

SUPPORTING INFORMATION FOR

2,6-bis(1,2,4-triazine-5,6-diisopropyl-3-yl)pyridine: A highly selective N-donor ligand studied by TRLFS, liquid-liquid extraction and molecular dynamics

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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 fluorescence emission is 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 short-lived fluorescence of organic ligands are discriminated by a delay time of 1.0 μ s before the fluorescence is recorded. The quartz cuvette is temperature controlled at T = 25 °C. Titrations are performed by stepwise addition of a ⁱPr-BTP solution in MeOH:H₂O 1:1 (vol.) to a Cm(III) and Eu(III) solution, respectively, in the same solvent mixture. The solutions are allowed to equilibrate for 10 minutes before the fluorescence spectrum is recorded.

Selected Cm(III) and Eu(III) emission spectra

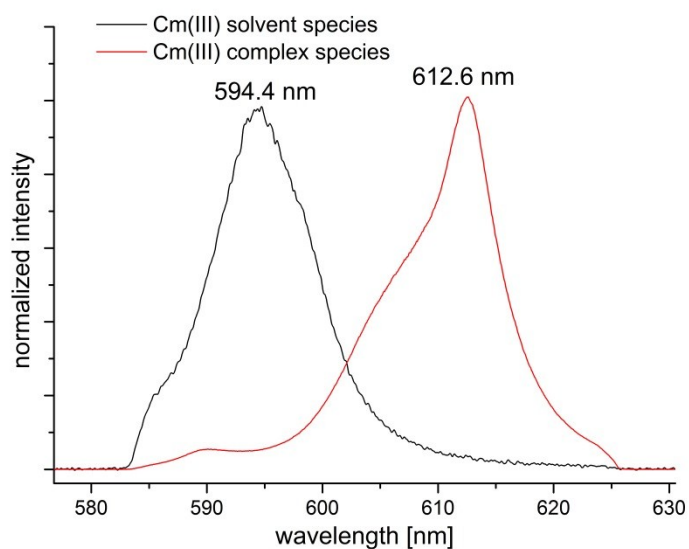


Figure S1 Emission spectra of the solvated Cm(III) ion and the Cm(III)-*i*Pr-BTP complex species in MeOH:H₂O 1:1 (vol.).

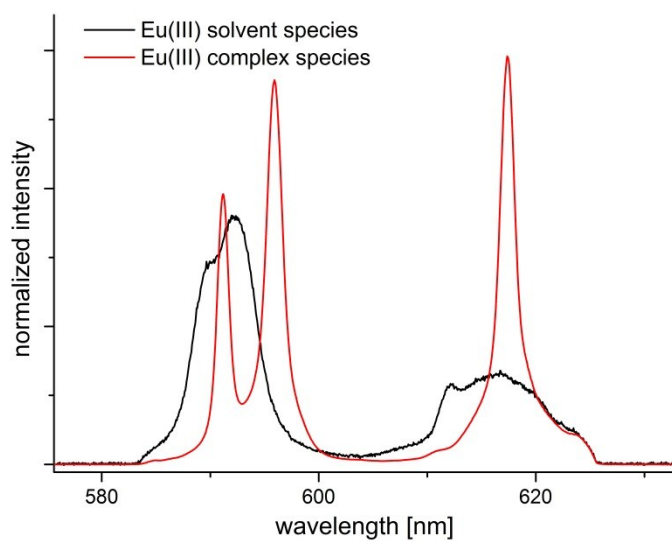


Figure S2 Eu(III) emission spectra resulting from the ${}^5D_0 \rightarrow {}^7F_{1/2}$ transition of the solvated Eu(III) ion and the Eu(III)-*i*Pr-BTP complex species in MeOH:H₂O 1:1 (vol.).

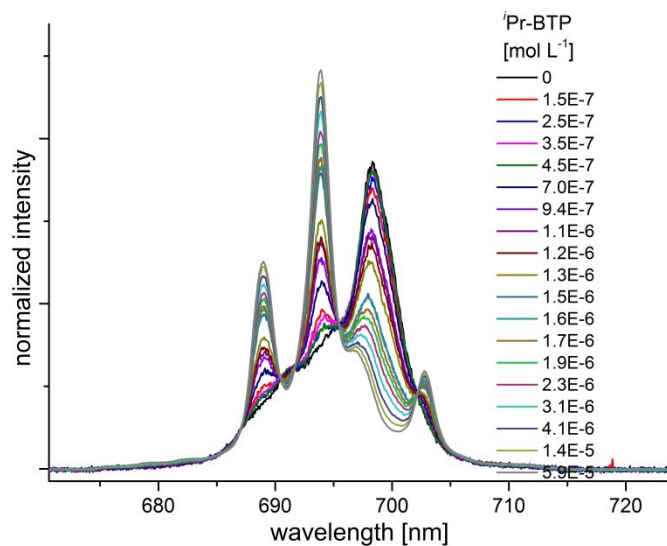


Figure S3 Eu(III) emission spectra resulting from the $^5D_0 \rightarrow ^7F_4$ transition as a function of the ligand concentration in MeOH:H₂O 1:1 (vol.); $[Eu(III)]_{ini} = 1.0 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$.

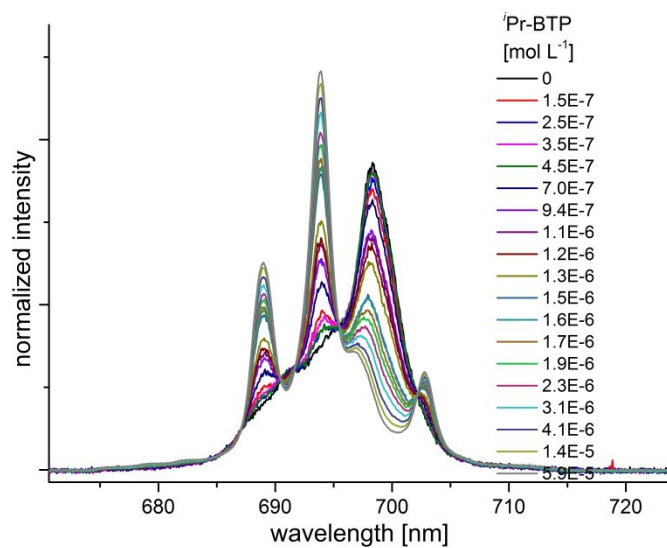


Figure S4 Eu(III) emission spectra resulting from the $^5D_0 \rightarrow ^7F_4$ transition of the solvated Eu(III) ion and the Eu(III)-*i*Pr-BTP complex species in MeOH:H₂O 1:1 (vol.).

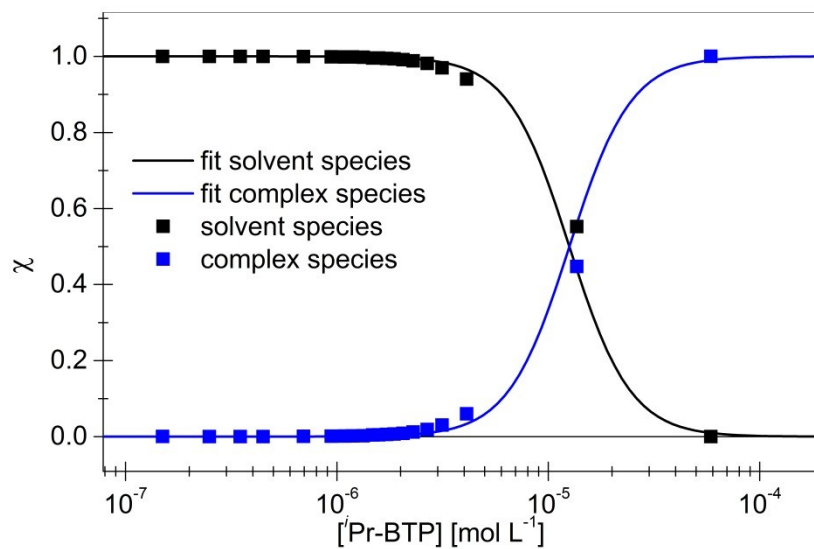


Figure S5 Species distribution of the Eu(III) complex species in MeOH:H₂O 1:1 (vol.) determined from deconvolution of the $^5D_0 \rightarrow ^7F_4$ bands; $[Eu(III)]_{ini} = 1 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; lines calculated with $\log \beta_3 = 14.9$.

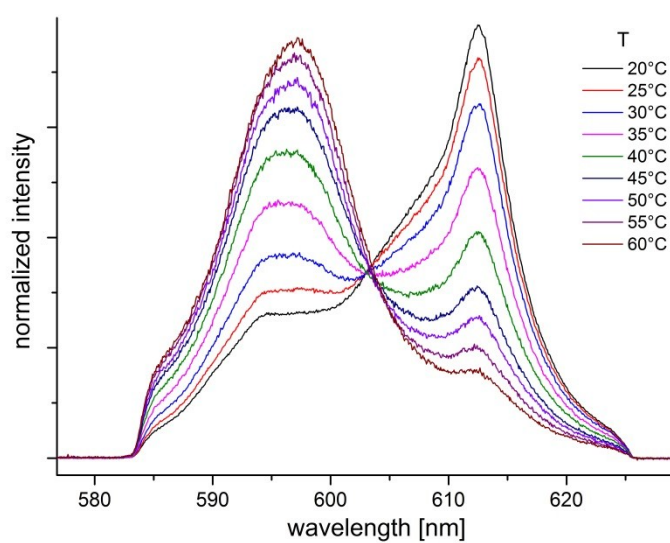


Figure S6 Normalized Cm(III) emission spectra as a function of the temperature in MeOH:H₂O 1:1 (vol.); $[Cm(III)] = 1 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$, $[Pr-BTP] = 1.2 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$.

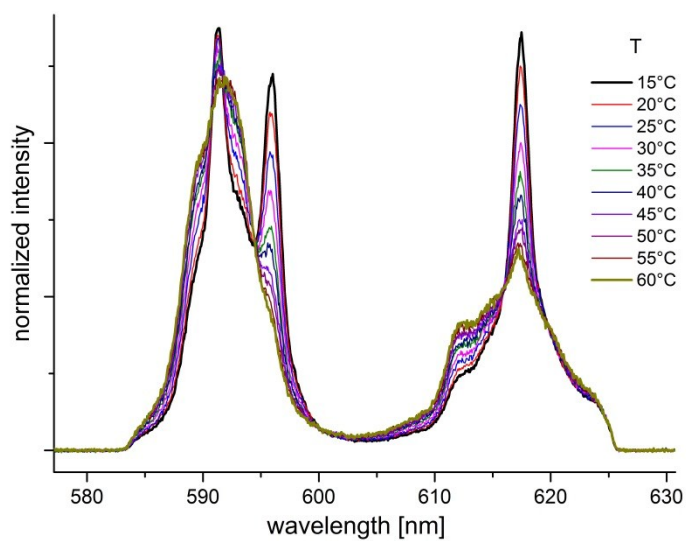


Figure S7 Normalized ${}^5D_0 \rightarrow {}^7F_{1/2}$ emission spectra of Eu(III) as a function of the temperature in MeOH:H₂O 1:1 (vol.); [Eu(III)] = $1.0 \cdot 10^{-5}$ mol·L⁻¹, [iPr-BTP] = $1.2 \cdot 10^{-6}$ mol·L⁻¹.

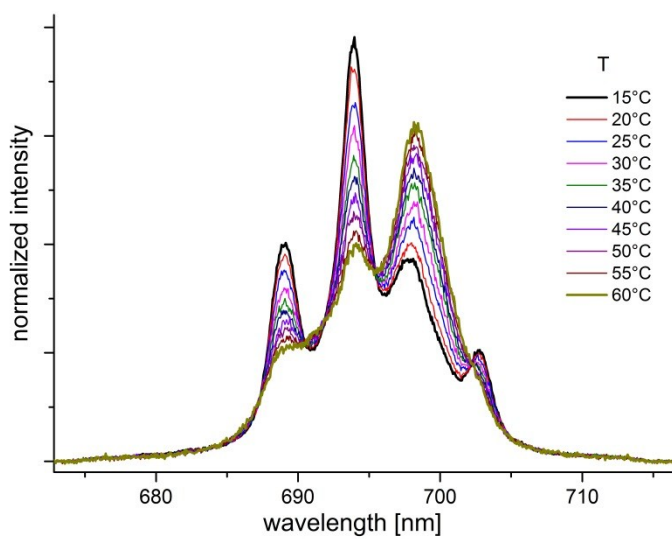


Figure S8 Normalized ${}^5D_0 \rightarrow {}^7F_4$ emission spectra of Eu(III) as a function of the temperature in MeOH:H₂O 1:1 (vol.); [Eu(III)] = $1.0 \cdot 10^{-5}$ mol·L⁻¹, [iPr-BTP] = $1.2 \cdot 10^{-6}$ mol·L⁻¹.

ICP-MS analysis

Solvent extraction experiments were carried out using the kerosene:1-octanol = 7:3 diluent mixture and aqueous phases containing Ln(III) + Y(III) total concentrations of 0.25 and 2.5 g L⁻¹, spiked with ²⁴¹Am and ¹⁵²Eu. The phases were contacted for different contacting times and separated by centrifugation. The phases are separated from the precipitate by centrifugation and sampled for ICP-MS, gamma, and LSC analysis. Distribution ratios were calculated as $D = [M(III)_{org}]/[M(III)_{aq}]$ for each metal ion measured. The distribution ratios of ²⁴¹Am and ¹⁵²Eu obtained from gamma and LSC counting and ICP-MS were in good agreement. The mass balances were calculated according to the following equation:

$$\text{Mass balance} = ([M(III)_{org}] + [M(III)_{aq}]) \cdot 100\% / [M(III)_{ini}]$$

The expected mass balance for the total recovery is 100%. Deviations < 100% give a lacking of mass, e.g. by the formation of precipitates. The so determined distribution ratios are given in table S1 and S2.

Table S1 Distribution ratios and mass balances as a function of mixing time using 10 mmol·L⁻¹ iPr-BTP in kerosene:1-octanol (7:3 vol.). ²⁴¹Am(III) + ¹⁵²Eu(III) (spike concentrations) + 0.25 g·L⁻¹ Ln(III) in 1.0 mol·L⁻¹ HNO₃.

t(min)	Distribution ratio						Mass balance [%]					
	2	5	10	20	50	100	2	5	10	20	50	100
Y	0.01	<0.01	<0.01	0.01	<0.01	<0.01	96.5	97.7	101.4	101.1	96.7	95.2
La	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	95.2	94.8	97.6	97.2	97.2	96.2
Ce	0.02	0.01	<0.01	<0.01	<0.01	<0.01	97.2	97.0	99.2	99.1	97.5	99.3
Pr	0.01	0.01	0.01	0.01	0.01	<0.01	96.1	97.7	101.4	99.7	96.7	96.1
Nd	0.01	0.02	0.04	0.03	0.02	0.01	96.7	98.2	101.9	97.0	91.4	88.0
Sm	0.01	0.04	0.09	0.12	0.05	0.03	95.0	97.0	101.1	87.9	72.3	66.2
Eu	0.01	0.04	0.09	0.13	0.06	0.04	94.0	96.3	102.0	85.8	70.2	63.5
Gd	0.01	0.03	0.07	0.09	0.05	0.03	94.0	97.2	99.8	88.9	76.5	68.2
Tb	0.02	0.04	0.10	0.14	0.08	0.05	94.0	96.0	99.6	85.0	66.8	56.4
Dy	0.01	0.04	0.09	0.12	0.08	0.05	94.6	96.9	100.5	86.8	68.9	56.6
Ho	0.01	0.03	0.08	0.10	0.07	0.05	93.9	95.3	99.2	88.2	73.6	61.2
Er	0.01	0.03	0.06	0.07	0.06	0.04	95.0	95.1	98.7	89.7	77.2	66.4
Tm	0.01	0.02	0.04	0.05	0.05	0.03	93.8	94.8	98.4	93.4	82.5	72.0
Yb	0.01	0.02	0.03	0.04	0.03	0.02	93.1	93.8	96.9	92.5	87.2	80.0
Lu	0.01	0.01	0.02	0.02	0.02	0.02	93.9	94.1	98.0	94.9	90.5	87.4
Am	0.63	2.11	9.97	53.7	20.3	7.89	100	98.4	94.1	39.2	3.7	1.6

Table S2 Distribution ratios and mass balances as a function of mixing time using 10 mmol·L⁻¹ Pr-BTP in kerosene:1-octanol (7:3 vol.). ²⁴¹Am(III) + ¹⁵²Eu(III) (spike concentrations) + 2.5 g·L⁻¹ Ln(III) in 1.3 mol·L⁻¹ HNO₃.

t(min)	Distribution ratio						Mass balance [%]					
	2	5	10	20	50	100	2	5	10	20	50	100
Y	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	96.2	93.5	98.0	96.4	98.1	95.7
La	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	95.6	94.2	97.1	95.4	97.1	97.5
Ce	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	95.4	93.9	96.3	94.6	96.4	96.2
Pr	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	95.7	93.9	96.8	93.2	94.9	92.2
Nd	0.01	0.01	<0.01	<0.01	<0.01	<0.01	95.4	92.6	94.8	92.2	90.2	86.9
Sm	0.02	0.01	<0.01	<0.01	<0.01	<0.01	96.1	92.0	93.6	89.7	86.7	83.8
Eu	0.02	0.01	0.01	<0.01	<0.01	<0.01	95.8	91.1	92.1	88.5	86.5	82.1
Gd	0.02	0.01	<0.01	<0.01	<0.01	<0.01	95.1	92.4	94.3	90.4	88.8	85.4
Tb	0.02	0.01	0.01	0.01	<0.01	<0.01	94.9	90.8	91.1	86.9	82.2	77.0
Dy	0.02	0.01	0.01	0.01	<0.01	<0.01	95.3	92.0	91.8	88.3	83.3	77.4
Ho	0.02	0.01	0.01	0.01	<0.01	<0.01	95.5	92.9	92.6	88.5	83.6	78.6
Er	0.01	0.01	0.01	0.01	0.01	<0.01	96.8	94.9	93.7	91.1	86.6	83.0
Tm	0.01	0.01	0.01	0.01	<0.01	<0.01	95.3	92.2	94.7	90.1	88.0	83.9
Yb	0.01	0.01	0.01	0.01	<0.01	<0.01	97.3	96.1	96.7	94.5	93.6	90.7
Lu	0.01	0.01	0.01	0.01	<0.01	<0.01	96.2	96.1	95.5	93.6	94.1	92.3
Am	0.87	0.54	0.36	0.19	0.00	0.58	100	27.74	18.40	4.83	0.71	0.72