### **Supporting Information:**

# Transient FTIR spectroscopy after one- and two-colour excitation on a highly luminescent chromium(III) complex

Pit Boden<sup>a</sup>, Patrick Di Martino-Fumo<sup>a</sup>, Gereon Niedner-Schatteburg<sup>a</sup>, Wolfram Seidel<sup>b</sup>, Katja Heinze<sup>\*c</sup> and Markus Gerhards<sup>a†</sup>

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<sup>a.</sup> Department of Chemistry and Research Center OPTIMAS, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany.

<sup>b.</sup> Institute of Chemistry, University of Rostock, Albert-Einstein-Straße 3a, 18059 Rostock, Germany. E-mail: wolfram.seidel@uni-rostock.de

 <sup>c.</sup> Department of Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, 55128 Mainz, Germany.
E-mail: katja.heinze@uni-mainz.de

<sup>+</sup> During manuscript finalisation, Prof. Markus Gerhards deceased.

### Luminescence investigations



**Fig. S1:** Phosphorescence spectra of  $1(BF_4)_3$  as KBr pellet between 290 K and 10 K at  $\lambda_{ex}$  = 420 nm. The inset shows the region of the transition at about 739 nm, where the low energy emission is normalized to 1 for better visibility of the high energy band at 739 nm.



**Fig. S2:** Phosphorescence spectra of  $1(BF_4)_3$  as KBr pellet between 290 K and 170 K at a)  $\lambda_{ex} = 355$  nm and b)  $\lambda_{ex} = 420$  nm (offset corrected).



**Fig. S3:** Boltzmann plot for  $1(BF_4)_3$  as KBr pellet showing the correlation between the relative intensities of the two phosphorescence bands (I<sub>HE</sub>/I<sub>LE</sub>, HE = high energy emission, LE = low energy emission) and temperature between 290 K and 170 K at a)  $\lambda_{ex}$  = 355 nm and b)  $\lambda_{ex}$  = 420 nm. For the series with  $\lambda_{ex}$  = 355 nm the spectrum at 170 K was not considered due to the low intensity of the high energy band.



**Fig. S4:** Phosphorescence spectra of  $1(BF_4)_3$  as KBr pellet between 100 K and 10 K at a)  $\lambda_{ex} = 355$  nm and b)  $\lambda_{ex} = 420$  nm.

## Determination of the spectral overlap of aromatic CH overtones with the phosphorescence

The non-radiative deactivation by relaxation *via* CH overtones mainly concerns the CH groups closest to the metal centre. Hence, the mainly aromatic CH stretching vibrations involving the  $\alpha$ -CH groups of the terminal pyridine rings (Cr···H distances down to 3.0 Å<sup>[1]</sup>) should be considered here. The FTIR ground state vibration at 3071 cm<sup>-1</sup> in KBr is dominated by the stretching motion of the  $\alpha$ -CH groups according to DFT calculations (Fig. S5). The spectral frequency of the relevant fourth overtone was estimated by a Birge-Sponer extrapolation of the corresponding fundamental frequency of the static ground state spectrum, preceded by a gaussian convolution. The general anharmonicity constant with  $x_e \approx 59 \text{ cm}^{-1}$  was applied here, which had been determined in earlier works by NIR measurements on a model ligand of ddpd (6,6′-dimethyl-2,2′-bipyridine).<sup>[1]</sup> The spectral overlap of the phosphorescence with the mentioned vibrational overtone is significant at 290 K, but decreases upon cooling and is close to zero at 170 K due to the vanishing high energy emission band.



**Fig. S5:** a) Ground state FTIR spectra of  $1(BF_4)_3$  as KBr pellet in the aromatic CH stretching region at 290 K (red) and 20 K (black) as well as calculated frequency of the aromatic CH stretching vibration of of  $1^{3+}$  involving mainly the  $\alpha$ -CH groups of the terminal pyridines and b) representation of the mentioned vibration  $\nu(C_{PY-6}-H)_{arom-}$  Calculation: UDFT/B3LYP/def2-TZVP, scaled by 0.96.



**Fig. S6:** Luminescence spectra of  $1(BF_4)_3$  as KBr pellet in the temperature range of 290 K – 10 K ( $\lambda_{ex}$  = 355 nm) normalized to the low energy emission bands and approximated fourth CH overtone of the aromatic CH stretching mode involving mainly the  $\alpha$ -CH groups of the terminal pyridines.

#### Discussion of the electron configurations of the excited doublet states

For the  ${}^{2}T_{1}$ -derived microstate calculated at the ground state geometry a larger contribution of the  $(d_{yz})^{2}(d_{xz})^{0}(d_{xy})^{1}$  configuration has been calculated as 65 % with a smaller admixture of  $(d_{yz})^{0}(d_{xz})^{2}(d_{xy})^{1}$  with 28 %.<sup>[2]</sup> This unbalanced electron distribution might well accompany a stronger distortion along x or y axes, leaving the Cr-N distances along the z axis (the central pyridine rings) almost unaffected. Supposed that the  $(d_{yz})^{2}(d_{xz})^{0}(d_{xy})^{1}$  configuration dominates in the lowest excited doublet state, the significant difference to the ground state electron configuration  $(d_{yz})^{1}(d_{xz})^{1}(d_{xy})^{1}$  becomes obvious and electron density has been transferred from the xz plane to the yz plane of the complex in the lowest excited state. In a true spin-flip state (<sup>2</sup>E) (^)(^)(\downarrow) such a redistribution of electron density between d orbitals would be absent.

### Vibrational spectroscopy of ground and excited states



**Fig. S7:** Ground state FTIR spectrum of  $1(BF_4)_3$  as KBr pellet (red) with DFT calculated  ${}^{4}A_2$  ground state IR absorption frequencies (blue) and calculated  ${}^{4}A_2$  ground state IR absorption spectrum of  $1^{3+}$  (green) (DFT/B3LYP/def2-TZVP, FWHM = 15 cm<sup>-1</sup>, pseudo-Voigt profile, scaled by 0.98).



**Fig. S8:** Ground state Raman spectrum of  $\mathbf{1}(BF_4)_3$  as solid (black) with DFT calculated  ${}^{4}A_2$  ground state Raman absorption frequencies (red) and calculated  ${}^{4}A_2$  ground state Raman absorption spectrum of  $\mathbf{1}^{3+}$  (orange) (DFT/B3LYP/def2-TZVP, FWHM = 8 cm<sup>-1</sup>, pseudo-Voigt profile, scaled by 0.98).



**Fig. S9:** Ground state Raman spectra of  $1(BF_4)_3$  as solid at different excitation wavelengths ( $\lambda_{ex} = 633 \text{ nm}$  (red); 532 nm (green) and 473 nm (blue) as well as DFT calculated  ${}^{4}A_2$  ground state Raman absorption spectrum of  $1^{3+}$  (orange) (DFT/B3LYP/def2-TZVP, FWHM = 15 cm<sup>-1</sup>, pseudo-Voigt profile, scaled by 0.98).



Fig. S10: Ground state FTIR spectrum of NaBF<sub>4</sub> in KBr at room temperature.

$\tilde{\nu}$ / cm <sup>-1</sup>		Description
measured	calcd. (scaled by 0.98)	
1608	1612	Symmetric C <sub>2</sub> -C <sub>3</sub> /C <sub>5</sub> -C <sub>6</sub> stretching of terminal pyridine moieties
1584	1584	Symmetric C <sub>2</sub> -C <sub>3</sub> /C <sub>5</sub> -C <sub>6</sub> stretching of central pyridine moieties
1569	1571	Antisymmetric C <sub>4</sub> -C <sub>3</sub> /C <sub>4</sub> -C <sub>5</sub> stretching of all pyridine moieties
1498	1496	C-H scissoring in the pyridine moieties, accompanied with C-N and C-C stretching
1452	1456	C-H scissoring in the pyridine moieties, accompanied with C-N and C-C stretching
1435	1433	C-H rocking in the pyridine moieties
1368	1350	Antisymmetric N-C stretching of py- N-py, accompanied with C-H rocking of pyridine
1345	1334	Antisymmetric N-C stretching of py- N-py, accompanied with C-H rocking of pyridine
1239	1232	Symmetric N-C stretching of py-N- py, accompanied with C-H rocking of pyridine
1140	1138	C-H scissoring in the pyridine moieties, accompanied with C-N stretch of N-Me
1123	1118	C-H rocking of the methyl groups
1083	1091	C-N stretch of N-Me, accompanied with C-H scissoring in the pyridine moieties
1035	1012	Cr-N stretching, accompanied with breathing of the terminal pyridine rings
948	943	Cr-N rocking, accompanied with N-C stretching of py-N-py and C-H rocking of pyridine

**Table S1:** Wavenumbers and assignment of the vibrations of  $1(BF_4)_3$  in the ground state FTIR spectrum at 290 K (KBr).

ν̈́	′ cm <sup>-1</sup>	Description
measured	calcd. (scaled by 0.98)	•
1614	1613	Symmetric C <sub>2</sub> -C <sub>3</sub> /C <sub>5</sub> -C <sub>6</sub> stretching of terminal pyridine moieties
1586	1583	Antisymmetric $C_3$ - $C_4/C_4$ - $C_5$ stretching and C-N stretching of pyridine moieties
1571	1572	Antisymmetric $C_3$ - $C_4/C_4$ - $C_5$ stretching and C-N stretching of pyridine mojeties
1494	1502	C-H bending of the methyl moieties
1428	1433	Antisymmetric C-H in plane rocking of central pyridine moieties and C-H bending of methyl moieties
1346	1352	C-H in plane rocking of terminal pyridine moieties, accompanied with C-N stretching and C-H bending of methyl moieties
1315	1299	C-H in plane rocking of pyridine moieties, accompanied with C-C and C-N stretching of the pyridine moieties
1286	1281	C-H in plane rocking, accompanied with C-N stretching in the pyridine moieties
1266	1258	C-C and C-N stretching vibrations, accompanied with C-H in plane rocking of the pyridine moieties and C-H bending of the methyl moieties
1181	1208	C-H in plane bending of terminal pyridine moieties
1128	1118	C-H bending of methyl moieties
1066	1075	C-N stretching accompanied with C-H in plane bending of terminal pyridine moieties
1028	1016	Symmetric C-N streching of py-N-py, accompanied with breathing of the pyridine moieties
779	774	C-C and C-N in plane bending of pyridine moieties
717	714	Symmetric Cr-N stretching, accompanied with C-C and C-N in plane bending of the pyridine moieties
681	685	C-C and C-N out of plane of the central pyridine moieties, accompanied with C-C and C-N in plane bending of the terminal pyridines
627	623	Symmetric Cr-N stretching, coupled with C-C and C-N in plane bending of the pyridine moieties
526	527	C-C and C-N out of plane of the terminal pyridine moieties
513	505	py-N-py bending, accompanied with C-C and C-N bending of the terminal pyridine moieties
460	457	N-Cr-N bending accompanied with C-C and C-N bending of central pyridine moieties
414	411	Symmetric Cr-N stretching, accompanied with C-N stretching of py-N-py
283	280	Cr-N bending

**Table S2:** Wavenumbers and assignment of the vibrations of  $1(BF_4)_3$  in the Raman spectrum at 290 K (KBr).

positive bands in	Ground state (static FTIR)	Excited state (step-scan FTIR)	the step-scan
difference	1608	1600	spectrum at
200 1/	1584	1576	
290 K.	1569	1562	
	1498	1481	
	1452	1426	
	1435	1414	
	1368	-	
	1345	-	
	1239	1246	
	1140	-	
	1123	-	
	1083	-	
	1055	-	
	1035	1012	

Table S3: Wavenumbers of the vibrations of  $1(BF_4)_3$  in the ground state FTIR spectrum and of the



**Fig. S11:** Pump (355 nm)/step-scan FTIR probe spectrum of  $1(BF_4)_3$  0.5 to 5.0 µs after excitation and ground state FTIR spectrum (black) in acetonitrile-d<sub>3</sub> (red).



**Fig. S12:** Pump (355 nm)/step-scan FTIR probe spectra of  $1(BF_4)_3$  0.5 to 5.0 µs after excitation in acetonitrile-d<sub>3</sub> (black) and in KBr at 290 K (red). The ground state FTIR spectrum in acetonitrile-d<sub>3</sub> (grey) is depicted for comparison.

Table S4:	Ground state (static FTIR)	Excited state (step-scan FTIR)	Wavenumbers of
the vibrations of	1613	-	<b>1</b> (BF₄)₃ in the
ground state FTIR	1608	1603	spectrum and the
positive bands in	1586	1579	the step-scan
difference	1499	1478	spectrum in
acetonitrile-d₃.	1455	1431	
	1438	1416	
	1369	-	
	1240	1244	



**Fig. S13:** Pump (355 nm)/step-scan FTIR probe spectra of  $1(BF_4)_3$  as KBr pellet 0 to 2  $\mu$ s (red), 20 to 22  $\mu$ s (blue) and 48 to 50  $\mu$ s (black) after excitation at 20 K.



**Fig. S14:** Biexponential decay fits performed for the time traces of the intensity of the IR band at  $1500 \text{ cm}^{-1}$  of  $1(BF_4)_3$  as KBr pellet at a) 20 K (green) and b) 290 K (blue) in KBr. The dots represent the smoothed raw data.



**Fig. S15:** Time traces of the IR intensity of 11 prominent bands (dots represent the smoothed data) of  $1(BF_4)_3$  as KBr pellet at 290 K and global biexponential fits (convolution with Gaussian pulse shape).



**Fig. S16:** Time traces of the IR intensity of 9 prominent bands (dots represent the smoothed data) of  $1(BF_4)_3$  as KBr pellet at 20 K and global biexponential fits (convolution with Gaussian pulse shape).



**Fig. S17:** Biexponential decay fits performed for the time traces of the intensity of the IR band at  $1431 \text{ cm}^{-1}$  of  $1(BF_4)_3$  in acetonitrile-d<sub>3</sub>. The monoexponential components are illustrated for the latter one. The dots represent the smoothed raw data.



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medium	method	<i>t</i> <sub>1</sub> / ns	<i>t</i> ₂ / μs	<i>t</i> ₃ / μs	$A_{1} / \%$	A2/%	A3 / %
KBr / RT	Step-scan	/	1.3 ± 0.1	22 ± 1	/	14	86
	TCSPC*	87 ± 7	$1.0 \pm 0.1$	27 ± 3	2	7	91
KBr / 20 K	Step-scan	/	11.7 ± 0.3	145 ± 1	/	7	93
CD₃CN	Step-scan⁺	/	5.39 ± 0.04	105.0 ± 0.3	/	6	94
	TCSPC** <sup>[3]</sup>	/	/	810	/	/	/

Fig. S18: Time traces of the IR intensity of 10 prominent bands (dots represent the smoothed data) of

1(BF<sub>4</sub>)<sub>3</sub> in acetonitrile-d<sub>3</sub> at 290 K and global biexponential fits (convolution with Gaussian pulse shape).

**Table S5:** Lifetimes of  $1(BF_4)_3$  in the KBr matrix and in acetonitrile-d<sub>3</sub> according to step-scan FTIR and TCSPC.

(\*):  $\lambda_{ex}$  = 389 nm;  $\lambda_{em}$  = 780 nm (\*\*):  $\lambda_{ex}$  = 435 nm;  $\lambda_{em}$  = 780 nm

(+): The lower time constant of 104  $\mu$ s compared to 810  $\mu$ s in earlier works<sup>[3]</sup> probably results from O<sub>2</sub> contamination in the step-scan sample.



**Fig. S19:** Decay curve and triexponential fit obtained from TCSPC data at 290 K ( $\lambda_{ex}$  = 389 nm,  $\lambda_{em}$  = 780 nm, KBr).

### Pump/pump/probe (FTIR) and pump/dump/probe (FTIR) experiments



**Fig. S20:** Pump (781 nm)/step-scan FTIR probe spectra of  $1(BF_4)_3$  as KBr pellet 0.5 to 5.0 µs after excitation at 290 K (red) and 20 K (black) as well as ground state FTIR spectrum (grey) at 290 K. The bands marked with asterisks are discussed in the manuscript.



**Fig. S21:** Pump (355 nm)/pump (785 nm)/step-scan FTIR probe (black) and pump (355 nm)/step-scan FTIR probe (red) (355 nm) spectra of  $1(BF_4)_3$  as KBr pellet 0.5 to 5.0 µs after excitation, both at 20 K. The bands marked with asterisks are discussed in the manuscript.



**Fig. S22:** Pump (355 nm)/step-scan FTIR probe spectrum (red) of  $1(BF_4)_3$  as KBr pellet 0.5 to 5.0 µs after excitation and ground state FTIR spectrum (black) at 20 K. The bands marked with asterisks are discussed in the manuscript.



**Fig. S23.** Pump (355 nm)/pump (741 nm)/step-scan FTIR probe (black) and pump (355 nm)/step-scan FTIR probe (red) spectra of  $1(BF_4)_3$  as KBr pellet 0.5 to 5.0 µs after excitation, both at 20 K. The bands marked with asterisks are discussed in the manuscript.



**Fig. S24:** Pump (741 nm)/step-scan FTIR probe spectrum of  $1(BF_4)_3$  as KBr pellet 0.5 to 5.0  $\mu$ s (red) after excitation and ground state FTIR spectrum (black) at 20 K. The bands marked with asterisks are discussed in the manuscript.

### **References:**

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