**Goal:**



*Target compound*

**Synthetic schema:**



**Synthesis of complexes.**

N,N′-dimethyl-N,N″-dipyridin-2-ylpyridine-2,6-diamine (ddpd), EtCOO-tpy, [Cr(ddpd)2](BF4)3 and [Cr(tpy)2](PF6)3 have been synthesized according to the published procedures. Reagent grade acetonitrile (ACN) was distilled from CaH2. All other chemicals were purchased from commercial suppliers and used without further purification. Microwave heating was performed in a Biotage initiator plus, producing continuous irradiation at 2.45 GHz. Reaction mixtures were stirred with a magnetic stir bar during irradiation.

**[Cr(ddpd)Br3]**. A solution of the ligand ddpd (370 mg, 1.26 mmol) in propan-2-ol (30 mL) was dropwise added into a solution of CrBr3.6H2O (520 mg, 1.3 mmol) in 15 mL of the same solvent. The resulting green solution was heated to reflux during 10 h. The resulting mixture was filtered and the obtained green solid was washed with warm ethanol (2 x 10 mL) and diethyl ether (2 x 20 mL). The product was dried under vaccum to obtain an olive drab powder [Cr(ddpd)Br3] (yield 90%). ESI-MS (CH3CN) *m/z*: [Cr(ddpd)Br2]+ calc: 502.92, found: 502.9. Slow diffusion of diethyl ether in a concentrated solution of the complex in dimethylformamide led to the formation of green crystals suitable for X-ray diffraction.

**[Cr(tpy)Br3]**. A solution of the ligand tpy (293 mg, 1.26 mmol) in propan-2-ol (30 mL) was dropwise added into a solution of CrBr3.6H2O (520 mg, 1.3 mmol) in 15 mL of the same solvent. The resulting green solution was heated to reflux during 10 h. The resulting mixture was filtered and the obtained green solid was washed with warm ethanol (2 x 10 mL) and diethyl ether (2 x 20 mL). The product was dried under vaccum to obtain a dark green powder [Cr(tpy)Br3] (yield 88%). ESI-MS (CH3CN) *m/z*: [Cr(tpy)Br2]+ calc: 444.87, found: 444.9.

**[Cr(ddpd)(SO3CF3)3].** A mixture of [Cr(ddpd)Br3] (100 mg, 0.17 mmol) and AgCF3SO3 (132 mg, 0.51 mmol) in distilled acetonitrile (4 mL), was heated under microwave irradiation at 150°C during 0.5 h. After cooling to room temperature, the resulting red solution was filtered to remove the AgBr generated during the reaction. ESI-MS of the previous solution in CH3CN; *m/z*: [Cr(ddpd)(SO3CF3)2]+ calc: 640.99, found: 641. This solution was used directly for the next step.

**[Cr(tpy)(SO3CF3)3].** A mixture of [Cr(tpy)Br3] (0.089 mg, 0.17 mmol) and AgCF3SO3 (132 mg, 0.51 mmol) in distilled acetonitrile (4 mL) was heated under microwave irradiation at 150°C for 0.5 h. After cooling to room temperature, the resulting red solution was filtered in order to remove the AgBr generated during the reaction. ESI-MS of the previous solution in CH3CN; *m/z*: [Cr(tpy)(SO3CF3)2]+ calc: 582.94, found: 582.8. This solution was used directly for the next step.

**[Cr(ddpd)(tpy)](PF6)3.**A red solution ofeither [Cr(ddpd)(SO3CF3)3] or [Cr(tpy)(SO3CF3)3] in distillated acetonitrile was loaded into a 5 ml MW vial containing the ligand tpy (42 mg, 0.18 mmol) or ddpd (51 mg, 0.18 mmol) respectively. The solution was heated under microwave irradiation during 2h at 75°C. After cooling to room temperature, the solvent was removed under reduced pressure yielding an orange residue. ESI-MS (CH3CN) *m/z*: [Cr(ddpd)(tpy)](SO3CF3)2]+ calc: 874.09, found: 874. The orange residue was dissolved in ethanol (2 mL) and few drops of a saturated methanol solution of (*n-*Bu4)NPF6 were added. The yellow precipitate obtained was filtered and washed with cold MeOH (1 x 5 mL) and diethyl ether (2 x 15 mL) and finally dried under vaccum to give [Cr(ddpd)(tpy)](PF6)3 (70 mg, yield 45%). Slow diffusion of diethyl ether in a concentrated solution of the complex in acetonitrile led to the formation of orange crystals suitable for XRD.

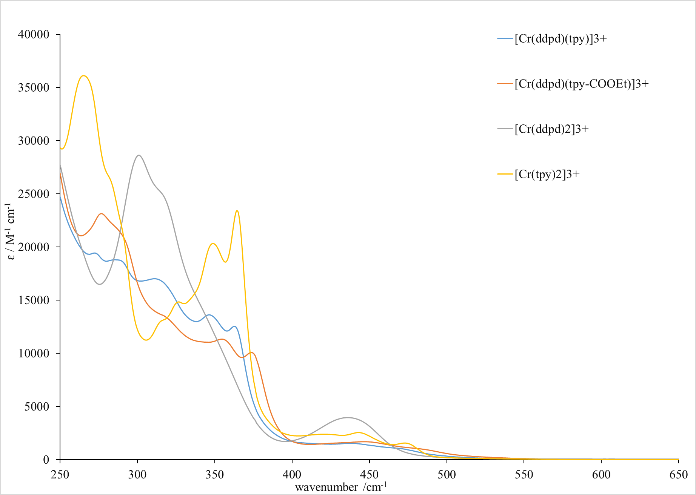
**[Cr(ddpd)(EtCOO-tpy)](PF6)3.** A red solution of[Cr(ddpd)(SO3CF3)3] in distillated acetonitrile was loaded into a 5 ml MW vial containing EtCOO-tpy (54 mg, 0.18 mmol). The solution was heated under microwave irradiation 2h at 75°C. After cooling to room temperature, the solvent was removed under reduced pressure yielding an orange residue. ESI-MS (CH3CN) *m/z*: [Cr(ddpd)(EtCOO-tpy)](SO3CF3)2]+ calc: 945.9, found: 946.0. The orange residue was dissolved in ethanol (2 mL) and few drops of a saturated methanol solution of (*n-*Bu4)NPF6 were added. The yellow precipitate obtained was filtered and washed with cold MeOH (1 x 5 mL) and diethyl ether (2 x 15 mL) and finally dried under vaccum to give [Cr(ddpd)(EtCOO-tpy)](PF6)3 (110 mg, yield 65%) as a fine yellow powder. Slow diffusion of diethyl ether in a concentrated solution of the complex in acetonitrile led to the formation of orange crystals suitables for XRD.

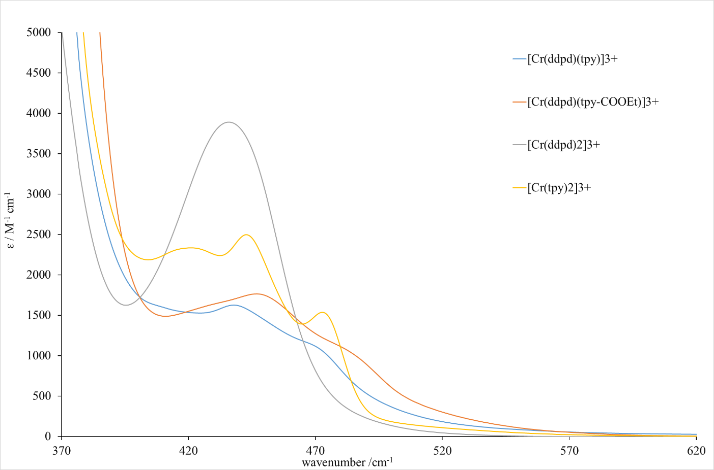
**Table of AE of compounds.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound** | **Found**  **C, H, N (%)** | **Calculated**  **C, H, N (%)** | **Molecular**  **Formula** | **Molecular weight (gmol-1)** |
| **[Cr(ddpd)Br3]** | 34.45, 3.14, 11.40 | 34.49, 3.06, 11.83 | C17H17N5Br3Cr 0.5H2O | 592.1 |
| **[Cr(tpy)Br3]** | 32.91, 2.61, 7.52 | 32.11, 2.69, 7.49 | C15H11N3Br3Cr 2H2O | 561 |
| **[Cr(ddpd)(tpy)](PF6)3** | 36.47, 3.18, 10.86 | 36.69, 3.08, 10.70 | C32H28CrF18N8P3 2H2O | 1047.5 |
| **[Cr(ddpd)(tpyCOOEt)](PF6)3** | 36.93, 3.23, 9.72 | 36.95, 3.37, 9.85 | C35H32CrF18N8O8P3 3H2O | 1137.6 |
| **[Cr(ddpd)2](BF4)3** | 43.86, 4.11, 15.10 | 43.77, 4, 15.01 | C34H34B4CrF12N10 1.5H2O | 932.9 |
| **[Cr(tpy)2](PF6)3** | 37.74, 2.31, 8.83 | 37.79, 2.33, 8.81 | C30H22CrF18N6P3F18 | 953.4 |

**UV-Vis spectroscopy**

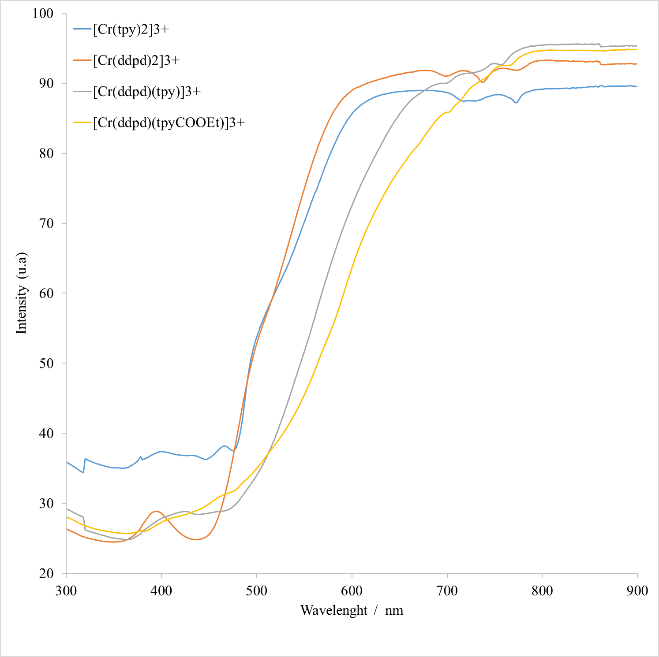
**Solution** Solvent CH3CN. Concentration 2.10-4 M

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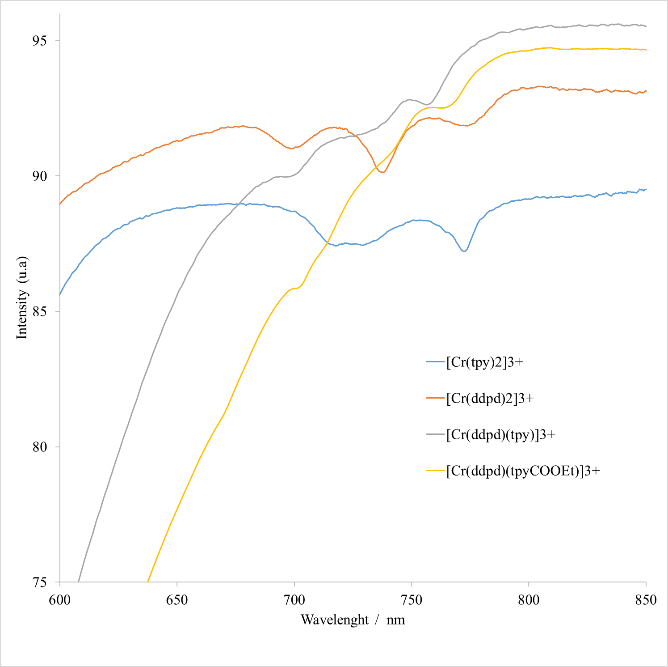


**Solid-State absorption**

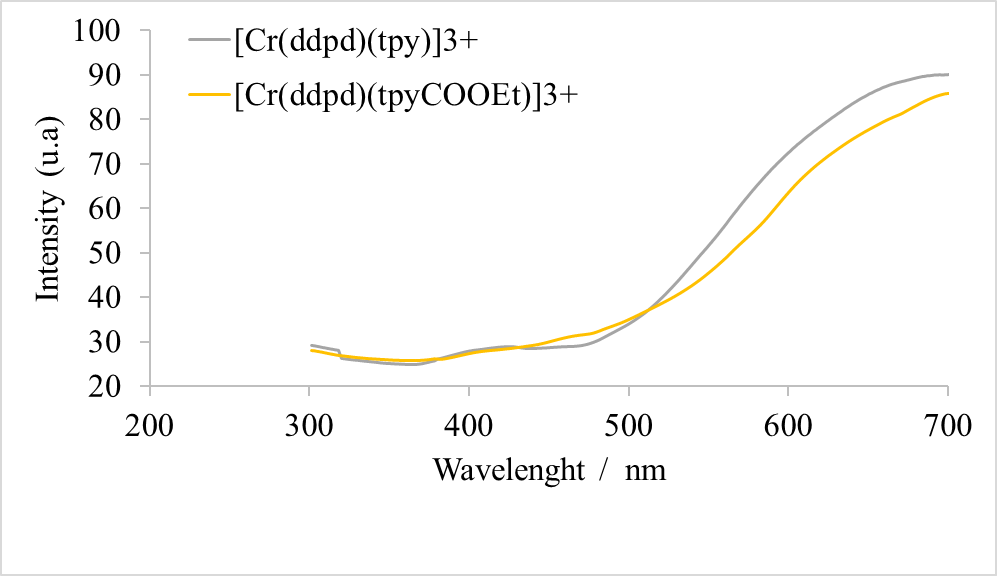
4Ag → 2T1 , 2Eg

****

π → π\* + LMCT

****

4Ag → 2T1 , 2Eg

****

Cr (4A2 → 4T2)

Table below summarizes all the electronic transitions observed in solution and the solid state for the four complexes. The values for the π → π\* and LMCT transitions were extracted from the solution spectra. The spin-flip transitions 4A2g → 2T1g and 4A2g → 2Eg were extracted from the solid-state spectra (first derivative has been done when needed).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | λ (nm) | ν (cm-1) | ε (L mol-1 cm-1) | assignments |
| **[Cr(ddpd)(tpy)]3+** | 273 | 36630 | 19417 | π → π\* |
| 289 | 34602 | 18734 |
| 314 | 31847 | 16922 |
| 344 | 29069 | 13525 |
| 363 | 27548 | 12539 |
| 410 | 24390 | 1600 | LMCT |
| 438 | 22831 | 1625 |
| 470 | 21276 | 1117 |
| **698** | **14327** |  | **4A2g → 2T1g** |
| **730** | **13699** |  |
| **758** | **13192** |  | **4A2g → 2Eg** |
| **[Cr(ddpd)(tpyCOOEt)]3+**   |  | | --- | |  | | 277 | 36101 | 23123 | π → π\* |
| 291 | 34364 | 20925 |
| 318 | 31446 | 13224 |
| 356 | 28090 | 11300 |
| 372 | 26882 | 11154 |
| 427 | 23419 | 1605 | LMCT |
| 449 | 22272 | 1758 |
| 486 | 20576 | 1020 |
| **700** | **14285** |  | **4A2g → 2T1g** |
| **712** | **14044** |  |
| **735** | **13605** |  |
| **760** | **13157** |  | **4A2g → 2Eg** |
| **[Cr(ddpd)2]3+**   |  | | --- | |  | | 301 | 33223 | 28608 | π → π\* |
| 316 (sh) | 31646 | 24960 |
| 341 | 29326 | 14421 |
| 437 | 22883 | 3936 | LMCT |
| **697** | **14347** |  | **4A2g → 2T1g** |
| **738** | **13550** |  |
| **775** | **12903** |  | **4A2g → 2Eg** |
| **[Cr(tpy)2]3+** | 265 | 37736 | 36102 | π → π\* |
| 282 (sh) | 35461 | 26458 |
| 290 | 34483 | 21698 |
| 315 | 31746 | 13020 |
| 325 | 30769 | 14735 |
| 350 | 28571 | 20253 |
| 365 | 27397 | 23288 |
| 421 | 23752 | 2335 | LMCT |
| 442 | 22624 | 2492 |
| 474 | 21097 | 1537 |
| 525 | 19047 | 100 |
| **715** | **13986** |  | **4A2g → 2T1g** |
| **730** | **13698** |  |
| **773** | **12936** |  | **4A2g → 2Eg** |

Table below summarizes the obtained values of Δ and Racah parameters as well as the energies of the CrIII-centred excited states. These values have been extracted from the combination of the absorption spectra recorded for the complexes in solution and in solid state and using the equations:

*E*(4T2) = *Δ*

*E*(4T1) = 9*B* + 3*C* – 24(*B2*/*Δ*)

*E*(2E) = 9*B* + 3C – 50(B2/*Δ*)

The values of 2E, 2T1 and 4T2 have been extracted experimentally from the absorption spectra in both solution and solid state. The 2T2 and 2T1 levels have been re-calculated by using the equations:

*E*(2T2) = 15*B* + 5*C* – 176(*B2*/Δ)

*E*(4T1) = 1.5Δ + 7.5*B* –

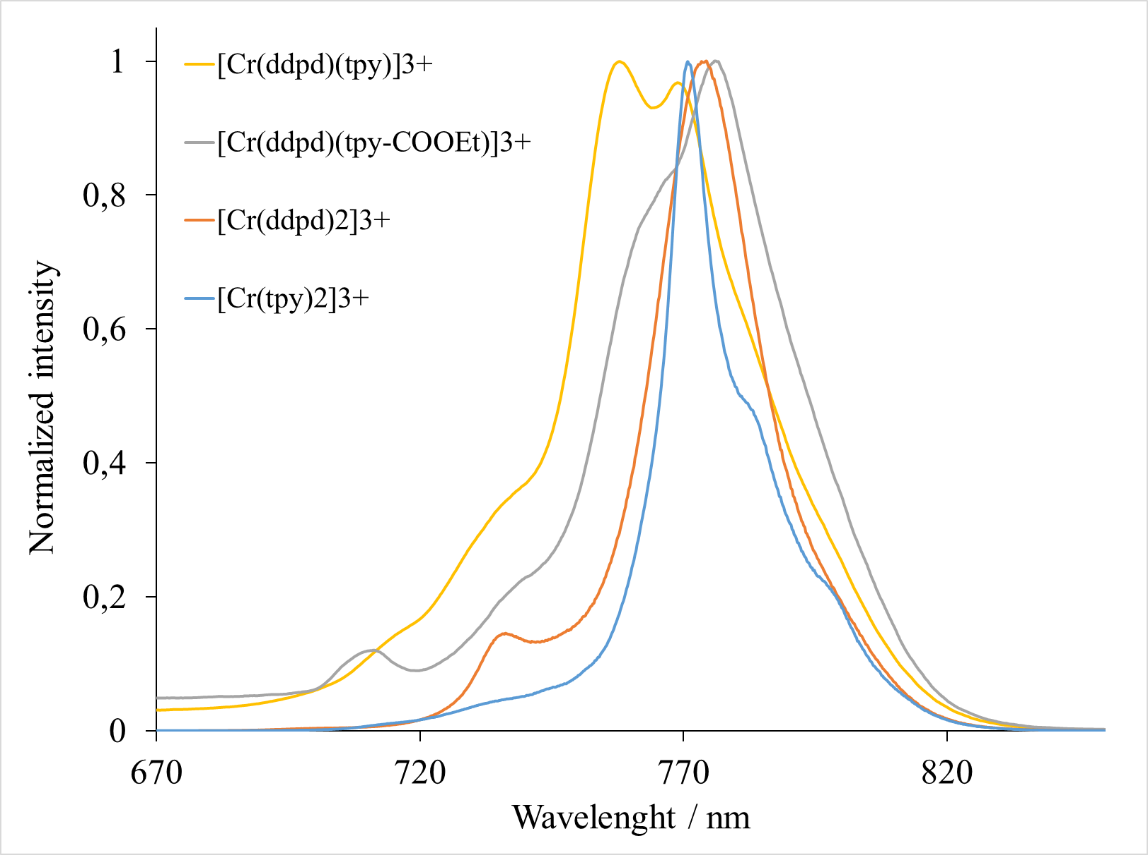
The Δ values for the [Cr(tpy)2] and [Cr(ddpd)2] are those reported in *Dalton* 2017, 46, 8992 and *Angew.* 2015, 54, 11572. However, B and C has been re-calculated for both complexes.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Compound | Δ/cm-1 | *B*/cm-1 | *C*/cm-1 | Δ/*B* | *C*/*B* | 2E  cm-1 | 2T1  cm-1 | 4T2  cm-1 | 2T2  cm-1 | 4T1  cm-1 |
| [Cr(tpy)2]3+ | 18750 | 790 | 2512 | 26 | 3.2 | 12936 | 13842 | 18750 | 18589 | 26640 |
| [Cr(ddpd)2]3+ | 22883 | 763 | 2442 | 30 | 3.2 | 12903 | 13949 | 22883 | 19176 | 30823 |
| [Cr(ddpd)(tpy)]3+ | 20121 | 791 | 2531 | 25 | 3.2 | 13192 | 14013 | 20121 | 19089 | 28083 |
| [Cr(ddpd)(tpyCOOEt)]3+ | 20408 | 798 | 2553 | 26 | 3.2 | 13157 | 13977 | 20408 | 19099 | 28368 |

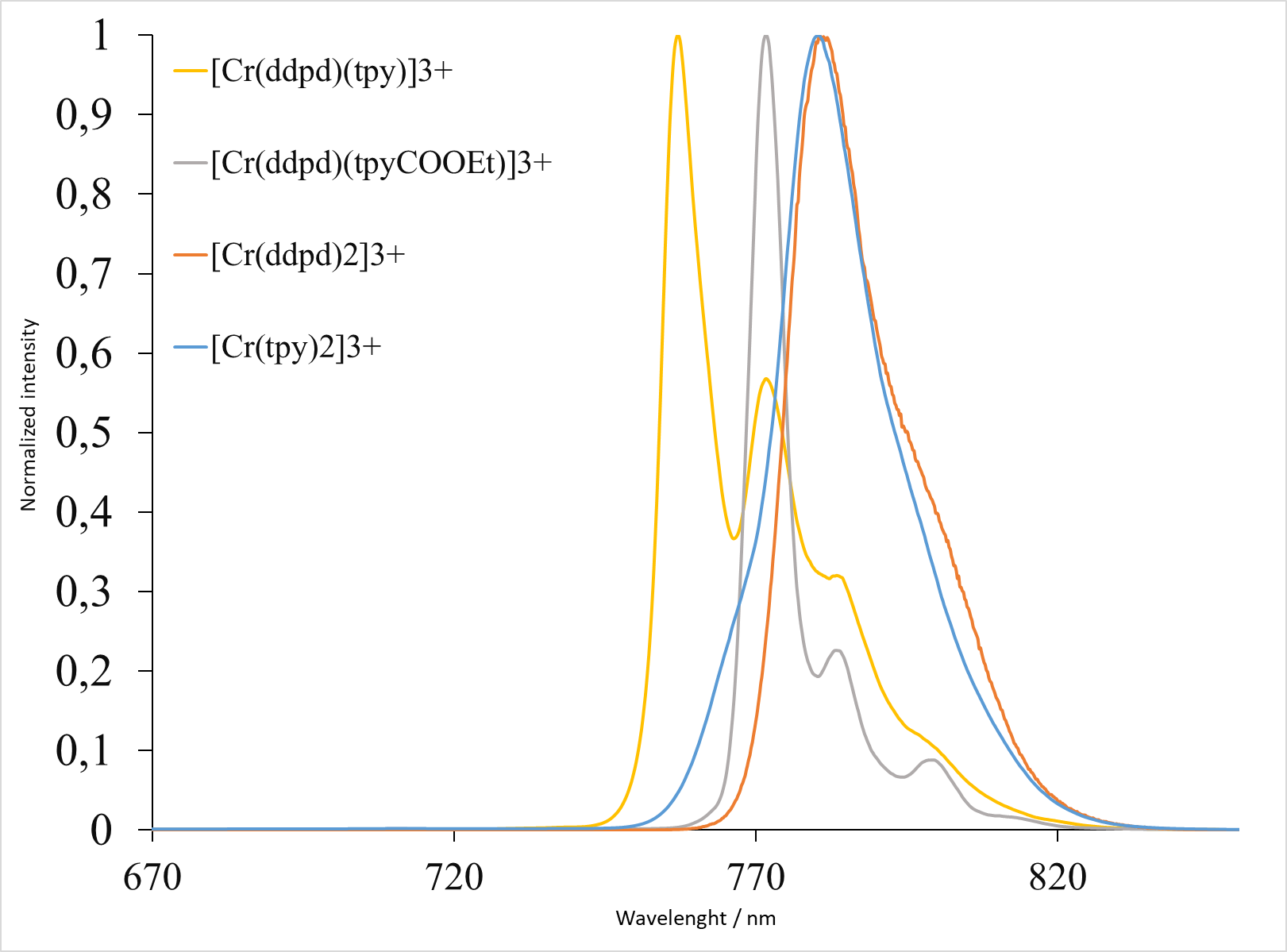
**Emission spectra of complexes in acetonitrile solution (10-5 M) 293 K. Exc. 355 nm.**

**Emission spectra of complexes in acetonitrile solution (10-5 M) 77 K**

**Emission in solution. Excitation at 355 nm.**



**Emission in solid state. Excitation at 355 nm.**

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**Table containing the maximum observed in the emission spectra.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Solid state | | Solution | |
| Compound | λmax (77 K) | λmax (293 K) | λmax (77 K) | λmax (293 K) |
| [Cr(tpy)2]3+ | 772  784  800 | 771  784  798 | 771  782  788  796 | 771  711 |
| [Cr(ddpd)2]3+ | 781  801 | 774  736 | 778  804 | 774  736 |
| [Cr(ddpd)(tpy)]3+ | 757  772  784  800 | 776  758  733  713 | 754  770  796 | **77**4  736 |
| [Cr(ddpd)(tpyCOOEt)]3+ | 765  781 | 776  762  733  713 | 761  796 | **77**4  736  711 |

**Lifetime of the 2E at 77 K and 293 K.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Solid state | | Solution | |
| Compound | τ77 K/μs | τ293 K/μs | τ77 K/μs | τ293 K/μs |
| [Cr(tpy)2]3+ | > 20 | > 20 | **670** | **> 20** |
| [Cr(ddpd)2]3+ | 492 | 211 | **1300** | **975** |
| [Cr(ddpd)(tpy)]3+ | 230 | > 20 | **1060** | **1002** |
| [Cr(ddpd)(tpyCOOEt)]3+ | 350 | > 20 | **1070** | **980** |

*Experimental lifetimes in solid state and in deaerated acetonitrile solution (10-5 M) at 77 K and 293 K. Excitation at 355 nm.*

**Excitation spectra vs absorption spectra at 293K in solution.**

434 nm

0 nm

470 nm

440 nm

435 nm

434 nm

438 nm

438 nm

Both homoleptic compounds fit quite well. However, for the heteroleptic compounds it does not. Actually, the excitation of the heteroleptique shows a maximum at 435 nm. This band can be found in the absorption spectrum. Interestingly this band is almost identical to that observed in the homoleptic [Cr(ddpd)2]3+. Is ddpd ligand the only responsible for ISC to the 2E?

**Excitation spectra in solution at 77 K**