydroxyethyl methyl triazolium chloride. After heating the reaction mixture to 90°C, a solution of 1.00 g (7.40 mmol) pyridine-2,6-dialdehyde in 12 ml dry 1,4-dioxane is added over a period of 4 hours. The solution is cooled to 50°C and stirred for additional 36 hours. After cooling to room temperature the precipitate is filtered off and discarded. The solvent is evaporated in high vaccum. The product is purified by column chromatography (SiO_2, EtOAc/dioxane 10:1). ^{1}H NMR ($CDCl_3$, 400.1 MHz, 27.0 °C): δ (ppm) 8.13 (2H, d, ^3J = 7.6 Hz, *m*H), 7.93 (1H, t, ^3J = 7.6 Hz, *p*H), 7.50 (2H, d, ^3J = 8.7 Hz, CH), 3.11 (4H, q, ^3J = 7.6 Hz, CH_2) 1.44 (6H, t, ^3J = 7.6 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$,100.6 MHz, 27.0 °C) δ 207.12 (s, CO), 199.57 (s, Py-CO), 152.13 (s, *o*-C), 137.96 (s, *p*-C), 124.91 (s, *m*-C), 37.02 (s, CH_2), 31.69 (s, CH_2), 29.97 (s, CH_2), 7.91 (s, CH_3).

Et-BDP **(1)** is obtained in a two-step synthesis of 2,6-Bis(1,4-dioxohex-1-yl)pyridine with hydrazinehydrate and subsequent aromatization with Pd/C and O_2.[S2] 2.24 g (7.4 mmol) 2,6-Bis(1,4-dioxohex-1-yl)pyridine is dissolved in 15.0 ml dry ethanol. The reaction mixture is heated to 70°C and 0.78 ml (15.0 mmol) hydrazinehydrate is added over a time period of one hour. After refluxing for 5 hours the reaction mixture is stirred for additional 48 hours at 50°C. The crude product is added to 0.14 g Pd/C and refluxed for 10 hours. The Pd/C is removed by filtration and the product dried in high vaccum.

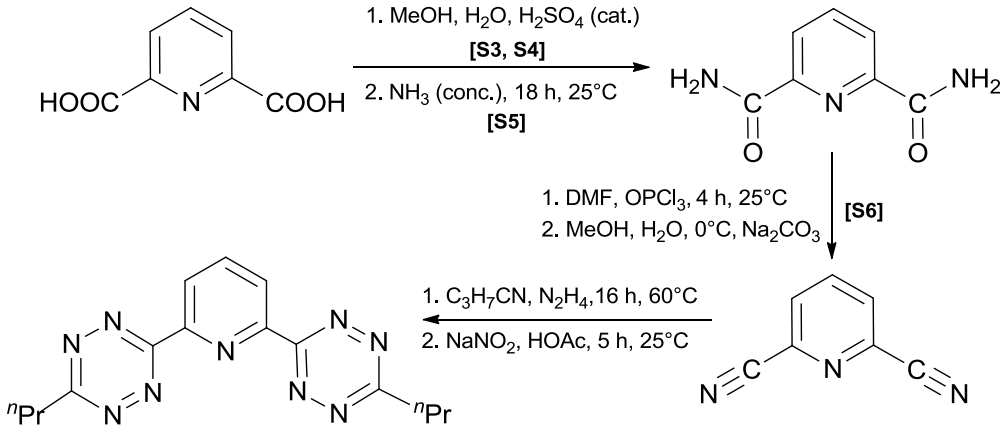
The product is first crystallized from methanol and then purified by column chromatography (1st column: 20 cm SiO_2, EtOAc:1,4-Dioxane:NEt_3 = 100:50:5; 2nd column: 38 cm SiO_2, EtOAc:1,4-Dioxane:NEt_3 = 100:50:5; The second column chromatography step is repeated five times) and the product obtained in 5.9% yield (124.0 mg, 0.426 mmol).

^{1}H NMR ($CDCl_3$, 400.1 MHz, 27.0 °C): δ (ppm) 8.76 (2H, d, ^3J = 7.9 Hz, *m*H), 8.59 (2H, d, ^3J = 8.7 Hz), 8.05 (1H, t, ^3J = 7.9 Hz CH), 7.50 (2H, d, ^3J = 8.7 Hz, CH), 3.11 (4H, q, ^3J = 7.6 Hz, CH_2) 1.44 (6H, t, ^3J = 7.6 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 27.0 °C) δ 164.68 (s, Et-C), 156.60 (s, Py-C), 153.11 (s, *o*C), 138.43 (s, *p*C), 126,76 (s, CH), 124.95 (s, CH), 122.17 (s, *m*C), 29.13 (s, CH_2), 13.54 (s, CH_3); ^{15}N-^{1}H *HMQC* NMR ($CDCl_3$, 40.6 MHz/400.1 MHz, 27.0 °C) δ 387.9 (pyridazine-N), 382.9 (pyridazine-N), 297.3 (pyridine-N). HR-ESI-MS: m/z 292.15580 ($(M+H)^+$, 63.8%, calc. 292.15622), m/z 314.13780 ($(M+Na)^+$, 66.6%, calc. 314.13816), m/z 330.11177 ($(M+K)^+$, 60.5%, calc. 330.11210), m/z 605.28621 ($(2M+Na)^+$, 100.0%, calc. 605.28656).

Synthesis of 2,6-bis(4-^{n}propyl-2,3,5,6-tetrazine-1-yl)pyridine (^{n}Pr-tetrazine, (2))

2,6-pyridine-carboxylic acid dimethylester[S3,S4], 2,6-pyridinedicarboxamide[S5] and 2,6-dicyano-pyridine[S6] are synthesized according to literature procedures. ^{n}Pr-tetrazine is received in a one-pot-reaction from 2,6-dicyanopyridine, butyronitrile and hydrazine (see scheme 1, step 3).

Formation of 2,3,5,6-tetrazine moieties from two nitriles and hydrazine and subsequent aromatization with sodium nitrite and acetic acid has been reported earlier[S7,S8] but not yet applied for the synthesis of 2,6-bis(*s*-tetrazine-1-yl)pyridine ligands.



Scheme S1 Three-step synthesis of 2,6-Bis(4-^{n}propyl-2,3,5,6-tetrazine-1-yl)pyridine **2** from 2,6-pyridine dicarboxylic acid.[S3-S8]

1.00 g (7.75 mmol) 2,6-dicyanopyridine, 10.9 ml (0.12 mol) butyronitrile and 3.0 ml hydrazine hydrate (62.0 mmol) are stirred for 16 hours at 60°C. The resulting orange-yellow solution is separated from the white precipitate that was formed during the reaction. The white precipitate is found to be pyridine-2,6-bisamidrazine by ^{1}H NMR spectroscopy and can be reacted with additional butyronitrile and used in subsequent aromatization.

20 ml water, 20 ml CH_2Cl_2 and 2.97 g (43.0 mmol) $NaNO_2$ are added without additional purification of the yellow solution. 2.34 ml (41.0 mmol) HOAc are added dropwise. After the solution is stirred for 5 hours at room temperature and the solvent evaporated in high vaccum the crude product is purified by column chromatography (SiO_2, CH_2Cl_2) and obtained in 23% yield (439 mg, 1.36 mmol) as purple solid.

^{1}H NMR ($CDCl_3$, 400.1 MHz, 27.0 °C): δ (ppm) 8.84 (2H, d, ^{3}J = 7.9 Hz, *m*H), 8.29 (1H, d, ^{3}J = 7.9 Hz, *p*H), 3.43 (4H, t, ^{3}J = 7.9 Hz, CH_2), 2.05 (4H, sex, ^{3}J = 7.5 Hz, CH_2), 1.01 (6H, t, ^{3}J = 7.4 Hz, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 27.0 °C) δ 171.07 (s, ^{n}Pr-C), 163.60 (s, Py-CN), 151.83 (s, *o*C), 139.03 (s, *p*CH), 126.12 (s, *m*CH), 30.31 (s, CH_2), 21.82 (s, CH_2), 13.70 (s, CH_3). ESI-MS: m/z 324.2 ($(M+H)^+$, 36.1%, calc. 324.3), m/z 346.2 ($(M+Na)^+$, 36.0%, calc. 346.3), m/z 669.9 ($(2M+Na)^+$, 25.8%, calc. 669.7).

References

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