

## **Bulky Ligands protect Molecular Ruby from Oxygen Quenching**

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### **Supplementary Information**

## General procedures

All reagents (pyridines, boronic acids, solvents, etc.) were used as received from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer, Sigma-Aldrich and TCI). Air and/or moisture-sensitive reactions were performed in dried glassware under an inert gas atmosphere (argon, quality 4.6). 1,4-Dioxane was refluxed over sodium, THF over potassium, dichloromethane and acetonitrile over calcium hydride and distilled under argon prior to use in moisture-sensitive reactions. A glovebox (UniLab/MBraun, Ar 4.8, O<sub>2</sub> < 1 ppm, H<sub>2</sub>O < 1 ppm) was used for storage and weighing of sensitive compounds.

**NMR spectra** were recorded on a Bruker Avance DRX 400 spectrometer at 400.1 MHz (<sup>1</sup>H), 100.7 MHz (<sup>13</sup>C{<sup>1</sup>H}). All resonances are reported in ppm versus the solvent signal as internal standard [CDCl<sub>3</sub> (<sup>1</sup>H:  $\delta$  = 7.26, <sup>13</sup>C:  $\delta$  = 77.16)]. <sup>1</sup> (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet.

**ESI<sup>+</sup> mass spectra** were recorded on an Agilent 6545 QTOF-MS spectrometer with analyte solutions in acetonitrile.

**Elemental analyses** of ligands and [Cr(ddpd<sup>5Me</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> were performed by the central analytical service of the department of chemistry of the University of Mainz using an Elementar Vario EL Cube. Elemental analyses of complexes [Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> and [Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> were performed by the Mikroanalytisches Labor Kolbe, c/o Fraunhofer Institut UMSICHT, Oberhausen, Germany.

**IR spectra** were recorded with a Bruker Alpha II FT-IR spectrometer with a Platinum Di-ATR unit under inert conditions in a glovebox.

**UV/Vis absorption spectra** were recorded on a Jasco V770 spectrometer using 1.0 cm quartz cells.

**Emission spectra and luminescence decay curves** were recorded at 293 K on an Edinburgh Instruments spectrometer (FLS 1000) equipped with the cooled red and NIR sensitive photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the spectral range between 200 nm and 1700 nm. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were performed in the multi-channel scaling mode employing the  $\mu$ s-xenon flashlamp  $\mu$ F2 (pulse width ca. 2  $\mu$ s) as excitation source. Absolute luminescence quantum yields  $\Phi$  were determined using an integrating sphere from Edinburgh Instruments. Relative uncertainty of  $\Phi$  is estimated to be  $\pm 10\%$ .

The solution samples of the complexes (10<sup>-4</sup> M) were prepared in long neck 1.0 cm quartz cuvettes with a Schott valve containing a stir bar. The spectroscopy grade acetonitrile was stirred in a beaker to ensure complete air saturation of the solvent. After measurement of the air saturated solutions the sample solutions, were purged for about 30 minutes with argon using a cannula. The absence of molecular oxygen was verified by the missing <sup>1</sup>O<sub>2</sub> emission band at around 1275 nm after excitation.

Temperature dependent luminescence decay curves were recorded from 278 K to 338 K in 5 K steps with 300 s equilibration time, while stirring the solution.

**Emission spectra** for Stern-Volmer analyses were recorded on an Edinburgh Instruments spectrometer (FSP 920) using a xenon arc lamp. Luminescence decay curves in the  $\mu$ s-range were measured with the same spectrometer using a  $\mu$ s xenon flashlamp and multi-channel scaling mode. All luminescence measurements were performed using magic angle conditions (polarization 0° in the excitation and 54.7° in the emission channel). Oxygen was removed from the solvents by purging with argon and the oxygen concentration in the sample solutions was measured using a Neofox-GT (sensor Phosphor-R) optical detection system (OceanOptics).

**Stern-Volmer studies with oxygen:** The solution samples were sealed in a long-neck (ca. 15 cm) quartz cuvette with a precision seal rubber septum cap. After purging the samples with Ar using a long needle (that reaches the bottom of the cuvette) for 30 min, the emission spectra, and decays were recorded. These data were used as the starting point ( $I_0$  or  $\tau_0$ ) of the Stern-Volmer studies. The lifetime data under Ar-saturation were obtained by independently measuring the freshly prepared samples at least twice to ensure reproducibility of the data.

After recording the starting point emission data, the oxygen partial pressure was determined with a commercial fiber-optic oxygen meter Firesting O<sub>2</sub> from PyroScience and a solvent-resistant oxygen probe tip (OXSOVLPT), which was calibrated with air-saturated and oxygen-free solutions before measurements. The needle-shaped oxygen probe tip can pierce the septa cap and reach the cuvette bottom. The oxygen concentration was read out on-live on the PyroScience program. Measuring the sample for 1-2 min, a stable  $pO_2$  readout was recorded. This value is usually found in the range of 0.01 and 0.5 hPa, as there was still traces of air in the needle-shaped oxygen probe tip, which dissolved in the sample solutions. This value will be taken as the starting  $pO_2$  point correlated to the Ar-saturated data ( $I_0$  or  $\pi$ ).

An increase of the oxygen concentration was achieved by opening the septa cap for a few seconds to let air in and sealing the cuvette again. The sealed cuvette was shaken for ca. 1 min on a lab dancer. The oxygen concentration was determined again until a stable  $pO_2$  readout was obtained. Followed by subsequent emission measurements, the oxygen concentration was controlled again. In some cases, the averaged  $pO_2$  values (before and after emission measurements) are used for the Stern-Volmer studies. This measuring cycle was repeated 9 to 10 times with different  $pO_2$  to obtain a reliable Stern-Volmer plot.

**Density functional theory (DFT) calculations** were carried out using the ORCA program package 5.0.3.<sup>2</sup> All calculations were performed using the B3LYP functional<sup>3</sup> employing the RIJCOSX approximation.<sup>4</sup> Relativistic effects were calculated at the zeroth-order regular approximation (ZORA) level.<sup>5</sup> The ZORA keyword automatically invokes relativistically adjusted basis sets. To account for solvent effects, a conductor-like screening model (CPCM) modeling acetonitrile was used in all calculations.<sup>6</sup> Geometry optimizations were performed using Ahlrichs' polarized valence triple- $\zeta$  basis set (def2-TZVP).<sup>7</sup> Atompairwise dispersion correction was performed with the Becke-Johnson damping scheme (D3BJ).<sup>8</sup> The energy of the electronic states and the presence of energy minima were checked by numerical frequency calculations. Explicit counter ions and/or solvent molecules were not taken into account. TD-DFT calculations were performed at the same level of theory. Fifty vertical spin-allowed transitions were calculated. The assignment of the state characters has been done dividing the molecule into three fragments (metal center and two ligands) and calculating charge transfer (CT) numbers, as implemented in the TheoDore software package.<sup>9,10</sup>

### Crystal Structure Determinations

Intensity data for crystal structure determination of **[Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>** were collected with a STOE IPDS-2T diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The diffraction frames were integrated using the STOE X-Area<sup>11</sup> software package and were corrected for absorption with MULABS<sup>12</sup> of the PLATON software package.<sup>13</sup> Intensity data for crystal structure determination of **[Cr(ddpd<sup>5Me</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>** and of **[Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>** were collected with a STADIVARI diffractometer from STOE & CIE GmbH using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The diffraction frames were integrated using the STOE X-Area<sup>11</sup> software package and were corrected for absorption with STOE LANA<sup>14</sup> of the STOE X-Area software package.<sup>11</sup>

The structures were solved with SHELXT<sup>15</sup> and refined by the full-matrix method based on  $F^2$  using SHELXL<sup>16</sup> of the SHELX<sup>17</sup> software package and the ShelXle<sup>18</sup> graphical interface. All non-hydrogen atoms were refined anisotropically while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2125020 (**[Cr(ddpd<sup>5Me</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>**), 2125021 (**[Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>**) and 2125019 (**[Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>**).

## Syntheses

**ddpd** and **[Cr(ddpd)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> (Cr<sup>5H</sup>)** were synthesized according to literature procedures.<sup>19,20</sup>

**Synthesis of ddpd<sup>6Me</sup>** (adapted from literature procedures of similar compounds<sup>21,22</sup>): 2,6-Bis(methylamino)pyridine (1.00 g, 7.29 mmol, 1.0 eq) was added to a suspension of potassium bis(trimethylsilyl)amide (3.34 g, 16.76 mmol, 2.3 eq) in 1,4-dioxane (100 mL). After stirring for 30 min, 2-bromo-6-methylpyridine (3.13 g, 2 mL, 18.22 mmol, 2.5 eq) was added. The solution was refluxed for 5 days. After cooling to room temperature, water (150 mL) was added. The aqueous phase was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The brown solution of the combined organic phases was washed twice with water (50 mL), dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The red-brown residue was subjected to column chromatography (SiO<sub>2</sub>, PE/EtOAc, gradient 6:1 → 1:1 + 5 vol% NEt<sub>3</sub>) to yield ddpd<sup>6Me</sup> as a pale-yellow oil. Yield: 370 mg, 1.16 mmol, 16%.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 296 K)  $\delta$  / ppm = 7.44 (m, 3 H, H<sup>1</sup>, H<sup>6,6a</sup>), 7.03 (d, <sup>3</sup>J = 8.3 Hz, 2 H, H<sup>5,5a</sup>), 6.76 (d, <sup>3</sup>J = 7.4 Hz, 2 H, H<sup>7,7a</sup>), 6.66 (d, <sup>3</sup>J = 8.0 Hz, 2 H, H<sup>2,2a</sup>), 3.48 (s, 6 H, H<sup>9,9a</sup>), 2.41 (s, 6 H, H<sup>10,10a</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 296 K)  $\delta$  / ppm = 158.1 (C<sup>3,3a</sup>), 157.7 (C<sup>4,4a</sup>), 157.3 (C<sup>8,8a</sup>), 139.5 (C<sup>1</sup>), 138.3 (C<sup>6,6a</sup>), 117.1 (C<sup>7,7a</sup>), 113.3 (C<sup>5,5a</sup>), 106.1 (C<sup>2,2a</sup>), 36.3 (C<sup>9,9a</sup>), 24.5 (C<sup>10,10a</sup>).

MS (ESI<sup>+</sup>, MeCN): Calcd. for C<sub>19</sub>H<sub>22</sub>N<sub>5</sub><sup>+</sup>: *m/z* = 320.19. Found: *m/z* (%) = 320.19 (100, [ddpd<sup>6Me</sup>+H]<sup>+</sup>).

UV/Vis (MeCN):  $\lambda_{\max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 236 (72.1), 273 (88.2), 335 (11.3).

Emission (MeCN):  $\lambda_{\text{em}}$  / nm ( $\lambda_{\text{exc}}$  / nm): 423, 373 (sh) (334).

**Synthesis of ddpd<sup>5Me</sup>** (adapted from literature procedures of similar compounds<sup>21,22</sup>): A solution of 2,6-diaminopyridine (1.27 g, 11.63 mmol, 1.0 eq, dried under reduced pressure overnight at 40 °C) in THF (30 mL) was added to a suspension of NaH (1.40 g of 60 wt%, 34.89 mmol, 3.0 eq) in THF (30 mL). After stirring for 30 min, 2-bromo-5-methylpyridine (5.00 g, 29.07 mmol, 2.5 eq) was added. The solution was refluxed for 3 days. After solvent evaporation, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and extracted twice with water (2 x 25 mL). The organic phase was concentrated under reduced pressure and used in the next step without further purification. The brown solid was added to a suspension of powdered KOH (1.62 g, 28.83 mmol, 2.5 eq) in DMSO (50 mL) and the mixture was stirred at ambient temperature for 30 min. Methyl iodide (1.5 mL, 2.25 g, 15.86 mmol, 1.4 eq) was added to the red-brown suspension and stirring was continued for 15 h. Water (30 mL) was added and the yellow aqueous suspension was extracted with a 1:1 (v/v) mixture of Et<sub>2</sub>O/THF (3 x 10 mL). The combined organic phases were washed with saturated aqueous Na<sub>2</sub>CO<sub>3</sub>, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The red-brown residue was subjected to column chromatography (SiO<sub>2</sub>, PE/EtOAc, gradient 3:1 → 1:1 + 5 vol% NEt<sub>3</sub>) to yield ddpd<sup>5Me</sup> as a pale-yellow oil. Yield: 760 mg, 2.38 mmol, 20%.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 296 K):  $\delta$  / ppm = 8.14 (s, 2 H, H<sup>8,8a</sup>), 7.41 (m, 3 H, H<sup>1</sup>, H<sup>6,6a</sup>), 7.18 (d, <sup>3</sup>J = 8.4 Hz, 2 H, H<sup>5,5a</sup>), 6.53 (d, <sup>3</sup>J = 8.0 Hz, 2 H, H<sup>2,2a</sup>), 3.45 (s, 6 H, H<sup>9,9a</sup>), 2.24 (s, 6 H, H<sup>10,10a</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 296 K):  $\delta$  / ppm = 157.3 (C<sup>3,3a</sup>), 156.7 (C<sup>4,4a</sup>), 148.7 (C<sup>8,8a</sup>), 139.6 (C<sup>1</sup>), 138.6 (C<sup>6,6a</sup>), 127.8 (C<sup>7,7a</sup>), 117.0 (C<sup>5,5a</sup>), 104.5 (C<sup>2,2a</sup>), 36.3 (C<sup>9,9a</sup>), 17.7 (C<sup>10,10a</sup>).

MS (ESI<sup>+</sup>, MeCN): *m/z* (%) = 320.19 (100, [ddpd<sup>5Me</sup>+H]<sup>+</sup>), 382.11 (5, [ddpd<sup>5Me</sup>+Cu]<sup>+</sup>).

Elem. anal. calcd. for C<sub>19</sub>H<sub>21</sub>N<sub>5</sub> (319.18): C, 71.45; H, 6.63; N, 21.93. Found: C, 71.11; H, 6.53; N, 22.16.

UV/Vis (MeCN):  $\lambda_{\max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 238 (13.8), 274 (18.3), 336 (19.9).

Emission (MeCN):  $\lambda_{\text{em}}$  / nm ( $\lambda_{\text{exc}}$  / nm): 431, 370 (sh) (334).

**Synthesis of 5-bromo-N-methylpyridine-2-amine.** 2,5-Dibromopyridine (15.18 g, 62.80 mmol, 1 eq) and methylamine solution (33 wt% in EtOH; 80 mL, 642.62 mmol, 10 eq) were stirred and heated in an autoclave for 24 h at 160 – 170 °C. After cooling to room temperature, the solvent was removed under reduced pressure yielding an orange solid. The crude product was dissolved in 1 M aqueous HCl solution (100 mL), yielding a yellow solution with a small amount of insoluble residue. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and the organic phase containing the starting material was discarded.

The aqueous phase was brought to pH 11 with 1 M aqueous NaOH solution, resulting in the precipitation of a colorless solid. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL) dissolving the solid in the organic phase. The organic phase was dried over MgSO<sub>4</sub>, filtered and the solvent was removed under reduced pressure resulting in 2-methylamino-5-bromopyridine as a colorless solid. Yield: 11.54 g, 61.70 mmol, 98%.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$ /ppm = 8.08 (dd, <sup>3</sup>J<sub>HH</sub> = 2.6, 0.7 Hz, 1H, H<sup>1</sup>), 7.48 (dd, <sup>3</sup>J<sub>HH</sub> = 8.9, 2.5 Hz, 1H, H<sup>3</sup>), 6.31 (dd, <sup>3</sup>J<sub>HH</sub> = 8.9, 0.7 Hz, 1H, H<sup>4</sup>), 4.94 (s, 1H, NH), 2.86 (d, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, 3H, H<sup>6</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$ /ppm = 158.3 (C<sup>5</sup>), 148.5 (C<sup>1</sup>), 139.5 (C<sup>3</sup>), 107.5 (C<sup>4</sup>), 106.5 (C<sup>2</sup>), 28.9 (C<sup>6</sup>).

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 186.99 (100, [py<sup>5Br</sup>-NHMe+H]<sup>+</sup>).

**Syntheses of 5-mesityl-*N*-methyl-pyridine-2-amine and 5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine** (adapted from an analogous literature procedure<sup>23</sup>): 5-Bromo-*N*-methylpyridine-2-amine (1.00 eq), Pd(OAc)<sub>2</sub> (0.05 eq), XPhos (2-(dicyclohexylphosphano)-2',4',6'-triisopropyl-1,1'-biphenyl, 0.16 eq), K<sub>3</sub>PO<sub>4</sub> (3.00 eq) and the corresponding boronic acid (1.16 eq; **Ar = Mes** 2.41 g, 14.7 mmol; **Ar = Tripp** 1.73 g, 7.0 mmol) were suspended in a 5:1 mixture of 1,4-dioxane (10 mL) and H<sub>2</sub>O (2 mL). The solution was degassed and stirred at 90 °C for 48 h under argon. The reaction mixture was allowed to cool to room temperature, diluted with EtOAc (30 mL), washed with H<sub>2</sub>O (3 x 25 mL) and brine (60 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. The orange oily residue was recrystallized from hexane, giving **5-mesityl-*N*-methyl-pyridine-2-amine** and **5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine**, respectively, as colorless powders.

**5-mesityl-*N*-methyl-pyridine-2-amine**: Yield: 71%, 2.00 g, 8.8 mmol.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$ /ppm = 7.88 (dd,  $J$  = 2.3, 0.9 Hz, 1H, H<sup>5</sup>), 7.26 (dd,  $J$  = 8.5, 2.3 Hz, 1H, H<sup>3</sup>), 6.99 – 6.94 (m, 2H, H<sup>11,13</sup>), 6.51 (dd,  $J$  = 8.5, 0.9 Hz, 1H, H<sup>2</sup>), 5.09 (s, 1H, H<sup>7</sup>), 2.96 (s, 3H, H<sup>9</sup>), 2.33 (s, 3H, H<sup>17</sup>), 2.07 (s, 4H, H<sup>15,16</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$ /ppm = 158.5 (C<sup>1</sup>), 147.9 (C<sup>5</sup>), 138.7 (C<sup>3</sup>), 136.8 (C<sup>10,14</sup>), 136.6 (C<sup>12</sup>), 135.8 (C), 128.1 (C<sup>11</sup>, C<sup>13</sup>), 125.0 (C<sup>4</sup>), 105.7 (C<sup>2</sup>), 29.0 (C<sup>9</sup>), 20.8 (C<sup>17</sup>), 20.7 (C<sup>15,16</sup>).

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 227.15 (100, [py<sup>5Mes</sup>-NHMe+H]<sup>+</sup>).

**5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine**: Yield: 59%, 1.08 g, 3.5 mmol.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$ /ppm = 7.88 (dt,  $J$  = 2.2, 1.0 Hz, 1H, H<sup>5</sup>), 7.28 (ddd,  $J$  = 8.4, 2.4, 1.0 Hz, 1H, H<sup>3</sup>), 7.08 (s, 2H, H<sup>11,13</sup>), 6.49 (d,  $J$  = 8.0 Hz, 1H, H<sup>2</sup>), 4.89 (b,  $J$  = 5.6 Hz, 1H, H<sup>7</sup>), 3.02 – 2.87 (m, 5H, H<sup>9,21</sup>), 2.74 (pd,  $J$  = 6.8, 1.1 Hz, 2H, H<sup>15,18</sup>), 1.31 (dd,  $J$  = 7.0, 1.0 Hz, 6H, H<sup>22,23</sup>), 1.11 (td,  $J$  = 7.0, 1.0 Hz, 12H, H<sup>16,17, 19,20</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$ /ppm = 158.5 (C<sup>1</sup>), 148.3 (C<sup>12</sup>), 148.1 (C<sup>5</sup>), 147.8 (C<sup>10,14</sup>), 138.8 (C<sup>3</sup>), 134.0 (C<sup>8</sup>), 124.5 (C<sup>4</sup>), 120.5 (C<sup>11,13</sup>), 105.4 (C<sup>2</sup>), 34.4 (C<sup>21</sup>), 30.3 (C<sup>15,18</sup>), 28.9 (C<sup>9</sup>), 23.9 (C<sup>16,17,19,20,23</sup>).

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 311.25 (100, [py<sup>5Tripp</sup>-NHMe-H]<sup>+</sup>).

**Synthesis of ddpd<sup>5Mes</sup>** (adapted from an analogous literature procedure<sup>19</sup>): Potassium bis(trimethylsilyl)amide (2.49 g, 12.48 mmol, 3.2 eq) was suspended in freshly dried 1,4-dioxane (50 mL) under an argon atmosphere. Addition of 5-mesityl-*N*-methyl-pyridine-2-amine (2.00 g, 8.84 mmol, 2.3 eq) resulted in a yellow solution. A solution of 2,6-dibromopyridine (0.91 g, 3.84 mmol, 1.0 eq) in 1,4-dioxane (10 mL) was added. The reaction mixture was refluxed for 64 h. After cooling to room temperature, water (100 mL) was added. The solution was extracted with a 1:1 (v/v) mixture of Et<sub>2</sub>O/THF (4 x 50 mL). The combined organic phases were washed with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution (3 x 50 mL), dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure, yielding a brown oil. The crude product (2.4 g) was dissolved in as little diethyl ether as possible. Tetrafluoroboric acid diethyl ether complex (2.5 eq, 9.6 mmol, 2.6 mL) in diethyl ether (50 – 55 wt%) was added dropwise to the solution of the crude product, resulting in the formation of a colorless precipitate (1.54 g). A concentrated solution of this solid was recrystallized by diffusion of diethyl ether into the solution. The

tetrafluoroborate salt of protonated ddpd<sup>5Mes</sup> was suspended in water (100 mL). Diethyl ether (25 mL) was added and the pH of the aqueous phase was brought to 9 with a 1 M aqueous NaOH solution. The aqueous phase was extracted with diethyl ether (3 x 30 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure yielding ddpd<sup>5Mes</sup> as a colorless solid. Yield: 1.21 g, 2.30 mmol, 60%.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$  / ppm = 8.12 (dd,  $J$  = 2.3, 0.9 Hz, 2H, H<sup>5,28</sup>), 7.49 (t,  $^1J$  = 8.0 Hz, 1H, H<sup>21</sup>), 7.39 (dd,  $J$  = 8.5, 1.0 Hz, 2H, H<sup>2,31</sup>), 7.35 (dd,  $J$  = 8.5, 2.3 Hz, 2H, H<sup>3,30</sup>), 6.99 – 6.93 (m, 4H, H<sup>11,13,34,36</sup>), 6.81 (d,  $^1J$  = 8.0 Hz, 2H, H<sup>20,22</sup>), 3.64 (s, 6H, H<sup>23,25</sup>), 2.32 (s, 6H, H<sup>17,40</sup>), 2.06 (s, 12H, H<sup>15,16,38,39</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$  / ppm = 20.7 (C<sup>15,16,38,39</sup>), 35.6 (C<sup>23,25</sup>), 105.6 (C<sup>20,22</sup>), 114.5 (C<sup>2,31</sup>), 128.1 (C<sup>11,13,34,36</sup>), 129.5 (C<sup>8,32</sup>), 135.2 (C<sup>12,35</sup>), 136.5 (C<sup>1,14,33,37</sup>), 137.0 (C<sup>4,29</sup>), 137.9 (C<sup>3,30</sup>), 138.3 (C<sup>21</sup>), 148.0 (C<sup>5,28</sup>), 156.3 (C<sup>9,19</sup>), 156.3 (C<sup>1,26</sup>).

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 528.31 (100, [ddpd<sup>5Mes</sup>+H]<sup>+</sup>), 550.29 (6, [ddpd<sup>5Mes</sup>+Na]<sup>+</sup>), 1077.60 (6, [2 ddpd<sup>5Mes</sup>+Na]<sup>+</sup>).

Elem. Anal. calcd. for C<sub>35</sub>H<sub>37</sub>N<sub>5</sub> (527.30): C, 79.66; H, 7.07; N, 13.27. Found: C, 79.27; H, 7.02; N, 12.99.

UV/Vis (MeCN):  $\lambda_{max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 243 (sh, 20.7), 279 (26.0), 337 (26.7), 371 (sh, 4.9).

Emission (MeCN):  $\lambda_{em}$  / nm ( $\lambda_{exc}$  / nm): 415, 370 (sh) (337).

**Synthesis of ddpd<sup>5Tripp</sup>** (adapted from an analogous literature procedure<sup>19</sup>). Potassium bis(trimethylsilyl)amide (0.966 g, 3.36 mmol, 2.4 eq) was suspended in freshly dried 1,4-dioxane (20 mL) under an argon atmosphere. Addition of 5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine (1.00 g, 3.22 mmol, 2.3 eq) resulted in an orange-colored solution. A solution of 2,6-dibromopyridine (0.332 g, 1.44 mmol, 1.0 eq) in 1,4-dioxane was added. The reaction mixture was refluxed for 64 h. After cooling to room temperature, water (50 mL) was added and 1,4-dioxane was removed under reduced pressure. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The brown CH<sub>2</sub>Cl<sub>2</sub> solution was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. Suspending the crude product in diethyl ether (20 mL) led to the formation of a colorless precipitate. This solid was filtered and washed with diethyl ether (3 x 10 mL), giving ddpd<sup>5Tripp</sup> as a colorless powder. Yield: 0.89 g, 1.28 mmol, 88%.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$  / ppm = 8.16 (t,  $J$  = 1.6 Hz, 2H, H<sup>5,28</sup>), 7.52 (t,  $J$  = 8.0 Hz, 1H, H<sup>21</sup>), 7.39 (d,  $J$  = 1.6 Hz, 4H, H<sup>2,3,30,31</sup>), 7.10 (s, 4H, H<sup>11,13,34,36</sup>), 6.86 (d,  $J$  = 8.0 Hz, 2H, H<sup>20,22</sup>), 3.66 (s, 6H, H<sup>23,25</sup>), 2.95 (hept,  $J$  = 6.9 Hz, 2H, H<sup>17,40</sup>), 2.72 (hept,  $J$  = 6.9 Hz, 4H, H<sup>15,16,38,39</sup>), 1.31 (d,  $J$  = 6.9 Hz, 12H, H<sup>41,42,48,51</sup>), 1.13 (dd,  $J$  = 13.3, 6.9 Hz, 24H, H<sup>43,44,45,46,47,49,50,52</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$  / ppm = 156.3 (C<sup>1,9,19,26</sup>), 148.7 (C<sup>12,35</sup>), 148.1 (C<sup>5,28</sup>), 147.5 (C<sup>10,14,33,37</sup>), 138.4 (C<sup>21</sup>), 138.2 (C<sup>3,30</sup>), 133.5 (C<sup>4,29</sup>), 129.0 (C<sup>8,32</sup>), 120.6 (C<sup>11,13,34,36</sup>), 114.1 (C<sup>2,31</sup>), 105.8 (C<sup>20,22</sup>), 35.6 (C<sup>23,25</sup>), 34.4 (C<sup>17,40</sup>), 30.4 (C<sup>15,16,38,39</sup>), 23.9 (C<sup>41,42,48,51</sup>), 23.9 (C<sup>43,44,45,46,47,49,50,52</sup>).

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 696.50 (21, [ddpd<sup>5Tripp</sup>+H]<sup>+</sup>), 718.48 (23, [ddpd<sup>5Tripp</sup>+Na]<sup>+</sup>), 1414.98 (100, [2 ddpd<sup>5Tripp</sup>+Na]<sup>+</sup>), 1430.95 (6, [2 ddpd<sup>5Tripp</sup>+K]<sup>+</sup>).

Elem. Anal. calcd. for C<sub>47</sub>H<sub>61</sub>N<sub>5</sub> (696.04): C, 81.10; H, 8.83; N, 10.06. Found: C, 80.99; H, 9.07; N, 9.93.

UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 248 (sh, 20.5), 281 (29.4), 341 (32.1).

Emission (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{em}$  / nm ( $\lambda_{exc}$  / nm): 402, 370 (sh) (320).

**Synthesis of [Cr(ddpd<sup>5Me</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> ([Cr<sup>5Me</sup>][BF<sub>4</sub>]<sub>3</sub>**, adapted from an analogous literature procedure<sup>20</sup>): ddpd<sup>5Me</sup> (725 mg, 2.3 mmol, 1.8 eq) was dissolved in MeCN (20 mL) and water (20 mL) was added. The solution was degassed with argon for one hour. Adding CrCl<sub>2</sub> (155 mg, 1.3 mmol, 1.0 eq) yielded a dark green to blue solution. After stirring overnight, an aqueous NH<sub>4</sub>BF<sub>4</sub> solution (4 mL, 1 M) was added and the solution was exposed to air. The solution turned orange. The solvents were removed under reduced pressure and the residue dissolved in MeCN (30 mL). Insoluble residues were filtered and the orange solution was subjected to crystallization with Et<sub>2</sub>O, resulting in orange crystals suitable for X-ray crystallography. Yield: 381 mg, 0.4 mmol, 32%.

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 230.10 (74, [Cr(ddpd<sup>5Me</sup>)<sub>2</sub>]<sup>3+</sup>), 388.65 (100, {[Cr(ddpd<sup>5Me</sup>)<sub>2</sub>][BF<sub>4</sub>]}<sup>2+</sup>), 864.31 (54, {[Cr(ddpd<sup>5Me</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>}<sup>+</sup>).

IR (ATR):  $\tilde{\nu}$  / cm<sup>-1</sup> = 1601 (m), 1580 (m), 1506 (s), 1447 (s), 1387 (s), 1337 (m), 1251 (w), 1225 (w), 1176 (w), 1153 (m), 1051 – 1015 (vs br, BF), 948 (s), 826 (s), 807 (s), 747 (m), 674 (m), 591 (m), 519 (m), 492 (m), 449 (m), 419 (m).

Elem. anal. calcd. (%) for C<sub>38</sub>H<sub>42</sub>B<sub>3</sub>CrF<sub>12</sub>N<sub>10</sub> (951.23) x 2 H<sub>2</sub>O: C, 46.23; H, 4.70; N, 14.19. Found: C, 46.22; H, 4.84; N, 14.29.

UV/Vis (MeCN):  $\lambda_{\max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 444 (4.0, MC + LMCT), 323 sh (22.4, MC + LMCT), 305 (26.5, LMCT), 225 sh (52.7,  $\pi\pi^*$ ).

UV/Vis (H<sub>2</sub>O):  $\lambda_{\max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 444 (4.0, MC + LMCT), 324 sh (22.1, MC + LMCT), 306 (26.6, LMCT), 222 sh (52.9,  $\pi\pi^*$ ).

Emission (MeCN):  $\lambda_{\text{em}}$  / nm ( $\lambda_{\text{exc}}$  / nm): 740, 778 (444).

Emission (H<sub>2</sub>O):  $\lambda_{\text{em}}$  / nm ( $\lambda_{\text{exc}}$  / nm): 741, 779 (444).

**Syntheses of [Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> ([Cr<sup>5Mes</sup>][BF<sub>4</sub>]<sub>3</sub>) and [Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> ([Cr<sup>5Tripp</sup>][BF<sub>4</sub>]<sub>3</sub>).** The precursor [Cr(MeCN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> was prepared according to a literature procedure.<sup>24</sup> All following reactions were performed in a glove box under inert conditions. The ligand (ddpd<sup>5Mes</sup>, 1.40 g, 2.65 mmol; ddpd<sup>5Tripp</sup>, 0.39 g, 0.56 mmol, 2.0 eq) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). [Cr(MeCN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> (1.0 eq) was dissolved in MeCN (10 mL). The pale blue chromium complex solution was added dropwise to the clear brownish ligand solution. The reaction mixture was stirred overnight under inert conditions and then for 2 hours under air, resulting in a dark yellow solution. A solution of [<sup>n</sup>Bu<sub>4</sub>N][BF<sub>4</sub>] in MeCN (2 mL) was added (2.0 eq). After stirring for three hours, the CH<sub>2</sub>Cl<sub>2</sub> was removed under reduced pressure and the remaining orange MeCN solution was subjected to crystallization with Et<sub>2</sub>O, resulting in orange needles suitable for X-ray crystallography. Rapid addition of Et<sub>2</sub>O to a concentrated MeCN solution of the complex yields a yellow powder.

**[Cr<sup>5Mes</sup>][BF<sub>4</sub>]<sub>3</sub>:** Yield: 680 mg, 1.3 mmol, 96%.

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 368.85 (72, [Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>]<sup>3+</sup>), 596.78 (100, {[Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>][BF<sub>4</sub>]}<sup>2+</sup>), 1280.56 (60, {[Cr(ddpd<sup>5Mes</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>}<sup>+</sup>).

IR (ATR):  $\tilde{\nu}$  = 1603 (m), 1576 (w), 1502 (m), 1480 (m), 1448 (s), 1374 (m), 1333 (w), 1234 (w), 1150 (w), 1104 – 1006 (vs br, BF), 944 (w), 849 (w), 810 (w), 762 (w), 736 (w), 585 (w), 519 (w), 449 (w), 406 (w) cm<sup>-1</sup>.

Elem. anal. calcd. (%) for C<sub>70</sub>H<sub>74</sub>B<sub>3</sub>CrF<sub>12</sub>N<sub>10</sub> (1367.56): C, 61.47; H, 5.45; N, 10.24. Found: C, 61.13; H, 5.48; N, 10.20.

UV/Vis (MeCN):  $\lambda_{\max}$  / nm ( $\epsilon$  / 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 453 (2.8, MC + LMCT), 312 (21.6, LMCT), 257 (31.2), 236 sh (43.5,  $\pi\pi^*$ ).

Emission (MeCN):  $\lambda_{\text{em}}$  / nm ( $\lambda_{\text{exc}}$  / nm): 742, 782 (450).

**[Cr<sup>5Tripp</sup>][BF<sub>4</sub>]<sub>3</sub>:** Yield: 140 mg, 0.08 mmol, 10%.

MS (ESI<sup>+</sup>, MeCN):  $m/z$  (%) = 481.31 (62, [Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>]<sup>3+</sup>), 765.47 (100, {[Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>][BF<sub>4</sub>]}<sup>2+</sup>), 1616.93 (36, {[Cr(ddpd<sup>5Tripp</sup>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>}<sup>+</sup>).

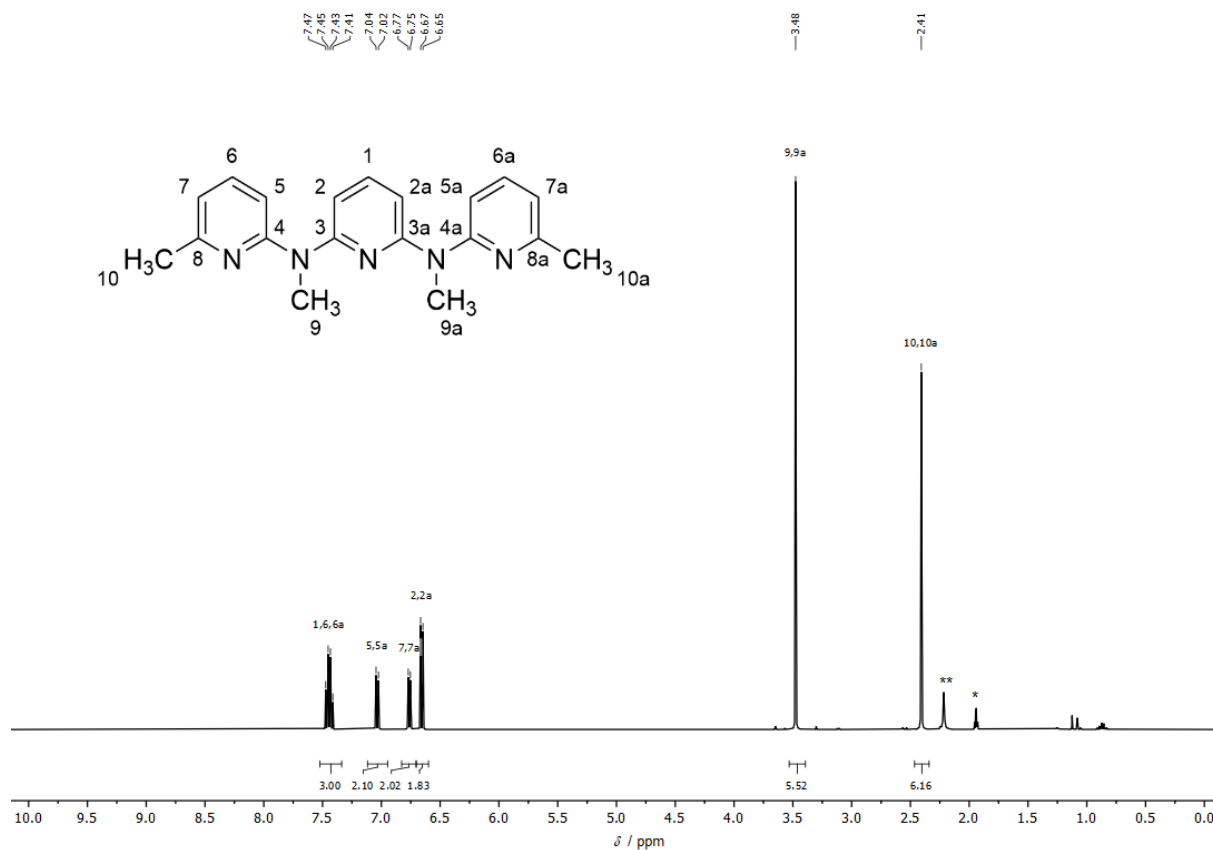
IR (ATR):  $\tilde{\nu}$  = 2959 (m), 2870 (w), 1601 (m), 1504 (m), 1444 (s), 1378 (s), 1333 (w), 1232 (w), 1148 (w), 1110 – 989 (vs br, BF), 946 (m), 878 (w), 812 (m), 760 (m), 649 (w), 581 (w), 519 (m), 457 (w), 406 (w) cm<sup>-1</sup>.

Elem. anal. calcd. (%) for C<sub>94</sub>H<sub>122</sub>B<sub>3</sub>CrF<sub>12</sub>N<sub>11</sub> (1442.92) x MeCN x Et<sub>2</sub>O: C, 66.01; H, 7.48; N, 8.47. Found: C, 65.70; H, 7.20; N, 8.14.

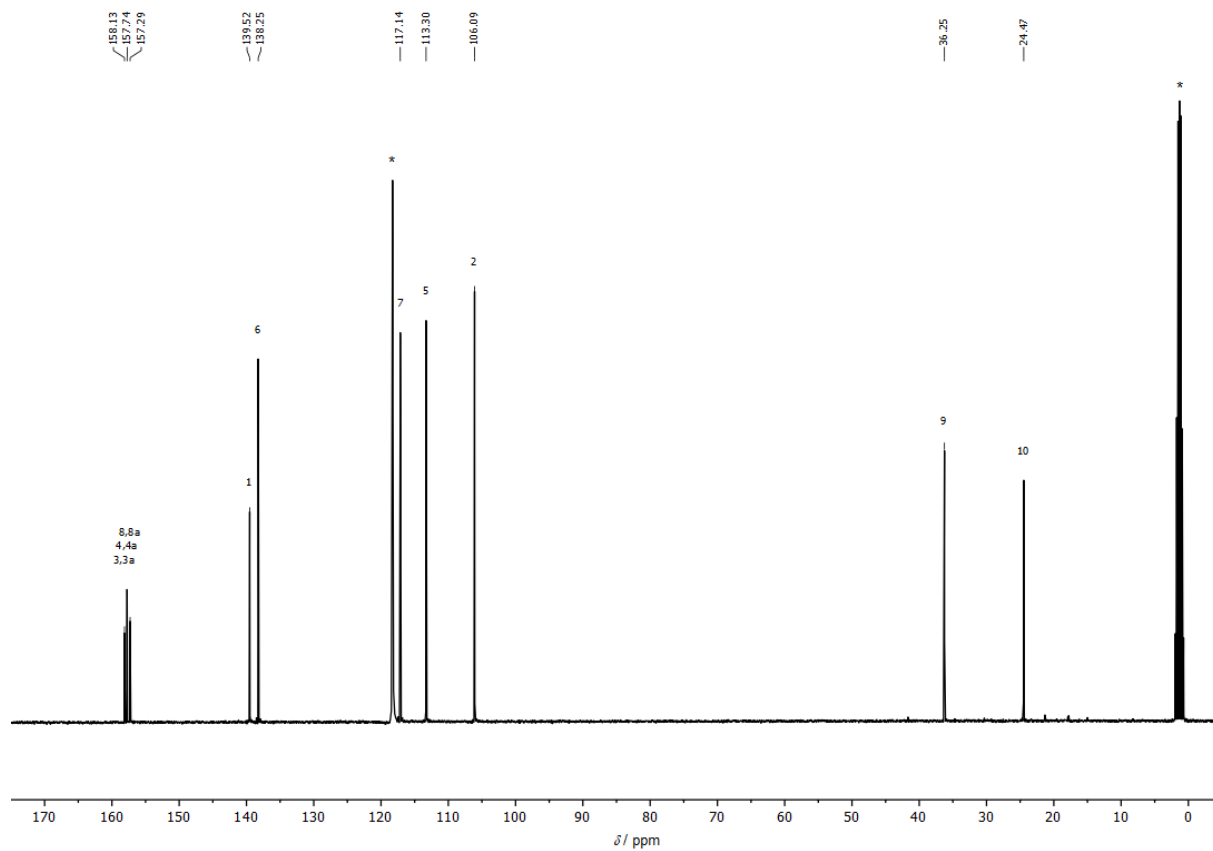
UV/Vis (MeCN):  $\lambda_{\max}$  / nm ( $\epsilon$  /  $10^3$  M<sup>-1</sup>cm<sup>-1</sup>): 455 (3.3, MC + LMCT), 319 (29.5, LMCT), 240 (sh, 55.1,  $\pi\pi^*$ ).

Emission (MeCN):  $\lambda_{\text{em}}$  / nm ( $\lambda_{\text{exc}}$  / nm): 740 (sh), 794 (454).

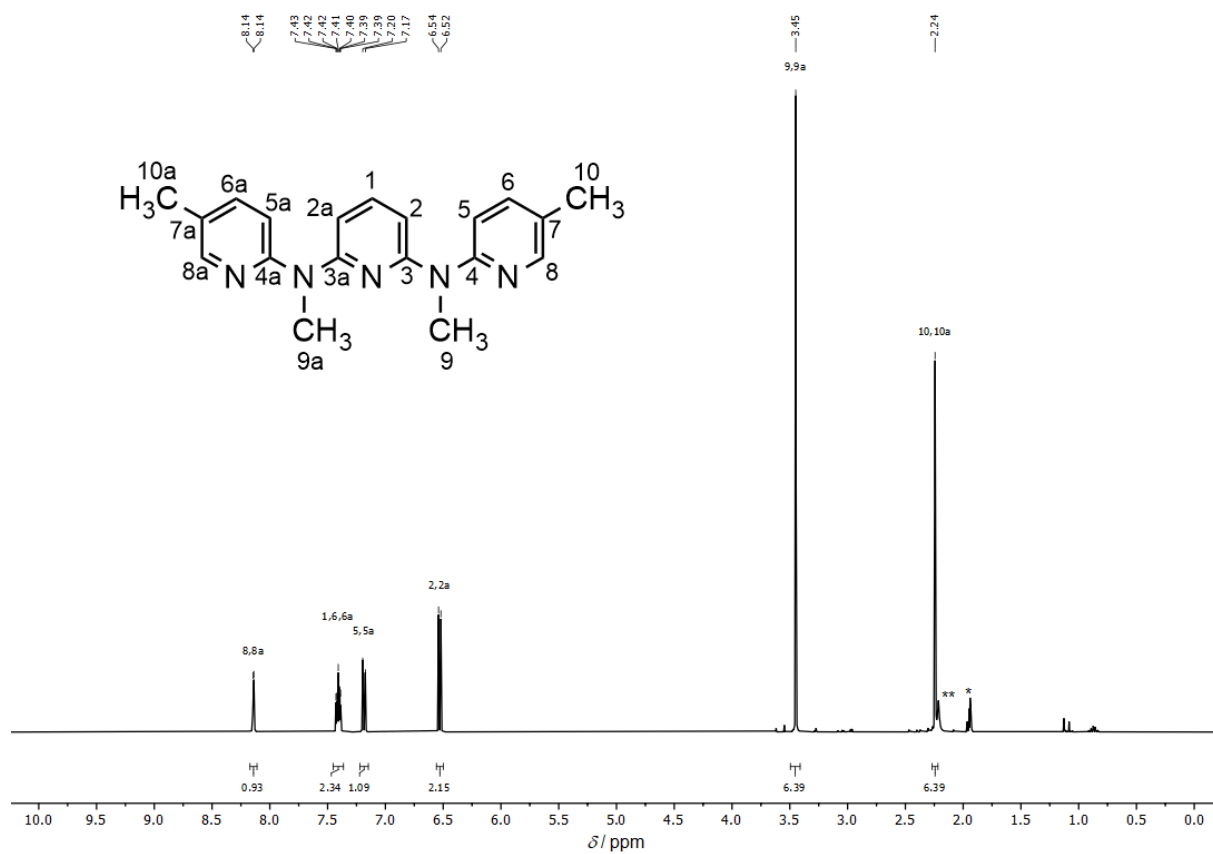




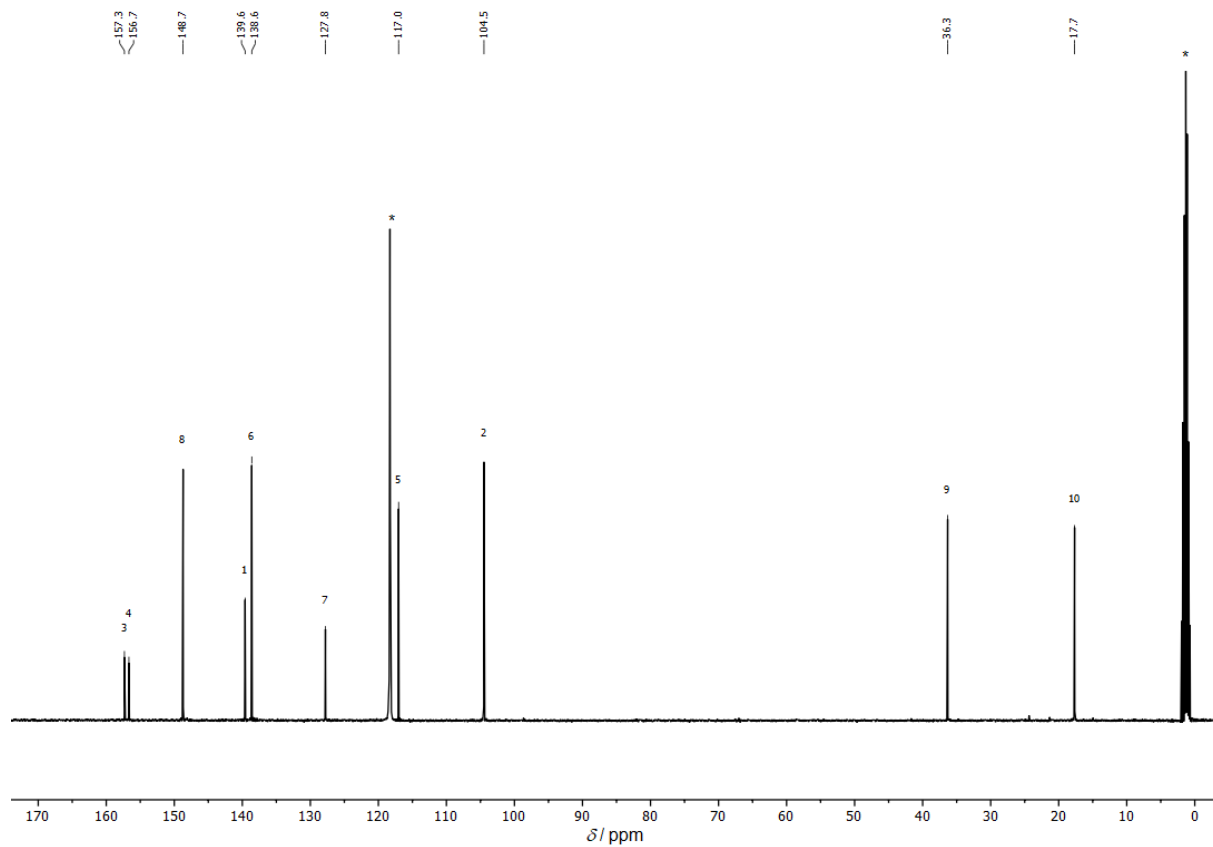
**Figure S1.** <sup>1</sup>H NMR spectrum of ddpd<sup>6Me</sup> in CD<sub>3</sub>CN. \* CH<sub>2</sub>DCN, \*\* water.



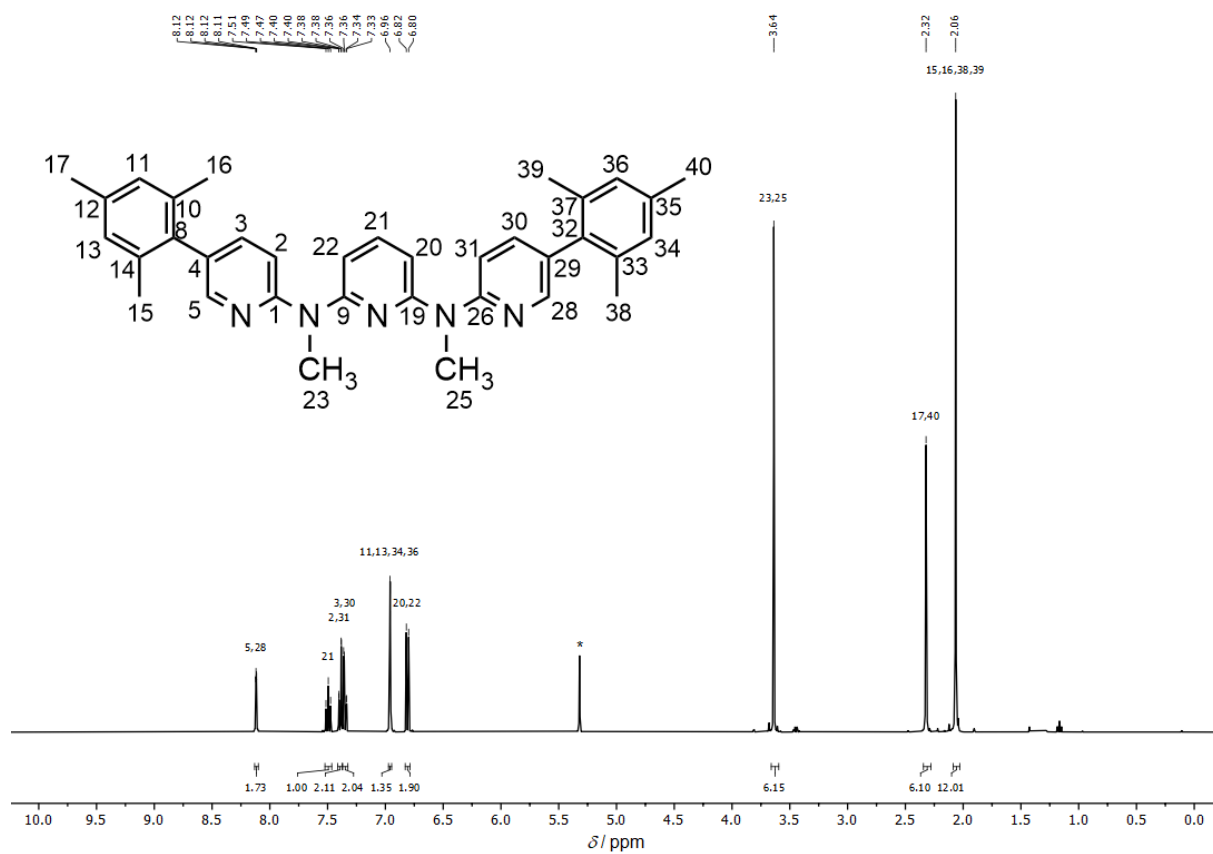
**Figure S2.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of ddpd<sup>6Me</sup> in CD<sub>3</sub>CN. \* CH<sub>2</sub>DCN.



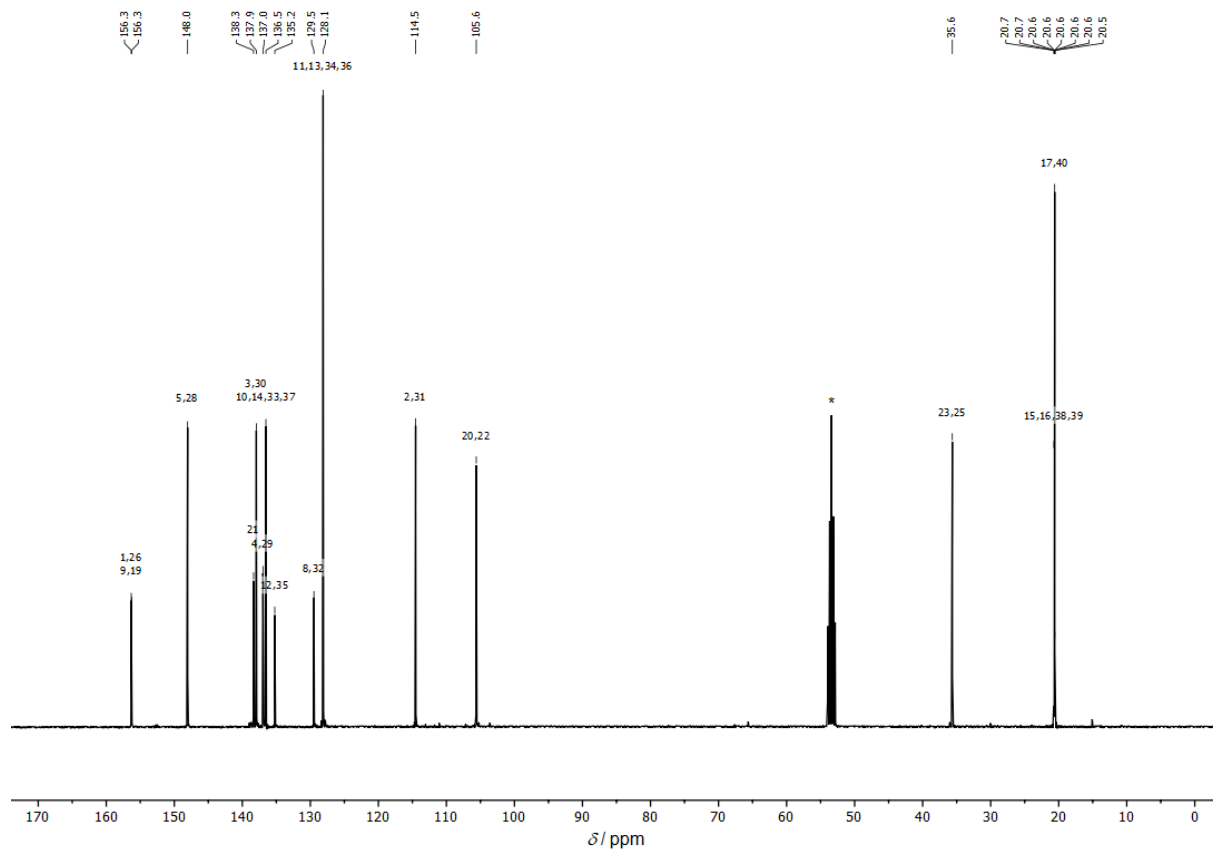
**Figure S3.** <sup>1</sup>H NMR spectrum of ddpd<sup>5Me</sup> in CD<sub>3</sub>CN. \* CH<sub>2</sub>DCN, \*\* water.



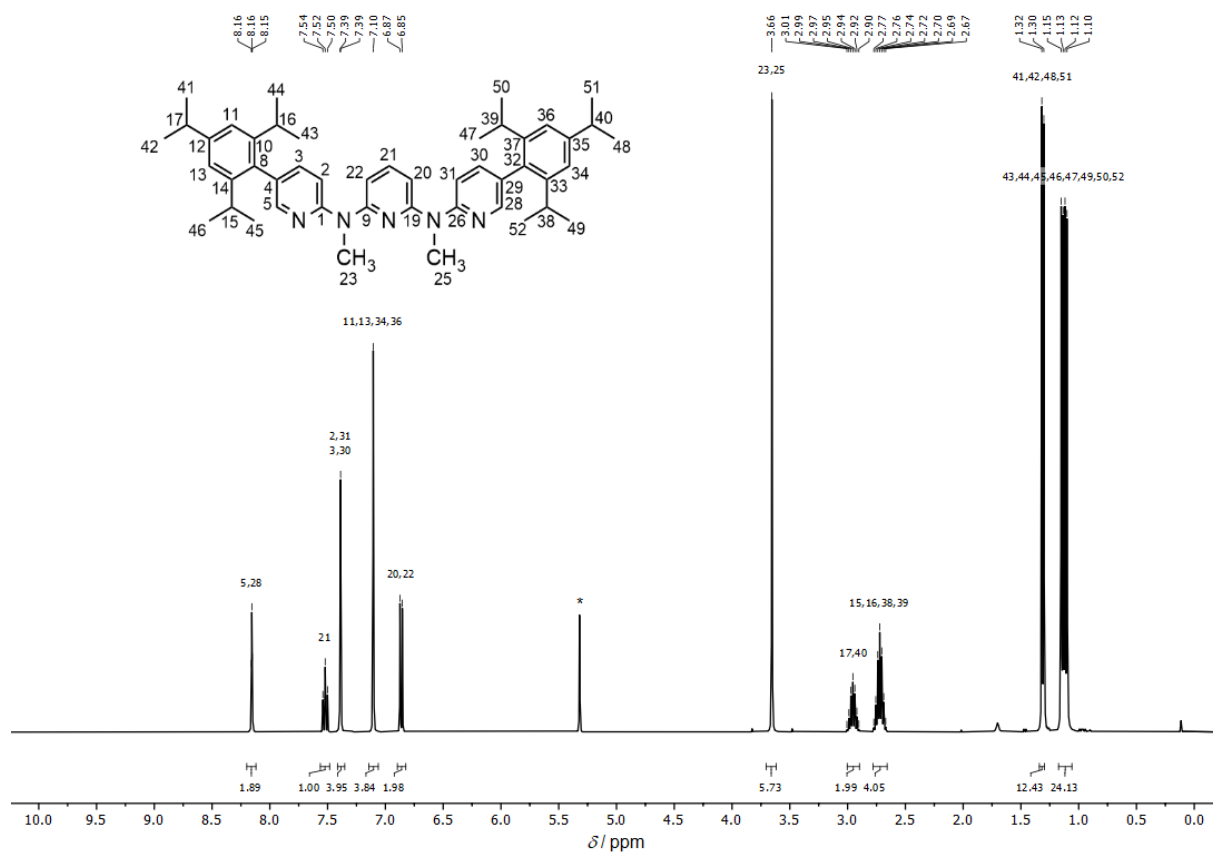
**Figure S4.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of ddpd<sup>5Me</sup> in CD<sub>3</sub>CN. \* CH<sub>2</sub>DCN.



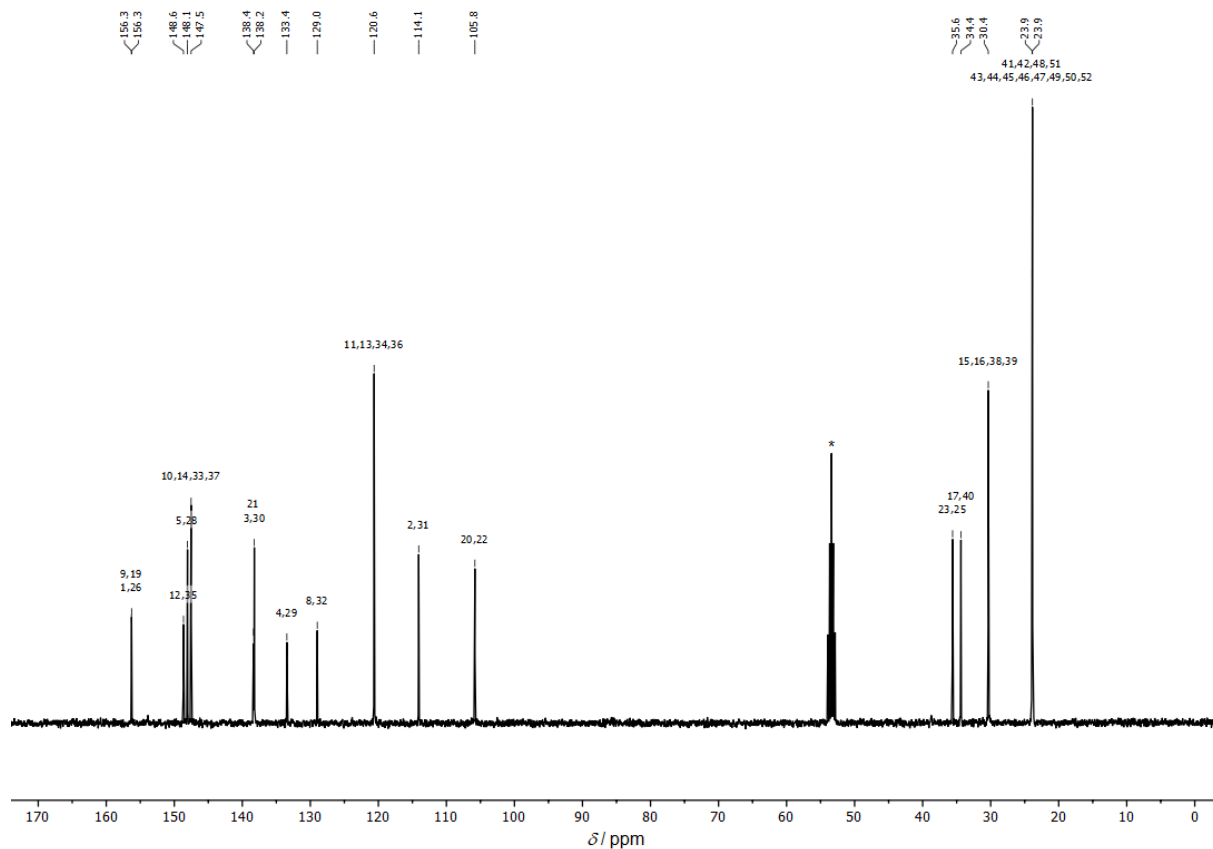
**Figure S5.** <sup>1</sup>H NMR spectrum of ddpd<sup>5</sup>Mes in CD<sub>2</sub>Cl<sub>2</sub>. \* CHDCl<sub>2</sub>.



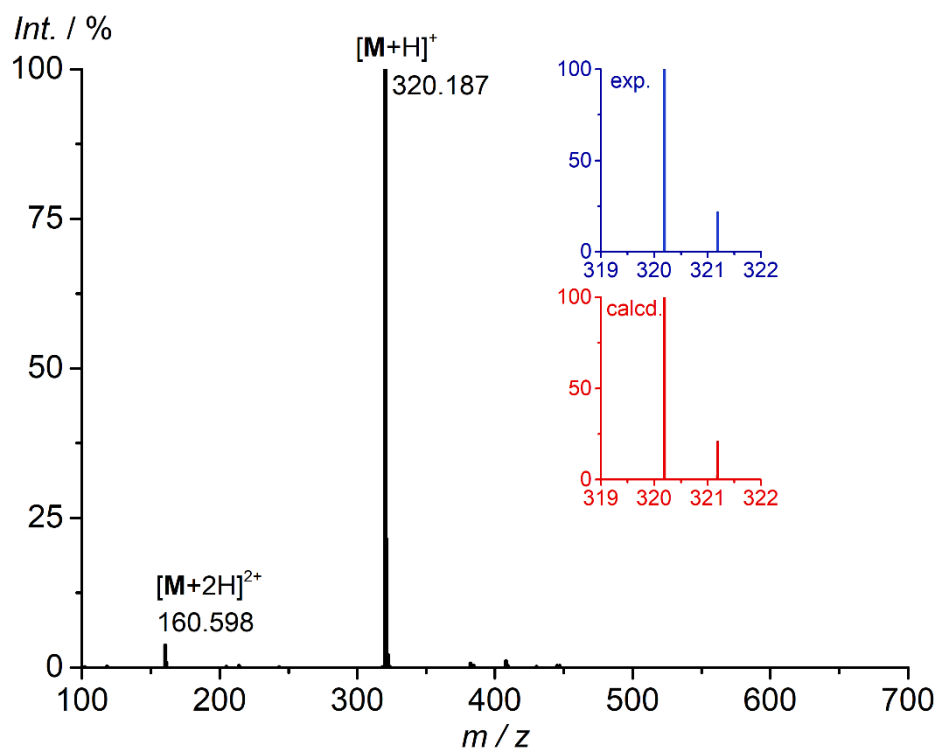
**Figure S6.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of ddpd<sup>5</sup>Mes in CD<sub>2</sub>Cl<sub>2</sub>. \* CHDCl<sub>2</sub>.



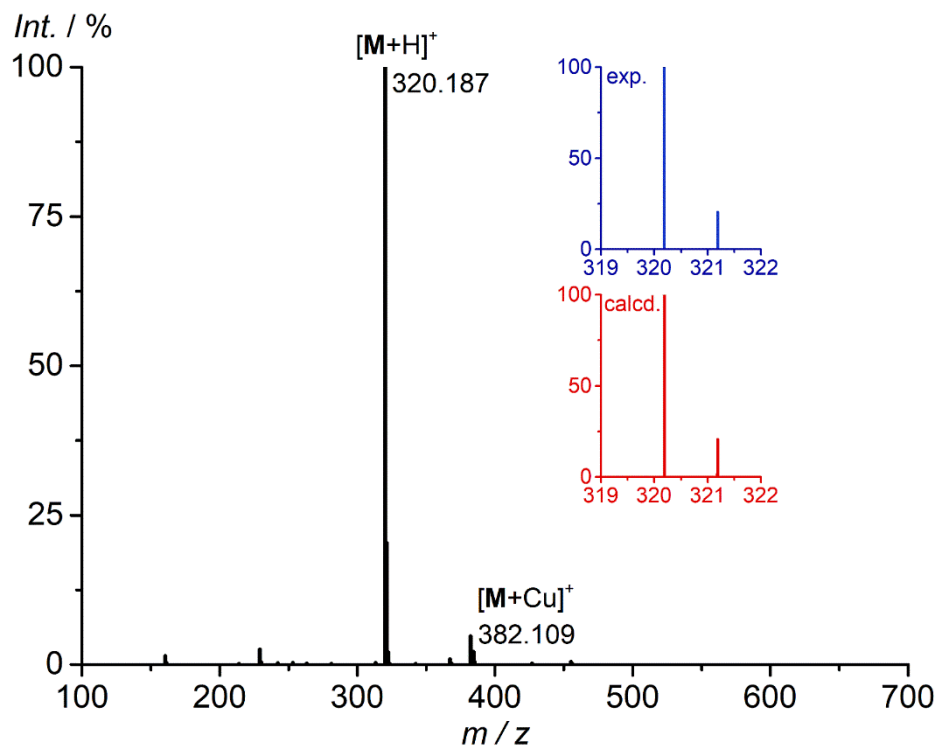
**Figure S7.**  $^1\text{H}$  NMR spectrum of  $\text{ddpd}^{\text{5Tripp}}$  in  $\text{CD}_2\text{Cl}_2$ . \*  $\text{CH}_2\text{Cl}_2$ .



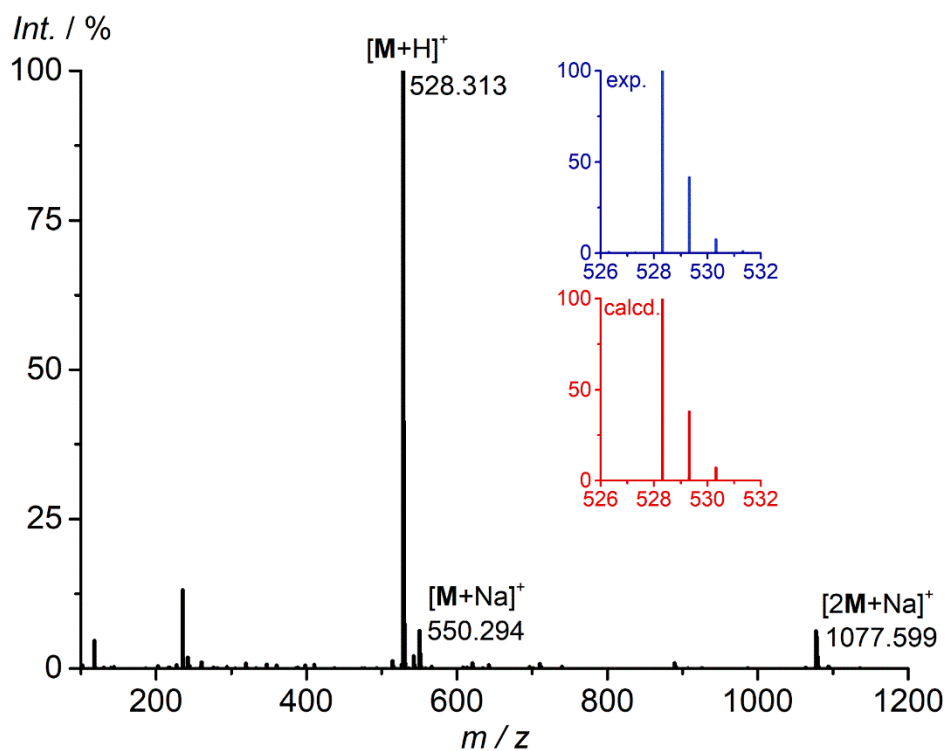
**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{ddpd}^{\text{5Tripp}}$  in  $\text{CD}_2\text{Cl}_2$ . \*  $\text{CH}_2\text{Cl}_2$ .



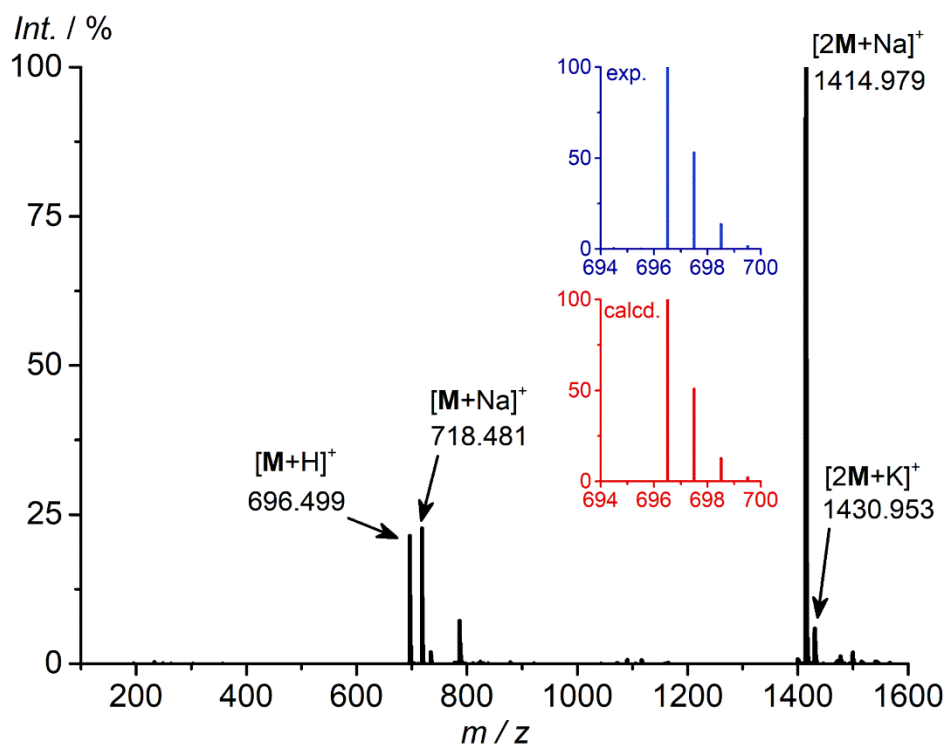
**Figure S9.** ESI<sup>+</sup> mass spectrum of ddpd<sup>6Me</sup> in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  320.



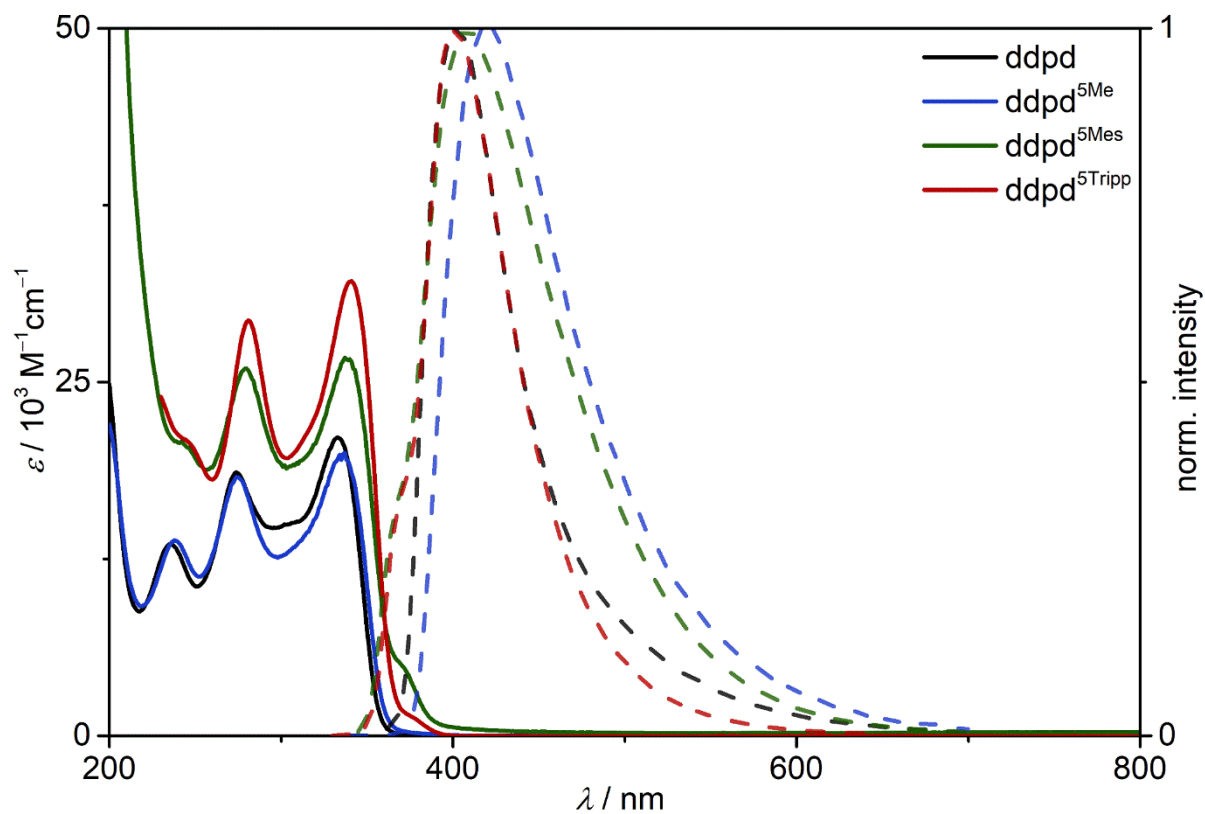
**Figure S10.** ESI<sup>+</sup> mass spectrum of ddpd<sup>5Me</sup> in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  320.



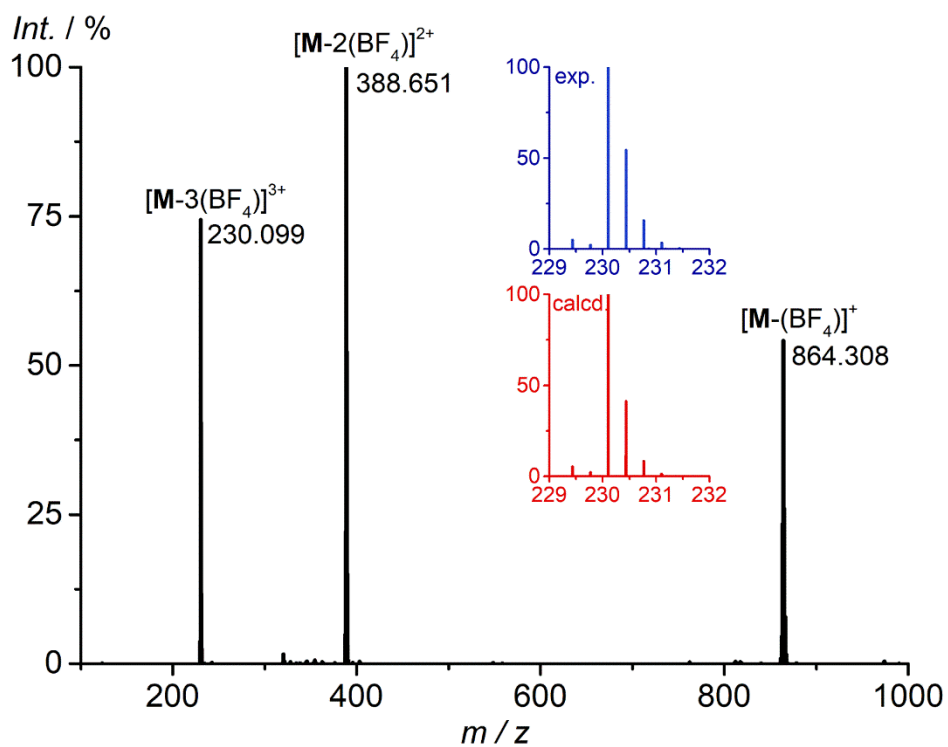
**Figure S11.** ESI<sup>+</sup> mass spectrum of ddpd<sup>5Mes</sup> in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  528.



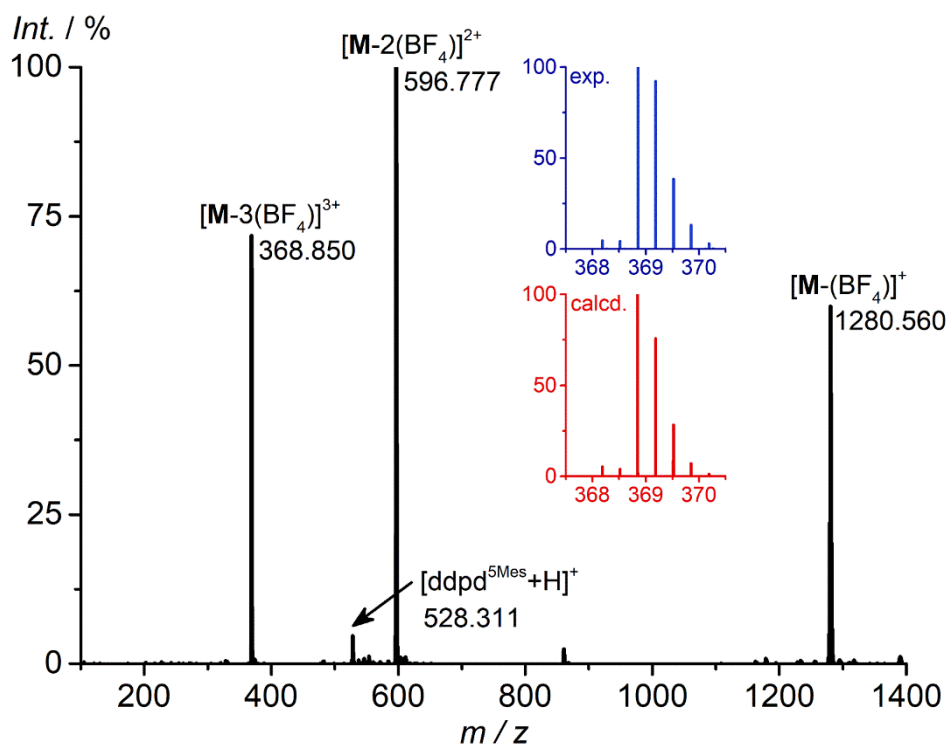
**Figure S12.** ESI<sup>+</sup> mass spectrum of ddpd<sup>5Tripp</sup> in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  696.



**Figure S13.** UV/Vis absorption (solid) and normalized emission spectra (dotted) of ligands ddpd ( $\lambda_{\text{exc}} = 333 \text{ nm}$ ), ddpd<sup>5Me</sup> ( $\lambda_{\text{exc}} = 334 \text{ nm}$ ), ddpd<sup>5Mes</sup> ( $\lambda_{\text{exc}} = 337 \text{ nm}$ ), in acetonitrile and ddpd<sup>5Tripp</sup> ( $\lambda_{\text{exc}} = 320 \text{ nm}$ ) in dichloromethane at 293 K.

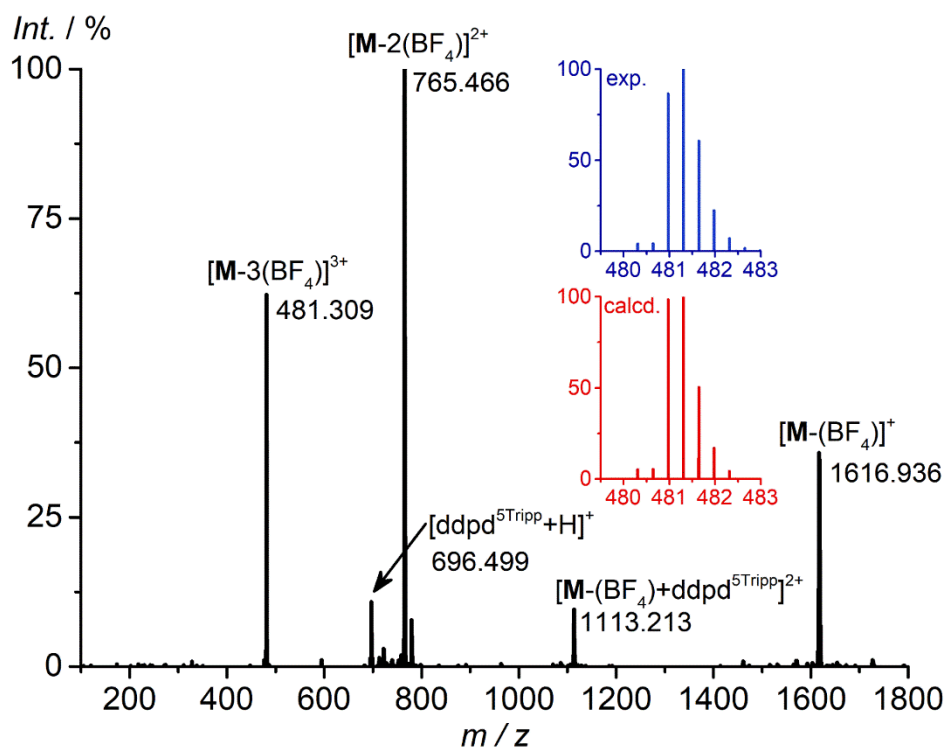


**Figure S14.** ESI<sup>+</sup> mass spectrum of  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$  in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  230.

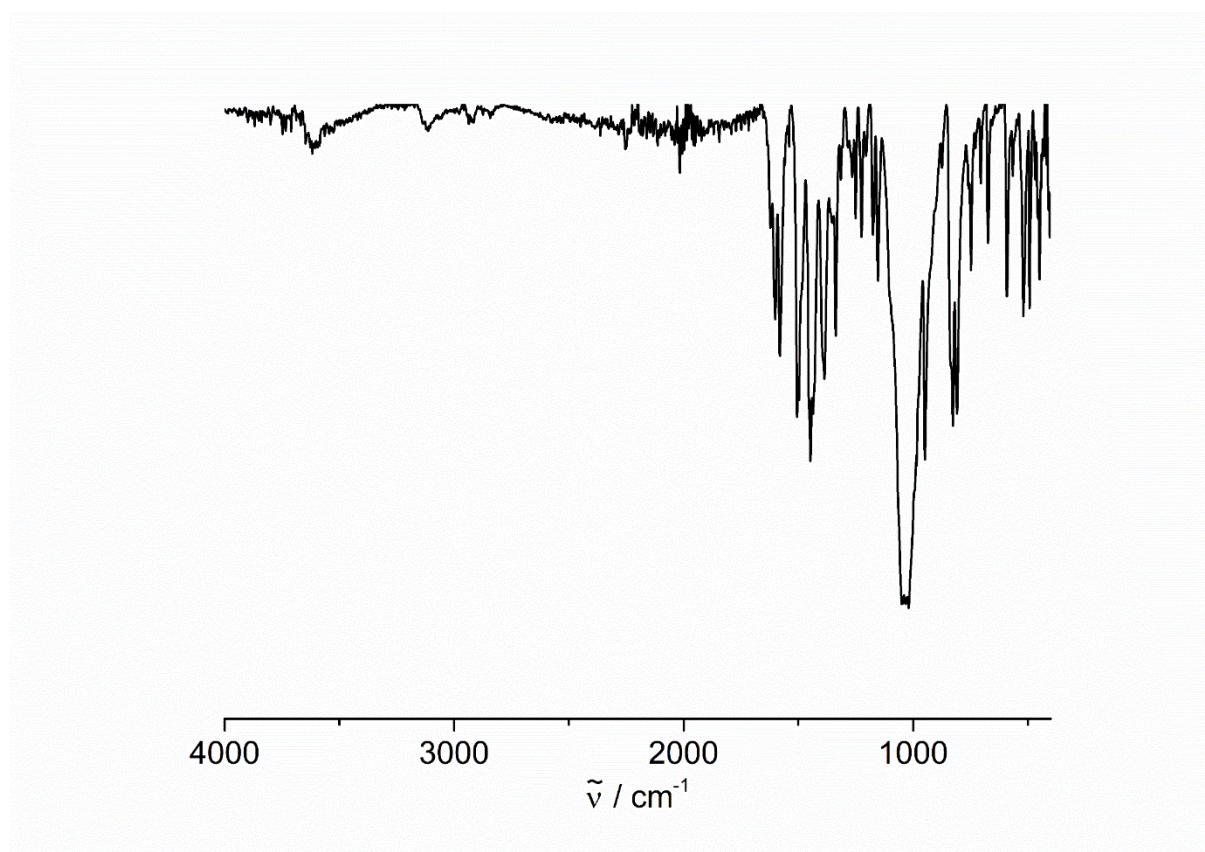


**Figure S15.** ESI<sup>+</sup> mass spectrum of  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  369.

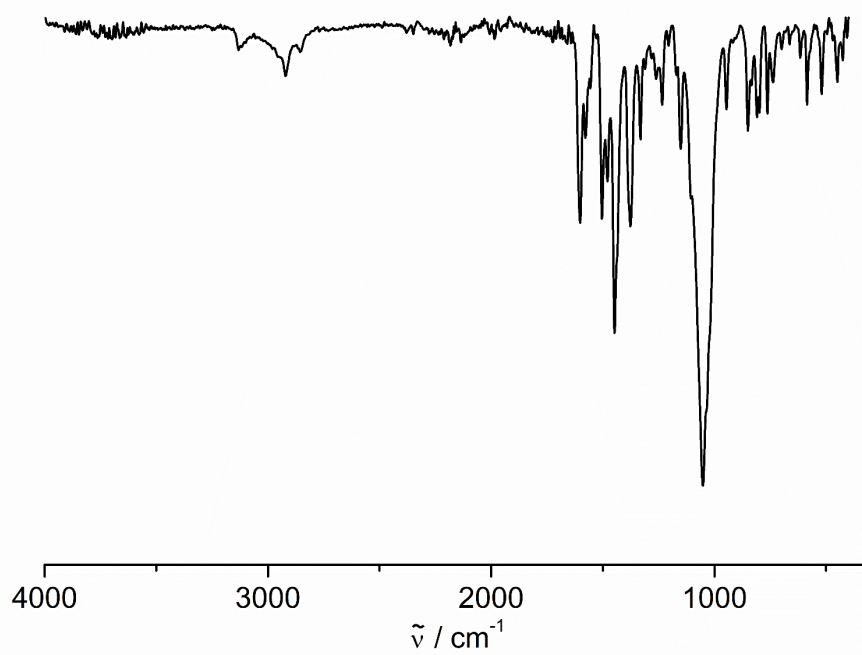




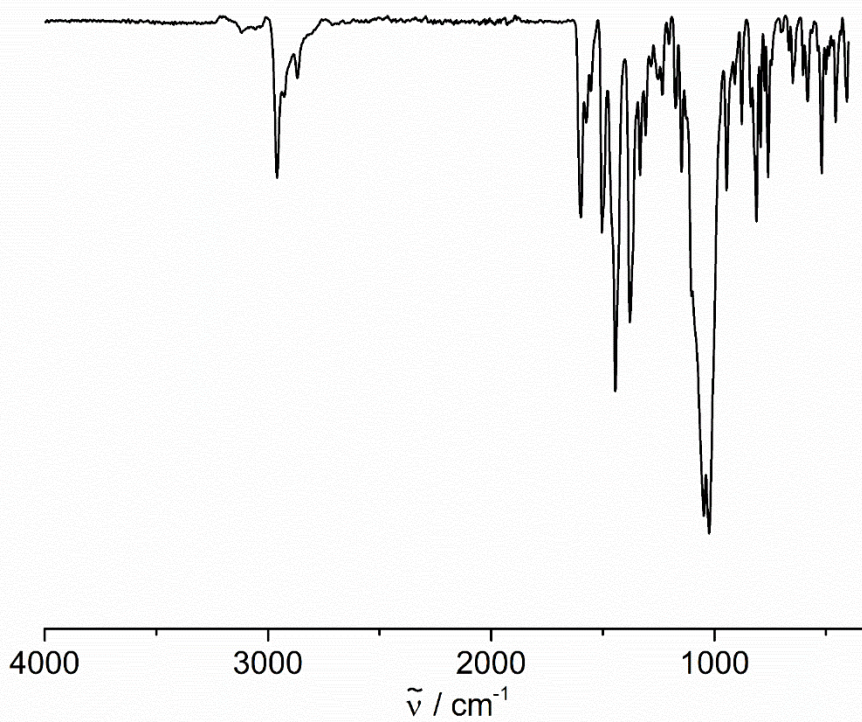
**Figure S16.** ESI+ mass spectrum of  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at  $m/z$  481.



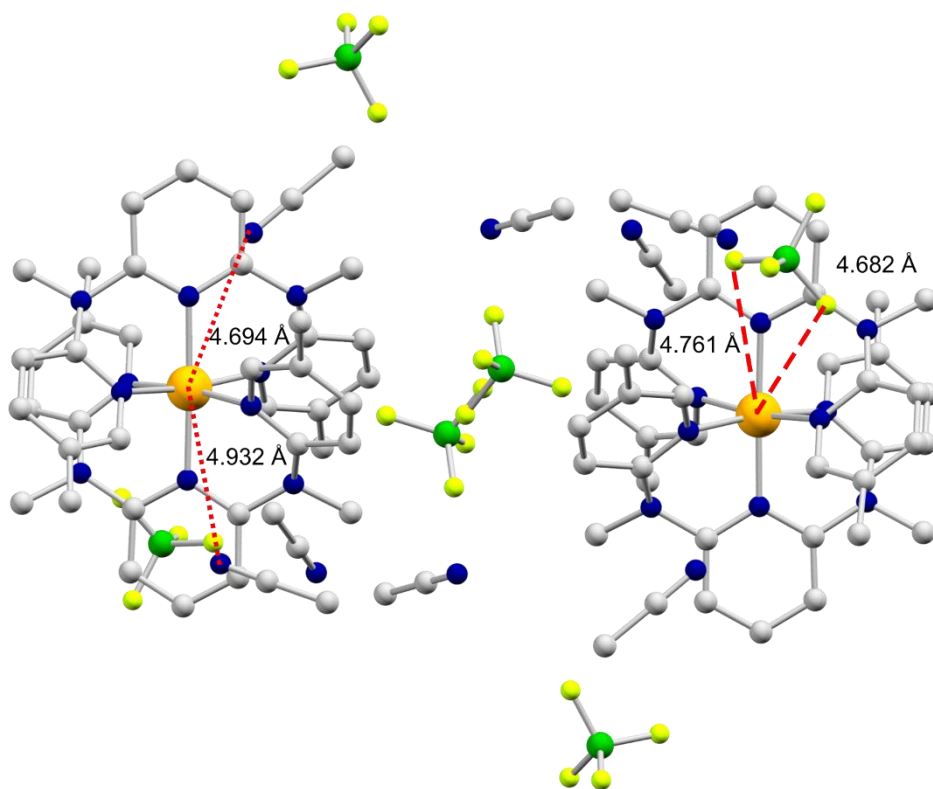
**Figure S17.** ATR-IR spectrum of  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ .



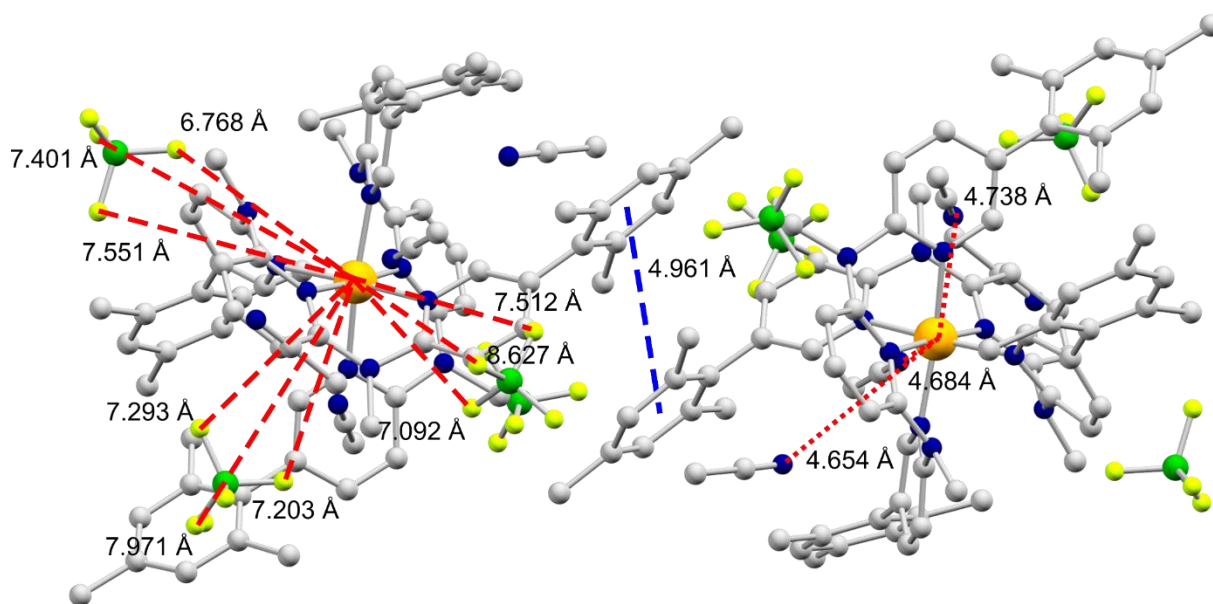
**Figure S18.** ATR-IR spectrum of [Cr<sup>5Mes</sup>][BF<sub>4</sub>]<sub>3</sub>.



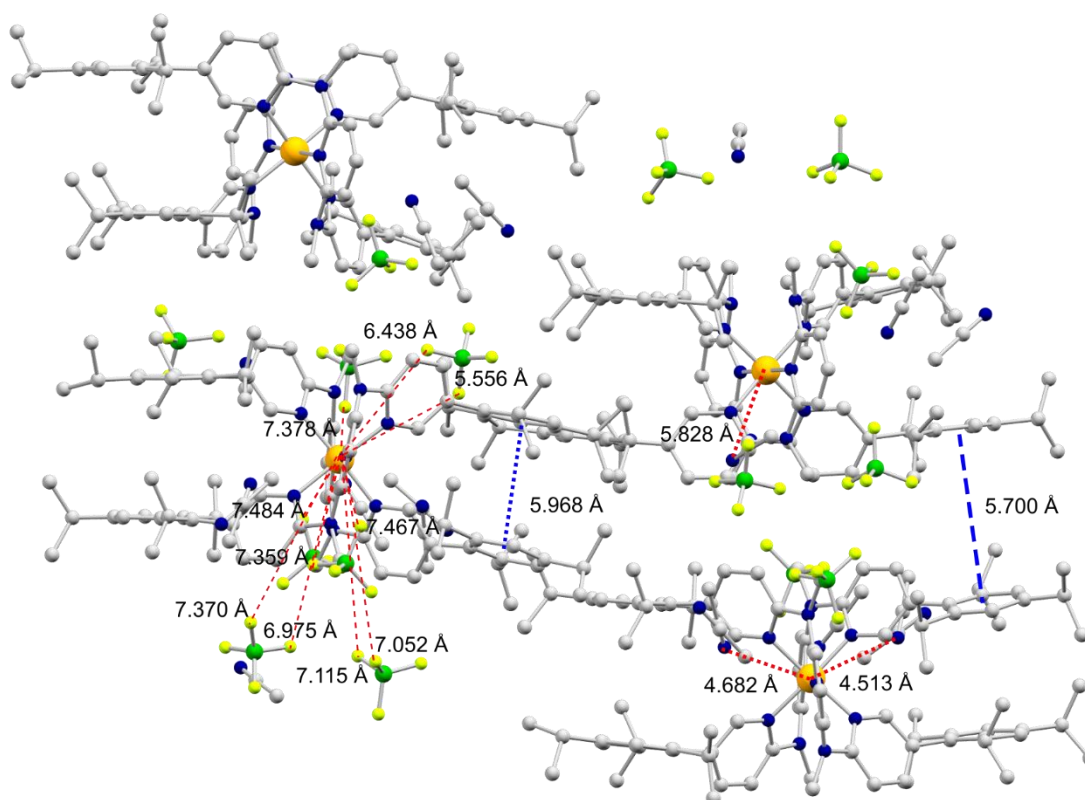
**Figure S19.** ATR-IR spectrum of [Cr<sup>5Tripp</sup>][BF<sub>4</sub>]<sub>3</sub>.



**Figure S20.** Packing of  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$  in the solid state with shortest  $\text{Cr}\cdots\text{F}$  (dashed,  $\text{BF}_4^-$ ) and  $\text{Cr}\cdots\text{N}$  (dotted, MeCN) distances indicated in red. Hydrogen atoms are omitted for clarity.



**Figure S21.** Packing of  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  in the solid state with intermolecular (blue dashed line)  $\pi$ - $\pi$  stacking indicated. The  $\pi$ - $\pi$  contact is denoted by the distance between ring centroids. Selected  $\text{Cr}\cdots\text{F}$  (dashed,  $\text{BF}_4^-$ ) and  $\text{Cr}\cdots\text{N}$  (dotted, MeCN) distances are indicated in red. Hydrogen atoms are omitted for clarity.



**Figure S22.** Packing of  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  in the solid state with average intramolecular (blue dotted lines) and intermolecular (blue dashed lines)  $\pi$ - $\pi$  stacking indicated. The  $\pi$ - $\pi$  contact is denoted by the distance between ring centroids. Selected Cr $\cdots$ F (dashed,  $\text{BF}_4^-$ ) and Cr $\cdots$ N (dotted, MeCN) distances are indicated in red. Hydrogen atoms are omitted for clarity.

**Table S1.** Selected atom and centroid distances / Å and angles between planes / deg in  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ ,  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  and  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  from XRD measurements.

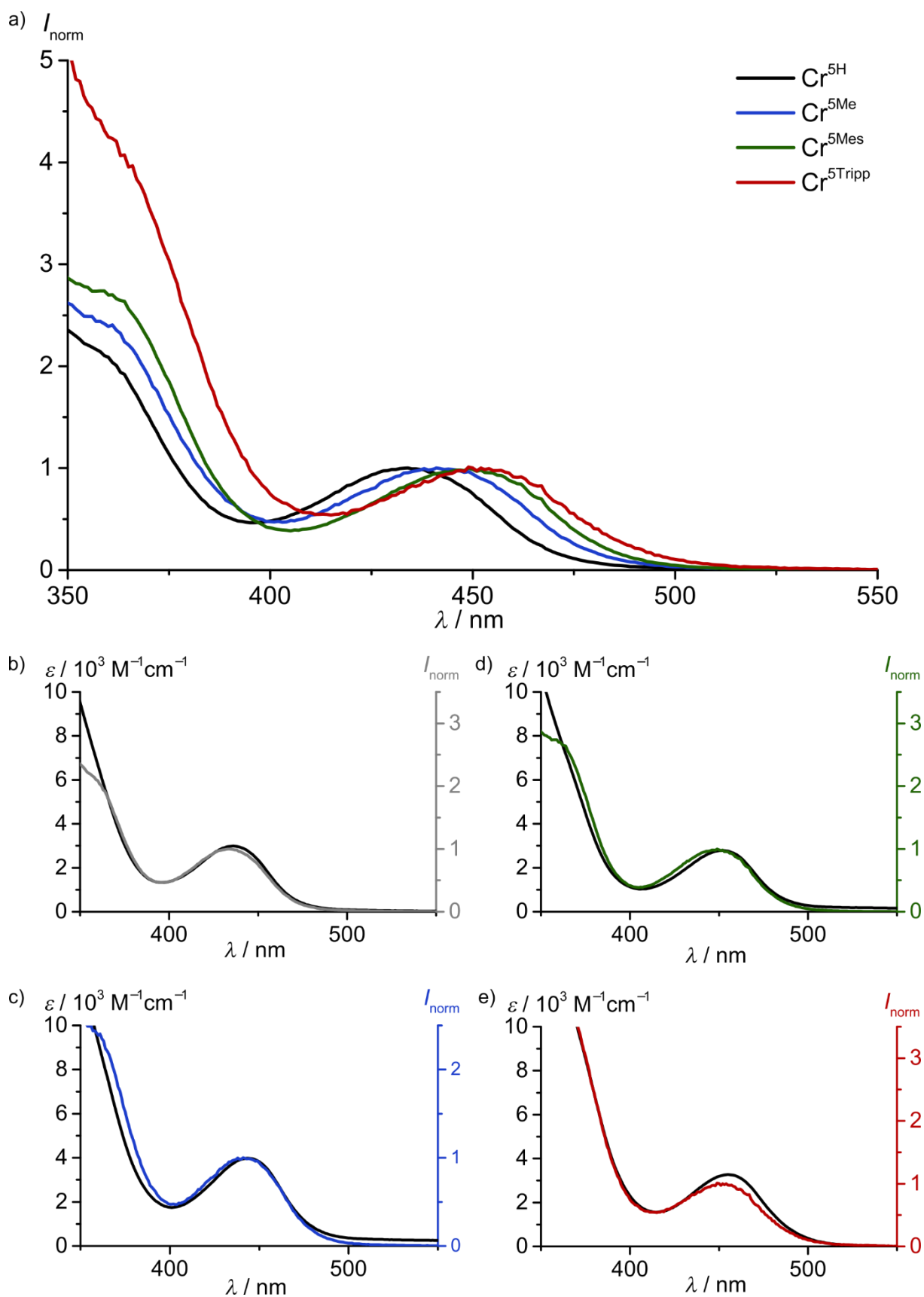
	$[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ <sup>20</sup>	$[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$	$[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$	$[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$
Intramol. centroids	-	-	-	5.968
Intermol. centroids	-	-	4.961	5.700
Shortest Cr $\cdots$ F ( $\text{BF}_4^-$ )	5.438	4.682	6.768	5.556
	6.140	4.761	7.401	6.438
	6.258	-	7.551	7.378
	-	-	7.203	6.975
	-	-	7.293	7.370
	-	-	7.971	7.052
	-	-	7.092	7.115
	-	-	7.512	7.467
	-	-	8.627	7.378
Shortest Cr $\cdots$ N (MeCN)	4.613	4.694	4.654	4.513
	4.815	4.932	4.684	4.682
	-	-	4.738	5.828
Py <sub>central</sub> -Cr-Py <sub>central</sub>	13.8	15.2	19.1	9.8

**Table S2.** Bond lengths / Å and angles / deg of  $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ , <sup>20</sup>  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ ,  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  and  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  from XRD measurements. Central pyridines, intraligand and interligand angles highlighted in purple, yellow and green, respectively.

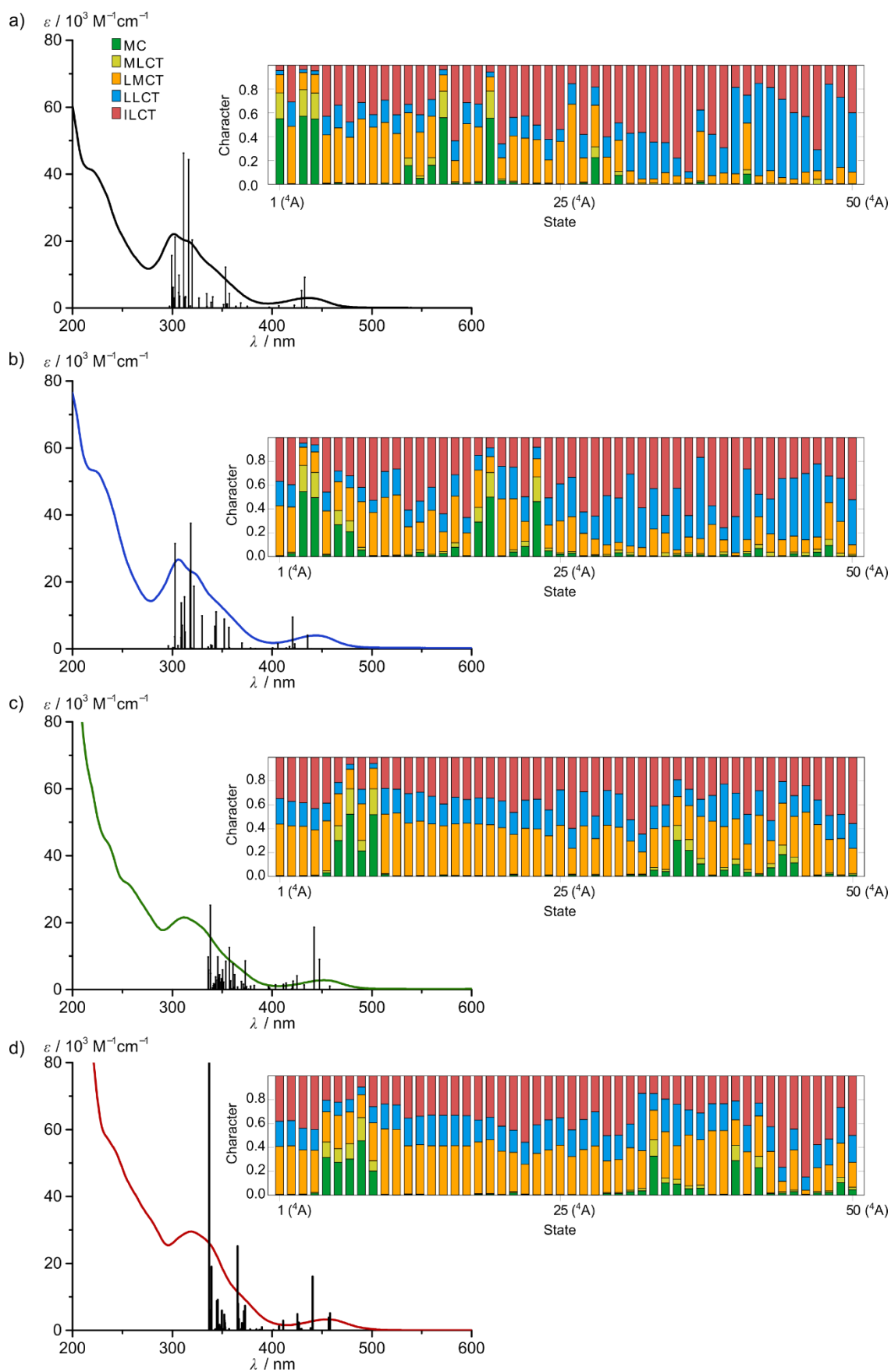
	$[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ <sup>20</sup>	$[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$	$[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$	$[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$
Cr1-N1	2.0485(18)	2.0448(14)	2.0577(17)	2.0523(14)
Cr1-N2	2.0393(18)	2.0294(14)	2.0268(17)	2.0222(14)
Cr1-N3	2.0394(19)	2.0471(14)	2.0623(18)	2.0561(14)
Cr1-N4	2.0446(17)	2.0492(13)	2.0579(18)	2.0576(14)
Cr1-N5	2.0444(18)	2.0300(14)	2.0215(17)	2.0238(14)
Cr1-N6	2.0485(18)	2.0403(13)	2.0549(18)	2.0449(14)
N1-Cr1-N2	85.13(8)	85.83(6)	87.63(7)	84.91(6)
N1-Cr1-N3	170.86(8)	172.00(5)	173.44(7)	170.02(6)
N1-Cr1-N4	91.06(87)	89.92(6)	88.71(7)	89.21(6)
N1-Cr1-N5	95.23(8)	93.47(6)	94.44(7)	95.40(6)
N1-Cr1-N6	89.49(7)	92.61(5)	91.25(7)	90.31(6)
N2-Cr1-N3	85.74(7)	86.18(6)	86.23(7)	85.26(6)
N2-Cr1-N4	95.10(7)	95.53(5)	91.65(7)	94.71(6)
N2-Cr1-N5	178.94(8)	178.31(5)	176.76(7)	179.13(6)
N2-Cr1-N6	94.02(7)	92.42(5)	95.71(7)	95.84(6)
N3-Cr1-N4	89.68(7)	90.31(6)	93.80(7)	93.29(5)
N3-Cr1-N5	89.68(7)	94.53(6)	91.79(7)	94.46(6)
N3-Cr1-N6	91.22(7)	88.26(5)	87.04(7)	89.00(6)
N4-Cr1-N5	85.89(7)	86.00(5)	85.91(7)	84.48(5)
N4-Cr1-N6	170.88(7)	171.81(5)	172.62(7)	169.35(6)
N5-Cr1-N6	84.99(7)	86.08(5)	86.74(7)	84.98(6)
Central pyridine, interligand trans, intraligand trans				

**Table S3.** Bond lengths / Å and angles / deg of  $[\text{Cr}^{5\text{H}}]^{3+}$ ,  $[\text{Cr}^{6\text{Me}}]^{3+}$ ,  $[\text{Cr}^{5\text{Me}}]^{3+}$ ,  $[\text{Cr}^{5\text{Mes}}]^{3+}$  and  $[\text{Cr}^{5\text{Tripp}}]^{3+}$  from DFT calculations. Central pyridines, intraligand and interligand angles highlighted in purple, yellow and green, respectively.

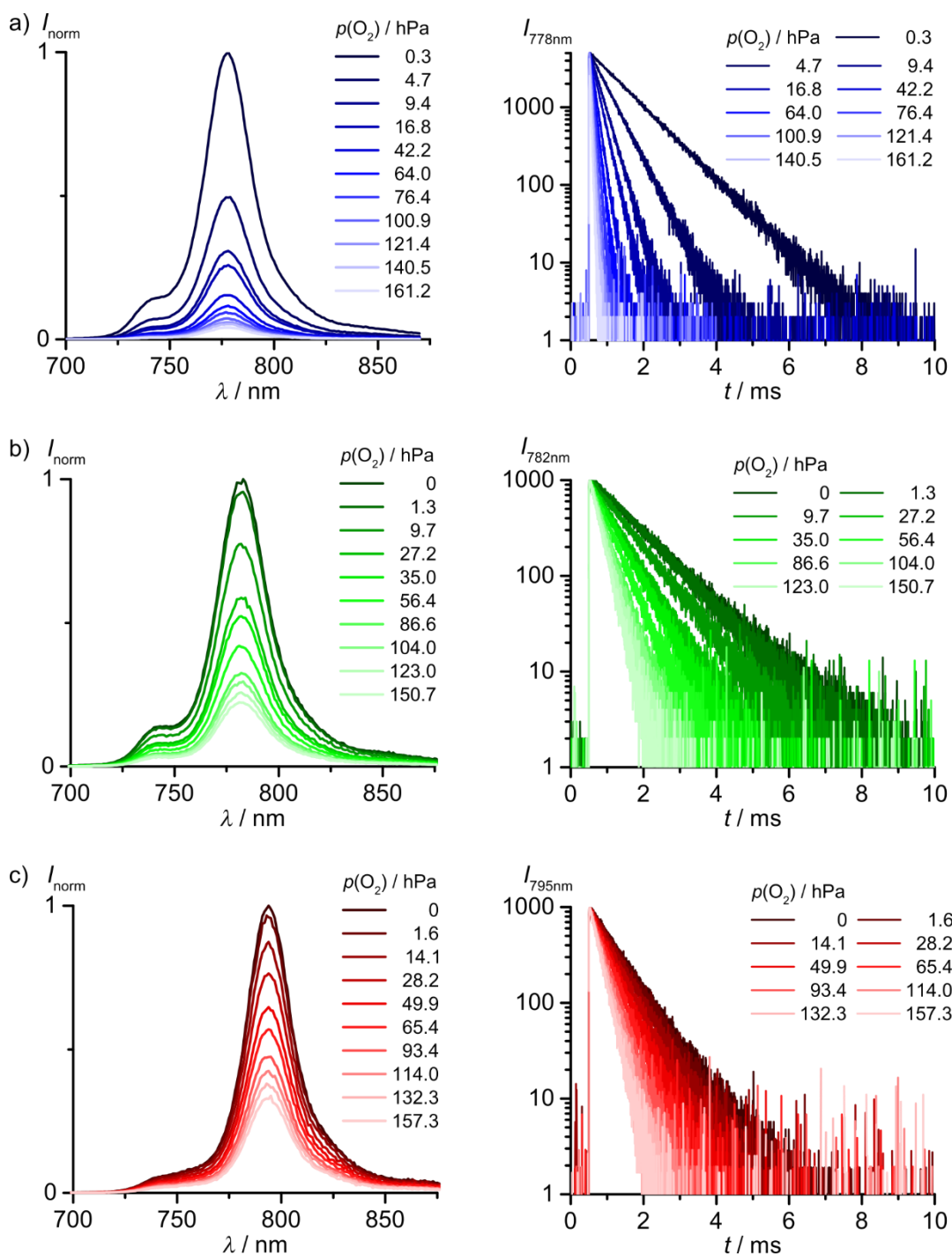
	$[\text{Cr}^{5\text{H}}]^{3+}$	$[\text{Cr}^{6\text{Me}}]^{3+}$	$[\text{Cr}^{5\text{Me}}]^{3+}$	$[\text{Cr}^{5\text{Mes}}]^{3+}$	$[\text{Cr}^{5\text{Tripp}}]^{3+}$
Cr1-N1	2.059	2.150	2.056	2.062	2.064
Cr1-N2	2.046	2.045	2.048	2.038	2.041
Cr1-N3	2.059	2.162	2.056	2.057	2.060
Cr1-N4	2.059	2.155	2.055	2.068	2.062
Cr1-N5	2.046	2.039	2.047	2.045	2.044
Cr1-N6	2.059	2.156	2.055	2.059	2.060
N1-Cr1-N2	86.46	87.30	86.49	85.65	84.95
N1-Cr1-N3	172.92	174.12	172.91	172.49	170.06
N1-Cr1-N4	91.40	87.00	91.29	94.35	92.24
N1-Cr1-N5	93.54	93.45	93.51	92.52	95.12
N1-Cr1-N6	89.04	92.97	89.11	88.51	88.54
N2-Cr1-N3	86.46	86.83	86.42	86.97	85.11
N2-Cr1-N4	93.54	92.97	93.56	91.51	95.16
N2-Cr1-N5	180.00	179.21	179.98	176.84	179.76
N2-Cr1-N6	93.54	93.24	93.49	94.92	94.65
N3-Cr1-N4	89.04	93.26	89.14	87.22	88.57
N3-Cr1-N5	93.54	92.42	93.59	94.86	94.82
N3-Cr1-N6	91.40	87.41	91.33	90.76	92.34
N4-Cr1-N5	86.46	87.30	86.46	86.06	85.07
N4-Cr1-N6	172.92	173.78	172.95	173.13	170.20
N5-Cr1-N6	86.46	86.49	86.49	87.58	85.13
Central pyridine, interligand trans, intraligand trans					



**Figure S23.** a) Normalized excitation spectra and superposition of absorption and excitation spectra of complexes b)  $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ , c)  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ , d)  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  and e)  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  in acetonitrile at 293 K ( $\lambda_{\text{em}} = 780 \text{ nm}$ ).

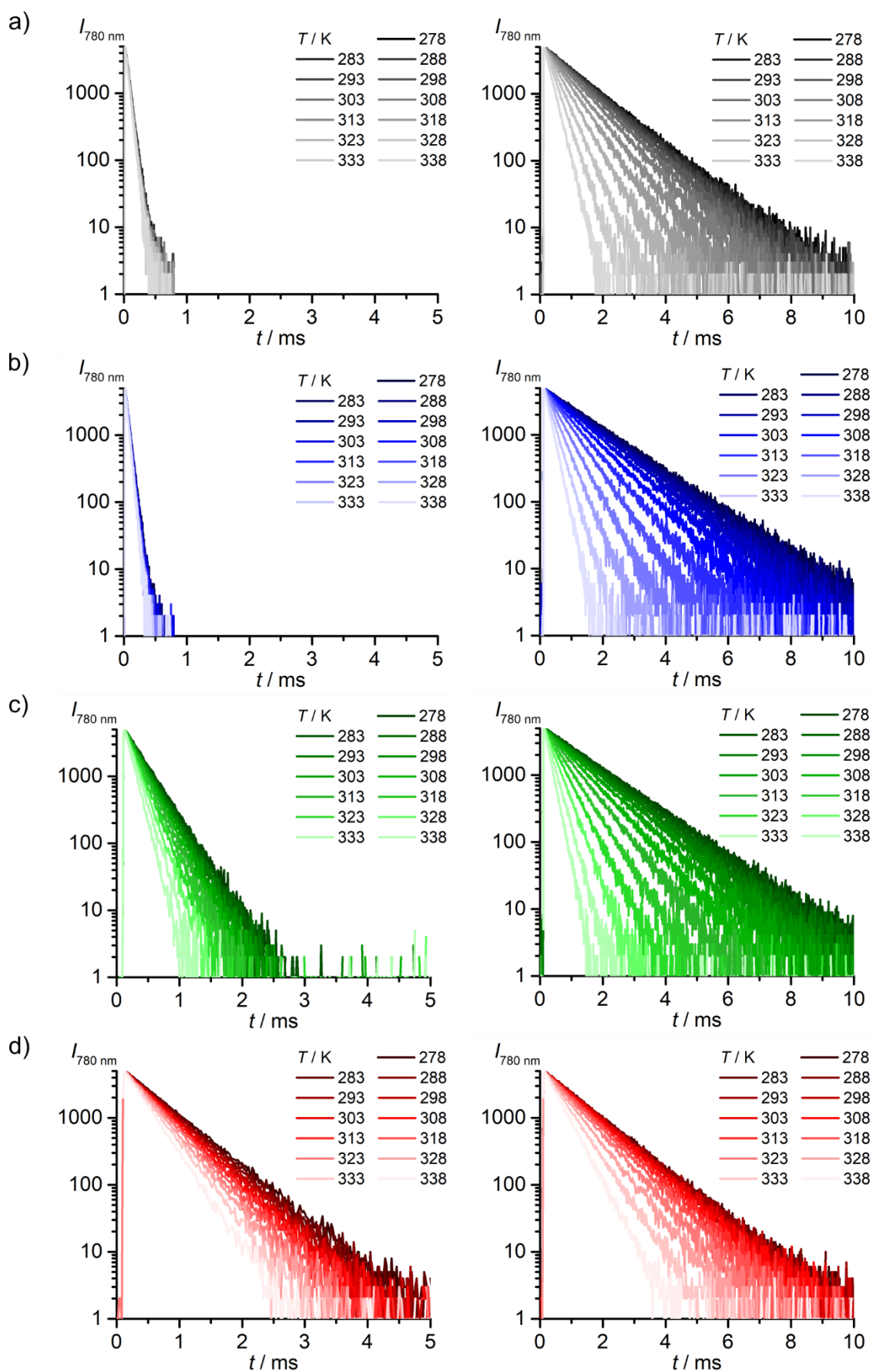


**Figure S24.** UV/Vis absorption spectra of a)  $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$  b)  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ , c)  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  and d)  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  in acetonitrile at 293 K including the 50 lowest-energy spin-allowed TD-DFT calculated transitions (oscillator strengths). The color code indicates the character of the transition according to charge transfer number analysis (green: MC, yellow: MLCT, orange: LMCT, blue: LLCT, red: ILCT).<sup>9,10</sup>



**Figure S25.** Oxygen quenching of luminescence intensity (left) and lifetime decay (right) of a) [Cr<sup>5Me</sup>][BF<sub>4</sub>]<sub>3</sub>, b) [Cr<sup>5Mes</sup>][BF<sub>4</sub>]<sub>3</sub> and c) [Cr<sup>5Tripp</sup>][BF<sub>4</sub>]<sub>3</sub> in acetonitrile at 293 K.

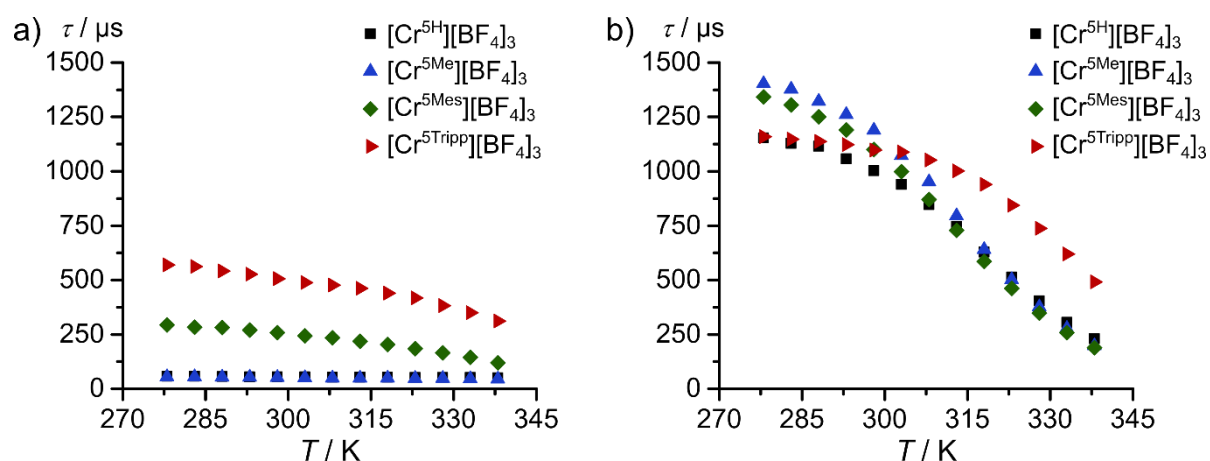




**Figure S26.** Temperature dependent luminescence decay of a) [Cr<sup>5H</sup>][BF<sub>4</sub>]<sub>3</sub>, b) [Cr<sup>5Me</sup>][BF<sub>4</sub>]<sub>3</sub>, c) [Cr<sup>5Mes</sup>][BF<sub>4</sub>]<sub>3</sub> and d) [Cr<sup>5Tripp</sup>][BF<sub>4</sub>]<sub>3</sub> in atmospheric (left) and under deoxygenated conditions (right) in acetonitrile.

**Table S4.** Emission lifetimes of  $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ ,  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ ,  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  and  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  at variable temperatures in atmospheric and under deoxygenated conditions in acetonitrile.

$T / \text{K}$	$\tau_{\text{O}_2}(T) / \mu\text{s}$				$\tau_{\text{Ar}}(T) / \mu\text{s}$			
	$\text{Cr}^{5\text{H}}[\text{BF}_4]_3$		$\text{Cr}^{5\text{Me}}[\text{BF}_4]_3$		$\text{Cr}^{5\text{Mes}}[\text{BF}_4]_3$		$\text{Cr}^{5\text{Tripp}}[\text{BF}_4]_3$	
278	57	1153	55	1402	294	1342	569	1160
283	57	1128	54	1377	283	1305	562	1148
288	56	1115	53	1322	282	1250	541	1137
293	55	1058	53	1261	270	1190	527	1122
298	54	1003	51	1189	258	1101	506	1098
303	54	939	50	1072	244	999	488	1089
308	53	846	49	951	234	870	476	1051
313	53	747	48	795	219	729	461	1001
318	53	628	48	640	204	585	439	940
323	52	513	47	502	184	462	418	843
328	51	404	47	376	165	348	382	738
333	51	306	46	278	144	258	349	620
338	50	230	44	197	119	189	311	491



**Figure S27.** Plot of temperature dependent excited state lifetimes of  $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ ,  $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ ,  $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$  and  $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$  in a) atmospheric and under b) deoxygenated conditions in acetonitrile.

**Table S5.** Cartesian coordinates of the calculated ground state geometry of  $[\text{Cr}^{5\text{H}}]^{3+}$  (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
24	0.000000	0.000000	0.000000
6	1.154209	2.726726	0.197888
6	1.180554	4.115108	0.198557
6	0.000108	4.806440	-0.000905
6	-1.180375	4.115091	-0.200089
6	-1.154102	2.726710	-0.198863
7	0.000035	2.045813	-0.000350
1	2.102258	4.641462	0.384612
1	-2.102053	4.641418	-0.386354
6	1.489211	-0.811393	2.438575
6	2.580962	-0.974575	3.252884
6	3.673329	-0.128995	3.064896
6	3.612947	0.863598	2.110309
6	2.457354	0.995242	1.330395
7	1.437725	0.127401	1.467847
1	4.559106	-0.229380	3.677786
1	0.626658	-1.453276	2.526980
1	2.581985	-1.749890	4.004488
1	4.432797	1.552395	1.990896
6	-2.457341	0.994868	-1.330706
6	-3.612958	0.862969	-2.110544
6	-3.673396	-0.129974	-3.064762
6	-2.581062	-0.975660	-3.252463
6	-1.489287	-0.812215	-2.438241
7	-1.437746	0.126938	-1.467861
1	-4.559192	-0.230557	-3.677590
1	-4.432787	1.551831	-1.991361
1	-2.582132	-1.751252	-4.003783
1	-0.626764	-1.454168	-2.526419
6	1.154173	-2.726739	-0.197967
6	1.180497	-4.115121	-0.198662
6	0.000050	-4.806440	0.000835
6	-1.180417	-4.115077	0.200071
6	-1.154123	-2.726696	0.198867
7	0.000018	-2.045812	0.000334
1	2.102186	-4.641485	-0.384765
1	-2.102097	-4.641393	0.386355
6	1.489148	0.811431	-2.438597
6	2.580878	0.974621	-3.252930
6	3.673234	0.129010	-3.065010
6	3.612862	-0.863614	-2.110456
6	2.457294	-0.995257	-1.330503
7	1.437674	-0.127396	-1.467898
1	4.558991	0.229402	-3.677926
1	0.626605	1.453335	-2.526950
1	2.581899	1.749960	-4.004509
1	4.432701	-1.552433	-1.991090
6	-2.457311	-0.994853	1.330767
6	-3.612902	-0.862951	2.110643
6	-3.673289	0.129967	3.064889
6	-2.580932	0.975628	3.252578
6	-1.489186	0.812183	2.438317
7	-1.437698	-0.126944	1.467908
1	-4.559061	0.230554	3.677752
1	-4.432745	-1.551800	1.991475
1	-2.581966	1.751195	4.003922
1	-0.626644	1.454113	2.526486
7	2.344554	-2.014881	-0.392565
6	3.585016	-2.662198	0.058369
1	3.984715	-3.362996	-0.676550
1	4.320278	-1.887509	0.259410
1	3.377073	-3.188034	0.985234
7	-2.344524	-2.014790	0.393176
6	-3.584959	-2.662275	-0.057586
1	-3.984679	-3.362824	0.677559
1	-4.320220	-1.887660	-0.258916
1	-3.376978	-3.188429	-0.984262
7	2.344587	2.014851	0.392442
7	-2.344517	2.014819	-0.393136
6	3.585039	2.662135	-0.058568
1	3.984793	3.362935	0.676319
1	4.320275	1.887427	-0.259637

1	3.377058	3.187961	-0.985430
6	-3.584934	2.662338	0.057629
1	-3.984647	3.362882	-0.677524
1	-4.320209	1.887742	0.258980
1	-3.376931	3.188504	0.984294
1	0.000138	5.888131	-0.001124
1	0.000064	-5.888131	0.001035

**Table S6.** Cartesian coordinates of the calculated ground state geometry of  $[\text{Cr}^{\text{6Me}}]^{3+}$  (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
6	1.227555	2.647677	0.174218
6	1.266675	4.034804	0.199839
6	0.096838	4.742037	-0.006219
6	-1.086929	4.061481	-0.219113
6	-1.076782	2.672940	-0.205725
7	0.068166	1.978374	-0.017520
1	2.195181	4.546349	0.394017
1	-2.004010	4.594735	-0.408580
6	1.690870	-0.801265	2.580027
6	2.884848	-0.904818	3.269363
6	3.961627	-0.104395	2.925012
6	3.806565	0.829430	1.927858
6	2.581245	0.918993	1.263153
7	1.559827	0.063824	1.525006
1	4.901899	-0.183693	3.453921
1	4.606524	1.509893	1.693523
6	-2.455147	0.973934	-1.312999
6	-3.646972	0.967108	-2.036230
6	-3.822370	0.038427	-3.037537
6	-2.797871	-0.847879	-3.311682
6	-1.639022	-0.834356	-2.553985
7	-1.481413	0.048770	-1.521958
1	-4.734897	0.029918	-3.618359
1	-4.402233	1.710390	-1.848132
6	1.207007	-2.789118	-0.099133
6	1.232886	-4.177624	-0.069321
6	0.043532	-4.868285	0.063432
6	-1.146846	-4.172922	0.164859
6	-1.118547	-2.785970	0.129857
7	0.044136	-2.105022	-0.000095
1	2.165794	-4.705666	-0.176929
1	-2.081292	-4.692921	0.297759
6	1.845121	0.684250	-2.487551
6	3.028748	0.679439	-3.206774
6	4.037154	-0.210052	-2.888150
6	3.824094	-1.119021	-1.876332
6	2.611741	-1.103935	-1.188583
7	1.647508	-0.181462	-1.447414
1	4.966726	-0.218212	-3.441248
1	4.567424	-1.863609	-1.650074
6	-2.522344	-1.078294	1.179244
6	-3.743170	-1.070720	1.851938
6	-3.961847	-0.139828	2.842444
6	-2.950466	0.748102	3.155296
6	-1.757680	0.728101	2.451470
7	-1.553077	-0.160382	1.433200
1	-4.898614	-0.129043	3.383259
1	-4.489977	-1.813124	1.629821
7	2.401094	-2.076215	-0.206434
6	3.590719	-2.726178	0.366266
1	4.025845	-3.474070	-0.298501
1	4.330522	-1.960756	0.580198
1	3.300185	-3.198132	1.299742
7	-2.310680	-2.065626	0.212872
6	-3.497779	-2.716868	-0.362684
1	-3.952994	-3.442803	0.312820
1	-4.224579	-1.948089	-0.608978
1	-3.198454	-3.218332	-1.277892
7	2.414003	1.923591	0.313717
7	-2.273586	1.970870	-0.351705
6	3.624167	2.560517	-0.229985
1	4.081576	3.260756	0.470521
1	4.338919	1.782706	-0.483032

1	3.350964	3.088232	-1.138257
6	-3.478782	2.636386	0.167851
1	-3.898487	3.359623	-0.533020
1	-4.221244	1.875293	0.390050
1	-3.215377	3.143956	1.090631
1	0.108163	5.823571	-0.001030
1	0.044434	-5.949634	0.088987
24	0.043376	-0.060445	-0.002839
1	-2.884107	-1.566726	-4.113430
1	3.146002	1.385973	-4.015445
1	-3.071684	1.472267	3.947651
1	2.960276	-1.614430	4.079465
6	0.827197	1.701135	-2.909075
1	0.870440	1.801886	-3.992206
1	-0.182998	1.451129	-2.631699
1	1.070872	2.679492	-2.491138
6	0.544276	-1.621184	3.085478
1	-0.016852	-2.125628	2.313230
1	0.924389	-2.372132	3.773023
1	-0.149150	-0.987018	3.639322
6	-0.599470	-1.849001	-2.924810
1	-0.853644	-2.825708	-2.509298
1	-0.597293	-1.958219	-4.008031
1	0.396786	-1.590812	-2.607214
6	-0.736332	1.743694	2.869389
1	-0.775745	1.843865	3.952909
1	0.272518	1.493639	2.586966
1	-0.980228	2.722612	2.453538

**Table S7.** Cartesian coordinates of the calculated ground state geometry of  $[\text{Cr}^{\text{5Me}}]^{3+}$  (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
6	1.22197	2.660232	0.200775
6	1.261177	4.048657	0.191003
6	0.090814	4.749211	-0.034648
6	-1.092028	4.067366	-0.251902
6	-1.077986	2.678412	-0.244814
7	0.065784	1.988576	-0.017678
1	2.183893	4.567687	0.392305
1	-2.005296	4.600463	-0.459366
6	1.468932	-0.874154	2.465253
6	2.535667	-1.070962	3.310864
6	3.636319	-0.22289	3.133406
6	3.610896	0.772575	2.182934
6	2.477709	0.920155	1.373461
7	1.449522	0.065835	1.493676
1	4.510309	-0.332895	3.763438
1	0.59394	-1.502618	2.532062
1	4.443835	1.449468	2.085458
6	-2.36377	0.946522	-1.39677
6	-3.496722	0.812383	-2.208845
6	-3.539865	-0.194747	-3.146287
6	-2.457038	-1.068556	-3.307837
6	-1.389334	-0.882982	-2.460914
7	-1.353428	0.069389	-1.501923
1	-4.413574	-0.294563	-3.778397
1	-4.315334	1.508104	-2.123379
1	-0.527605	-1.530559	-2.51597
6	1.180199	-2.799209	-0.148906
6	1.194031	-4.188083	-0.13336
6	0.001304	-4.866726	0.034387
6	-1.178735	-4.163362	0.190258
6	-1.139088	-2.775005	0.182317
7	0.026878	-2.106495	0.011269
1	2.116208	-4.724381	-0.285827
1	-2.110725	-4.67968	0.35186
6	1.600605	0.728236	-2.404107
6	2.708336	0.898195	-3.201703
6	3.779769	0.024647	-2.975558
6	3.689259	-0.967534	-2.025923
6	2.519452	-1.085168	-1.265513
7	1.516872	-0.208731	-1.432692
1	4.682342	0.112456	-3.567592
1	0.743134	1.374915	-2.511955

1	4.500088	-1.664485	-1.891407
6	-2.447293	-1.019842	1.270365
6	-3.616779	-0.865104	2.024708
6	-3.687485	0.141169	2.961116
6	-2.597159	0.992985	3.179753
6	-1.491669	0.788111	2.387312
7	-1.426122	-0.163269	1.428689
1	-4.58977	0.257049	3.548777
1	-4.443283	-1.544712	1.896621
1	-0.620952	1.418072	2.487914
7	2.378887	-2.098511	-0.321416
6	3.604652	-2.74789	0.16274
1	4.014897	-3.461707	-0.55395
1	4.341668	-1.975813	0.367339
1	3.375248	-3.259479	1.092749
7	-2.324852	-2.04944	0.341821
6	-3.56149	-2.68304	-0.135065
1	-3.987072	-3.376885	0.592191
1	-4.283266	-1.900616	-0.354322
1	-3.339694	-3.214498	-1.055728
7	2.39901	1.938569	0.428263
7	-2.267567	1.975342	-0.464287
6	3.656431	2.565605	-0.000879
1	4.050796	3.266413	0.737189
1	4.385556	1.780091	-0.181514
1	3.475405	3.08803	-0.935523
6	-3.51427	2.630626	-0.045982
1	-3.893466	3.330148	-0.793169
1	-4.258131	1.86065	0.141187
1	-3.326343	3.160203	0.883289
1	0.100615	5.830887	-0.041171
1	-0.008652	-5.948376	0.043711
24	0.046441	-0.058776	-0.002875
6	2.76668	1.97681	-4.240973
1	3.579374	2.673065	-4.023398
1	2.954264	1.551518	-5.228879
1	1.833888	2.538303	-4.277466
6	1.22197	2.660232	0.200775
6	1.261177	4.048657	0.191003
6	0.090814	4.749211	-0.034648
6	-1.092028	4.067366	-0.251902
6	-1.077986	2.678412	-0.244814
7	0.065784	1.988576	-0.017678
1	2.183893	4.567687	0.392305
1	-2.005296	4.600463	-0.459366
6	1.468932	-0.874154	2.465253
6	2.535667	-1.070962	3.310864
6	3.636319	-0.22289	3.133406
6	3.610896	0.772575	2.182934

**Table S8.** Cartesian coordinates of the calculated ground state geometry of  $[\text{Cr}^{5\text{Mes}}]^{3+}$  (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
24	8.926913	9.429243	8.465156
7	7.734977	10.739418	7.415496
7	8.106973	12.377064	9.079042
7	10.06575	11.038023	9.010373
7	11.98582	9.638553	8.913485
7	10.195834	8.308991	9.653338
7	10.018037	9.125668	6.741729
7	9.920281	6.809635	7.134349
7	7.88654	7.765601	7.914506
7	5.9059	8.78993	8.721076
7	7.670319	9.544198	10.08938
6	7.154787	10.347907	6.261301
1	7.434197	9.370372	5.902089
6	6.247021	11.116493	5.561355
6	5.671864	10.642064	4.278193
6	6.528875	10.328738	3.205172
6	8.023745	10.496235	3.293453
1	8.451835	10.571059	2.295385
1	8.49681	9.643651	3.785293
1	8.307058	11.38766	3.853285
6	5.978478	9.876258	2.009456

1	6.642376	9.651672	1.182072
6	4.605011	9.716544	1.843797
6	4.039661	9.184751	0.555499
1	4.612741	9.538722	-0.302822
1	2.998838	9.483186	0.426994
1	4.074102	8.09141	0.541067
6	3.775503	10.050077	2.90915
1	2.70201	9.945264	2.798119
6	4.27969	10.520651	4.120579
6	3.302191	10.894733	5.205198
1	3.036103	11.953482	5.14223
1	3.700487	10.723179	6.202436
1	2.381659	10.321138	5.099018
6	5.922738	12.357716	6.121387
1	5.227341	13.014042	5.616454
6	6.51351	12.773833	7.293198
1	6.287188	13.748287	7.693304
6	7.452975	11.951349	7.922377
6	7.440454	13.428588	9.859899
1	7.536884	14.416683	9.406206
1	7.87637	13.445716	10.851605
1	6.388394	13.170411	9.948126
6	9.488006	12.239677	9.249692
6	10.244249	13.328925	9.668361
1	9.777736	14.285719	9.833457
6	11.608094	13.175289	9.825612
1	12.212295	14.013147	10.146329
6	12.20252	11.952569	9.570661
1	13.26174	11.814838	9.713022
6	11.405005	10.892501	9.165732
6	13.387797	9.624143	8.477929
1	13.573375	8.684772	7.963522
1	14.089541	9.729394	9.307438
1	13.540408	10.435572	7.77478
6	11.522266	8.504038	9.578082
6	12.401865	7.596876	10.175817
1	13.467926	7.716311	10.07414
6	11.891851	6.592843	10.97008
1	12.570025	5.919083	11.476765
6	10.511894	6.476596	11.174234
6	9.928151	5.561489	12.189915
6	9.105211	4.485736	11.823395
6	8.818082	4.170295	10.379772
1	8.230861	4.955101	9.899553
1	8.258738	3.239577	10.294777
1	9.742532	4.065547	9.809561
6	8.558142	3.683882	12.822857
1	7.928309	2.849237	12.536044
6	8.804099	3.92102	14.1728
6	8.168279	3.067983	15.236052
1	7.184087	3.461564	15.507285
1	8.774207	3.048496	16.142566
1	8.025534	2.043582	14.889499
6	9.62416	4.992846	14.512426
1	9.815773	5.20399	15.5583
6	10.185547	5.824172	13.547207
6	11.010667	7.008086	13.981549
1	12.065778	6.885064	13.72825
24	8.926913	9.429243	8.465156
7	7.734977	10.739418	7.415496
7	8.106973	12.377064	9.079042
7	10.06575	11.038023	9.010373
7	11.98582	9.638553	8.913485
7	10.195834	8.308991	9.653338
7	10.018037	9.125668	6.741729
7	9.920281	6.809635	7.134349
7	7.88654	7.765601	7.914506
7	5.9059	8.78993	8.721076
7	7.670319	9.544198	10.08938
6	7.154787	10.347907	6.261301
1	7.434197	9.370372	5.902089
6	6.247021	11.116493	5.561355
6	5.671864	10.642064	4.278193
6	6.528875	10.328738	3.205172
6	8.023745	10.496235	3.293453
1	8.451835	10.571059	2.295385
1	8.49681	9.643651	3.785293

1	8.307058	11.38766	3.853285
6	5.978478	9.876258	2.009456
1	6.642376	9.651672	1.182072
6	4.605011	9.716544	1.843797
6	4.039661	9.184751	0.555499
1	4.612741	9.538722	-0.302822
1	2.998838	9.483186	0.426994
1	4.074102	8.09141	0.541067
6	3.775503	10.050077	2.90915
1	2.70201	9.945264	2.798119
6	4.27969	10.520651	4.120579
6	3.302191	10.894733	5.205198
1	3.036103	11.953482	5.14223
1	3.700487	10.723179	6.202436
1	2.381659	10.321138	5.099018
6	5.922738	12.357716	6.121387
1	5.227341	13.014042	5.616454
6	6.51351	12.773833	7.293198
1	6.287188	13.748287	7.693304
6	7.452975	11.951349	7.922377
6	7.440454	13.428588	9.859899
1	7.536884	14.416683	9.406206
1	7.87637	13.445716	10.851605
1	6.388394	13.170411	9.948126
6	9.488006	12.239677	9.249692
6	10.244249	13.328925	9.668361
1	9.777736	14.285719	9.833457
6	11.608094	13.175289	9.825612
1	12.212295	14.013147	10.146329
6	12.20252	11.952569	9.570661
1	13.26174	11.814838	9.713022
6	11.405005	10.892501	9.165732
6	13.387797	9.624143	8.477929
1	13.573375	8.684772	7.963522
1	14.089541	9.729394	9.307438
1	13.540408	10.435572	7.77478
6	11.522266	8.504038	9.578082
6	12.401865	7.596876	10.175817
1	13.467926	7.716311	10.07414
6	11.891851	6.592843	10.97008
1	12.570025	5.919083	11.476765
6	10.511894	6.476596	11.174234
6	9.928151	5.561489	12.189915
6	9.105211	4.485736	11.823395
6	8.818082	4.170295	10.379772
1	8.230861	4.955101	9.899553
1	8.258738	3.239577	10.294777
1	9.742532	4.065547	9.809561
6	8.558142	3.683882	12.822857
1	7.928309	2.849237	12.536044
6	8.804099	3.92102	14.1728
6	8.168279	3.067983	15.236052
1	7.184087	3.461564	15.507285
1	8.774207	3.048496	16.142566
1	8.025534	2.043582	14.889499
6	9.62416	4.992846	14.512426
1	9.815773	5.20399	15.5583

**Table S9.** Cartesian coordinates of the calculated ground state geometry of  $[\text{Cr}^{\text{Tripp}}]^{3+}$  (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
24	0.158588	-0.02335	0.02619
7	1.483885	-1.599333	-0.040323
7	2.370841	-0.881765	2.020611
7	0.041139	-0.433338	2.024911
7	-2.284598	0.024106	1.929483
7	-1.190457	1.481051	0.436786
7	-1.342024	-1.331068	-0.518483
7	-2.082216	0.253566	-2.094728
7	0.283226	0.381912	-1.970504
7	2.642298	0.498898	-1.74864
7	1.676591	1.355073	0.221214
6	1.435299	-2.506704	-1.039067
1	0.584421	-2.43753	-1.697047



6	2.386903	-3.487593	-1.218947
6	2.206202	-4.610821	-2.175825
6	2.066944	-4.398059	-3.558455
6	2.002175	-3.013987	-4.1775
1	2.173898	-2.282056	-3.391405
6	3.090546	-2.791691	-5.232766
1	4.082497	-2.968782	-4.812765
1	3.051154	-1.763068	-5.597707
1	2.959742	-3.456829	-6.088087
6	0.604695	-2.750968	-4.754305
1	-0.159588	-2.801141	-3.975764
1	0.355586	-3.489226	-5.518617
1	0.560589	-1.762885	-5.21127
6	1.961055	-5.503462	-4.401971
1	1.863251	-5.344611	-5.469083
6	1.974981	-6.805956	-3.922781
6	1.876941	-7.983181	-4.870289
1	1.832868	-7.575079	-5.884067
6	0.595778	-8.793151	-4.636706
1	0.580597	-9.219353	-3.631113
1	0.529841	-9.61579	-5.352191
1	-0.290275	-8.167181	-4.749918
6	3.11736	-8.880455	-4.779507
1	3.200892	-9.331465	-3.788176
1	4.028873	-8.310494	-4.969682
1	3.057719	-9.687744	-5.512629
6	2.065569	-6.99281	-2.546976
1	2.036229	-7.999023	-2.148824
6	2.171141	-5.927111	-1.66062
6	0.871872	-6.924228	0.253798
1	0.871173	-7.096473	1.331855
1	0.74987	-7.88964	-0.239611
1	0.003967	-6.312073	0.010319
6	2.175014	-6.235951	-0.169457
1	2.217506	-5.299548	0.382674
6	3.397856	-7.065342	0.239698
1	3.398816	-7.229595	1.319397
1	4.327207	-6.560705	-0.031257
1	3.391391	-8.04182	-0.24869
6	3.506717	-3.418167	-0.37806
1	4.321455	-4.116774	-0.512447
6	3.555253	-2.51952	0.664314
1	4.388149	-2.530289	1.347671
6	2.470174	-1.663648	0.871621
6	3.60169	-0.667274	2.792813
1	3.908557	-1.555407	3.348296
1	3.438219	0.151079	3.485576
1	4.390038	-0.380243	2.102061
6	1.155236	-0.780123	2.712133
6	1.10466	-1.041154	4.074599
1	1.995239	-1.326783	4.609208
6	-0.118445	-0.986207	4.716784
1	-0.181147	-1.20408	5.774308
6	-1.262199	-0.655906	4.013405
1	-2.214273	-0.586808	4.51305
6	-1.151836	-0.360762	2.661621
6	-3.587323	-0.459099	2.405736
1	-3.984418	0.144082	3.224397
1	-3.475078	-1.485602	2.737569
1	-4.283105	-0.443052	1.571004
6	-2.27809	1.19452	1.174123
6	-3.363323	2.074917	1.185777
1	-4.268861	1.827055	1.714092
6	-3.23077	3.306274	0.584287
1	-4.051998	4.008881	0.629959
6	-2.024209	3.687315	-0.020208
6	-1.060189	2.706523	-0.114991
1	-0.133675	2.893838	-0.632869
6	-1.783727	5.09009	-0.449522
6	-1.877845	6.11324	0.521804
6	-2.076592	5.834047	2.005531
1	-2.180882	4.761233	2.151013
6	-3.349801	6.49167	2.549644
1	-3.490157	6.228595	3.600252
1	-4.230885	6.164819	1.993785
1	-3.292849	7.579793	2.480873
6	-0.843438	6.256572	2.813298

1	-0.980179	6.00593	3.866901
1	-0.667913	7.331743	2.743955
1	0.053366	5.748467	2.45993
6	-1.712126	7.434981	0.124074
1	-1.777414	8.214164	0.872721
6	-1.442443	7.783762	-1.195619
6	-1.275165	9.231554	-1.608284
1	-1.093285	9.237355	-2.686763
6	-0.062626	9.877028	-0.926538
1	-0.188079	9.893462	0.158511
1	0.061916	10.907245	-1.267199
1	0.852109	9.326935	-1.150788
6	-2.548869	10.043177	-1.342859
1	-2.767196	10.087426	-0.27358
1	-3.409898	9.598935	-1.846048
1	-2.430677	11.067065	-1.704181
6	-1.308882	6.759899	-2.123178
1	-1.07091	7.016478	-3.148391
6	-1.463859	5.417422	-1.779168
6	-1.247217	4.371201	-2.857504
1	-1.479729	3.3961	-2.436007
6	-2.176221	4.562785	-4.060588
1	-3.22262	4.56193	-3.749141
1	-2.03185	3.750932	-4.776725
1	-1.976692	5.503785	-4.576262
6	0.224987	4.346419	-3.289578
1	0.881594	4.122251	-2.446239
1	0.523589	5.312868	-3.699985
1	0.385204	3.589896	-4.057201
6	-1.443845	-2.556378	0.040154
1	-0.594707	-2.880471	0.618663
6	-2.541134	-3.374794	-0.120494
6	-2.560964	-4.794185	0.320929
6	-2.76321	-5.794262	-0.657625
6	-2.799541	-5.498296	-2.150876
1	-2.704632	-4.425101	-2.29916
6	-1.599512	-6.13796	-2.859905
1	-1.615608	-7.225015	-2.767901
1	-0.657696	-5.780939	-2.442857
1	-1.613757	-5.890774	-3.923387
6	-4.122208	-5.932201	-2.792883
1	-4.973	-5.449588	-2.307866
1	-4.261505	-7.01258	-2.71948
1	-4.13381	-5.663864	-3.851427
6	-2.856982	-7.121109	-0.254173
1	-3.006614	-7.884413	-1.006988
6	-2.740616	-7.49937	1.079485
6	-2.85171	-8.951152	1.495587
1	-2.757275	-8.980513	2.584856
6	-1.71354	-9.792892	0.904684
1	-1.789372	-10.828114	1.244523
1	-0.740509	-9.402358	1.205533
1	-1.754267	-9.792058	-0.186857
6	-4.21884	-9.540633	1.127942
1	-5.029454	-8.95672	1.568249
1	-4.300453	-10.568044	1.489378
1	-4.360728	-9.553479	0.044983
6	-2.48924	-6.506785	2.016635
1	-2.361732	-6.793494	3.053457
6	-2.385261	-5.161096	1.667382
6	-2.028914	-4.161632	2.752391
1	-2.115665	-3.161078	2.334263
6	-2.973963	-4.22166	3.956398
1	-2.71608	-3.437345	4.670881
1	-2.903561	-5.180113	4.473128
1	-4.010835	-4.076463	3.647389
6	-0.568476	-4.358524	3.183721
1	-0.422515	-5.358991	3.595382
1	-0.292844	-3.63226	3.94768
1	0.113689	-4.244076	2.338566
6	-3.62941	-2.813425	-0.804788
1	-4.547696	-3.376799	-0.901821
6	-3.524038	-1.585646	-1.418185
1	-4.341801	-1.20502	-2.007306
6	-2.31516	-0.888473	-1.334859
6	-3.251799	0.916802	-2.685334
1	-4.006756	1.030049	-1.911703

1	-3.668798	0.359381	-3.526004
1	-2.957315	1.90507	-3.021293
6	-0.843114	0.462798	-2.717481
6	-0.784805	0.742346	-4.075713
1	-1.686876	0.786893	-4.663353
6	0.453704	0.909932	-4.667339
1	0.520663	1.116962	-5.726748
6	1.606701	0.81444	-3.910414
1	2.573882	0.973645	-4.357714
6	1.493335	0.562969	-2.549684
6	3.89361	0.093501	-2.402335
1	4.55988	-0.308195	-1.643404
1	4.382892	0.921268	-2.919006
1	3.670796	-0.694684	-3.11356
6	2.747249	1.258799	-0.586988
6	3.928764	1.930123	-0.260009
1	4.816967	1.80598	-0.856927
6	3.920386	2.823808	0.787186
1	4.819261	3.380798	1.014813
6	2.745959	3.076247	1.510964
6	1.671247	2.26464	1.21901
1	0.755387	2.339896	1.781693
6	2.655756	4.213623	2.463313
6	2.899945	5.513994	1.972456
6	3.099882	5.819497	0.494392
1	3.063561	4.886755	-0.063711
6	1.955734	6.687042	-0.04396
1	1.933304	7.663484	0.442463
1	0.988257	6.211894	0.115879
1	2.080155	6.849524	-1.116397
6	4.462354	6.464734	0.217708
1	5.278482	5.831473	0.571135
1	4.547268	7.432832	0.715239
1	4.593114	6.625509	-0.854556
6	2.884663	6.582406	2.866298
1	3.067285	7.583177	2.4936
6	2.618402	6.414069	4.218542
6	2.623485	7.596401	5.164788
1	2.865984	8.481338	4.569657
6	3.70396	7.44399	6.243039
1	3.500969	6.576587	6.875136
1	3.732368	8.328353	6.883313
1	4.69058	7.312914	5.794408
6	1.245564	7.82158	5.798853
1	1.264085	8.702126	6.444745
1	0.951221	6.964181	6.408184
1	0.481194	7.971065	5.035024
6	2.328979	5.130832	4.670097
1	2.085741	4.98305	5.714413
6	2.332327	4.028037	3.822038
6	1.93964	2.68025	4.399343
1	2.088864	1.923518	3.632679
6	0.448755	2.677563	4.764218
1	0.233745	3.440076	5.51525
1	0.156227	1.709958	5.171214
1	-0.173329	2.884651	3.890879
6	2.804439	2.272773	5.5964
1	2.521031	1.275341	5.938967
1	2.680336	2.961643	6.433649
1	3.861843	2.25427	5.325623

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