# **UV-VIS Titration Data for paper**

# Bipyridyldicarboxamides and f-metals: Electron effects influence the structure, stability, separation properties, and photophysics

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# UV-vis Titration Data in "dry" CH<sub>3</sub>CN

## 2-F ligand with trivalent lanthanide ions



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.22 mM titrant solution La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 1.97·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [La2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 316 nm; c) the method of continuous variation for 0,094 mM 2-F with 0,094 mM La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 316 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.79 mM titrant solution Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.08·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Ce2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 317 nm; c) the method of continuous variation for 0,099 mM 2-F with 0,099 mM Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 317 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.76 mM titrant solution Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.00·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Pr2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 318 nm; c) the method of continuous variation for 0,093 mM 2-F with 0,093 mM Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 318 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.69 mM titrant solution Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.02·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Nd2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 318 nm; c) the method of continuous variation for 0,108 mM 2-F with 0,108 mM Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 318 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.13 mM titrant solution Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 1.95·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Sm2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 318 nm; c) the method of continuous variation for 0,098 mM 2-F with 0,098 mM Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 318 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.66 mM titrant solution Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 1.99·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Eu2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm; c) the method of continuous variation for 0,108 mM 2-F with 0,108 mM Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 319 nm.

#### 2-F with Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.23 mM titrant solution Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.01·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Gd2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm; c) the method of continuous variation for 0,098 mM 2-F with 0,098 mM Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 319 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.34 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.01·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,098 mM 2-F with 0,098 mM Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.69 mM titrant solution Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.01·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Dy2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,104 mM 2-F with 0,104 mM Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.38 mM titrant solution Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 1.99·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Ho2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,096 mM 2-F with 0,096 mM Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.25 mM titrant solution Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.00·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Er2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,106 mM 2-F with 0,106 mM Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.19 mM titrant solution Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 1.91·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tm2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,094 mM 2-F with 0,094 mM Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 2.95 mM titrant solution Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 1.91·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Yb2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,094 mM 2-F with 0,094 mM Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.27 mM titrant solution Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 1.98·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Lu2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,097 mM 2-F with 0,097 mM Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 320 nm.

#### 3-F ligand with trivalent lanthanide ions



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.37 mM titrant solution La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.03·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [La3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm; c) the method of continuous variation for 0,122 mM 3-F with 0,127 mM La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 319 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.36 mM titrant solution Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Ce3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm; c) the method of continuous variation for 0,117 mM 3-F with 0,117 mM Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 320 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.35 mM titrant solution Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.00·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Pr3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 321 nm; c) the method of continuous variation for 0,101 mM 3-F with 0,101 mM Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 321 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.35 mM titrant solution Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 1.98·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Nd3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,097 mM 3-F with 0,097 mM Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.00 mM titrant solution Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.01·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Sm3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,109 mM 3-F with 0,109 mM Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 322 nm.

0.8

1.0



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.34 mM titrant solution Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.03·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Eu3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,109 mM 3-F with 0,109 mM Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.35 mM titrant solution Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.04·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Gd3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,097 mM 3-F with 0,097 mM Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 322 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.35 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.04·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,094 mM 3-F with 0,094 mM Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.39 mM titrant solution Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.03·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Dy3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,100 mM 3-F with 0,100 mM Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.34 mM titrant solution Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.19·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Ho3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,106 mM 3-F with 0,106 mM Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 322 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.46 mM titrant solution Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.21·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Er3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,107 mM 3-F with 0,106 mM Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.11 mM titrant solution Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 1.99·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tm3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,110 mM 3-F with 0,110 mM Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 2.316  $\mu$ l of 1.23 mM titrant solution Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 1.83·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Yb3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,101 mM 3-F with 0,101 mM Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1.91  $\mu$ l of 1.49 mM titrant solution Lu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O was added to 2 ml of 1.83·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Lu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and blue line – complex [Lu3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,099 mM 3-F with 0,099 mM Lu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O at 322 nm.

## 4-F ligand with trivalent lanthanide ions



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.44 mM titrant solution La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [La4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm; c) the method of continuous variation for 0,110 mM 4-F with 0,112 mM La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 319 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.36 mM titrant solution Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Ce4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 321 nm; c) the method of continuous variation for 0,110 mM 4-F with 0,110 mM Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 321 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.13 mM titrant solution Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.03·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Pr4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,111 mM 4-F with 0,111 mM Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.37 mM titrant solution Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Nd4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm; c) the method of continuous variation for 0,102 mM 4-F with 0,102 mM Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 322 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 2.76 mM titrant solution Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Sm4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,086 mM 4-F with 0,086 mM Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 323 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.38 mM titrant solution Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.12·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Eu4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,108 mM 4-F with 0,108 mM Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 323 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.62 mM titrant solution Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Gd4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,100 mM 4-F with 0,100 mM Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O at 323 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.36 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.14·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,091 mM 4-F with 0,091 mM Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.08 mM titrant solution Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.04·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Dy4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,091 mM 4-F with 0,091 mM Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.14 mM titrant solution Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.14·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Ho4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,110 mM 4-F with 0,110 mM Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.74 mM titrant solution Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.13·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Er4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,083 mM 4-F with 0,083 mM Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.





Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.41 mM titrant solution Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.03·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tm4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,107 mM 4-F with 0,107 mM Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.72 mM titrant solution Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.10·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Yb4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,093 mM 4-F with 0,093 mM Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.



Spectrophotometric titration in "dry" CH<sub>3</sub>CN solution: 1  $\mu$ l of 3.42 mM titrant solution Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 2.04·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Lu4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm; c) the method of continuous variation for 0,113 mM 4-F with 0,122 mM Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O at 323 nm.

## UV-vis Titration Data in "wet" CH<sub>3</sub>CN

## 2-F ligand with trivalent lanthanide ions



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.58 mM titrant solution La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.60·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [La2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 316 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.65 mM titrant solution Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.42·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Ce2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 317 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.48 mM titrant solution Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.65·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Pr2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 317 nm.





Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.18 mM titrant solution Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.50·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Sm2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 317 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.52 mM titrant solution Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.54·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Eu2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 317 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.29 mM titrant solution Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.53·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Gd2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.26 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 4.68·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.39 mM titrant solution Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 4.53·10<sup>-2</sup> mM 2-F: a) spectrophotometric data, where red line – 2-F spectrum, blue dashed lines – aliquots of Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Ho2-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 319 nm.

## 3-F ligand with trivalent lanthanide ions



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.31 mM titrant solution La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 5.59·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [La3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 317 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1 µl of 4.36 mM titrant solution Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of  $5.24 \cdot 10^{-2}$  mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex  $[Ce3-F](NO_3)_3$ ; b) titration curve at 320 nm.

3-F with  $Pr(NO_3)_3$ ·6H<sub>2</sub>O



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1 µl of 4.84 mM titrant solution  $Pr(NO_3)_3 \cdot 6H_2O$  was added to 2 ml of 4.60  $\cdot 10^{-2}$  mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Pr3- $F](NO_3)_3$ ; b) titration curve at 320 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.44 mM titrant solution  $Gd(NO_3)_3 \cdot 6H_2O$  was added to 2 ml of 5.40 $\cdot 10^{-2}$  mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Gd3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 320 nm.



3-F with  $Tb(NO_3)_3$ .5H<sub>2</sub>O

Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.68 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 5.33·10<sup>-2</sup> mM 3-F: a) spectrophotometric data, where red line – 3-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb3-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 321 nm.

## 4-F ligand with trivalent lanthanide ions



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 6.54 mM titrant solution Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.32·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Ce4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 321 nm.

#### 4-F with Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 5.56 mM titrant solution Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.31·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Pr4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 321 nm.

#### 4-F with Nd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.58 mM titrant solution Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.34·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Nd4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 321 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 5.85 mM titrant solution Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.37·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Sm4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm.

4-F with Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 5.56 mM titrant solution Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 2 ml of 4.29·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and blue line – complex [Gd4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 323 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 5.97 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 4.34·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 5.97 mM titrant solution Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 4.34·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Tb4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm.





Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 4.66 mM titrant solution Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 4.30·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Dy4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 322 nm.



Spectrophotometric titration in "wet" CH<sub>3</sub>CN solution: 1  $\mu$ l of 6.75 mM titrant solution Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added to 2 ml of 4.39·10<sup>-2</sup> mM 4-F: a) spectrophotometric data, where red line – 4-F spectrum, blue dashed lines – aliquots of Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and blue line – complex [Er4-F](NO<sub>3</sub>)<sub>3</sub>; b) titration curve at 324 nm.