Heteroleptic *mer*-[Cr(N∩N∩N)(CN)₃] complexes: synthetic challenge, structural characterization and photophysical properties.

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Supporting Information

(44 pages)

Table S1 Ligand field Δ and Racah B and C parameters reported for $[CrF_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Cr(CN)_6]^{3-}$, $[Cr(tpy)_2]^{3+}$, $[Cr(ddpd)_2]^{3+}$·and $[Cr(dqp)_2]^{3+}$ at 293 K.

Compound	Δ/cm^{-1}	B/cm^{-1}	C/cm^{-1}	Δ/B	C/B	Ref.
$[CrF_6]^{3-}$	15200	820	3280	18.5	4.0 [a]	S1
$[Cr(H_2O)_6]^{3+}$	17390	725	2900	24.0	4.0 [a]	S1
$[Cr(NH_3)_6]^{3+}$	21550	650	2600	33.2	4.0 [a]	S1
$[Cr(CN)_6]^{3-}$	26700	530	2120	50.4	4.0 [a]	S1
$[Cr(tpy)_2]^{3+}$	18750	790	2512	23.8	3.2	S2
$[Cr(ddpd)_2]^{3+}$	22883	763	2442	30.0	3.2	S3
$[Cr(dqp)_2]^{3+}$	24937	656	2791	38.0	4.3	S4

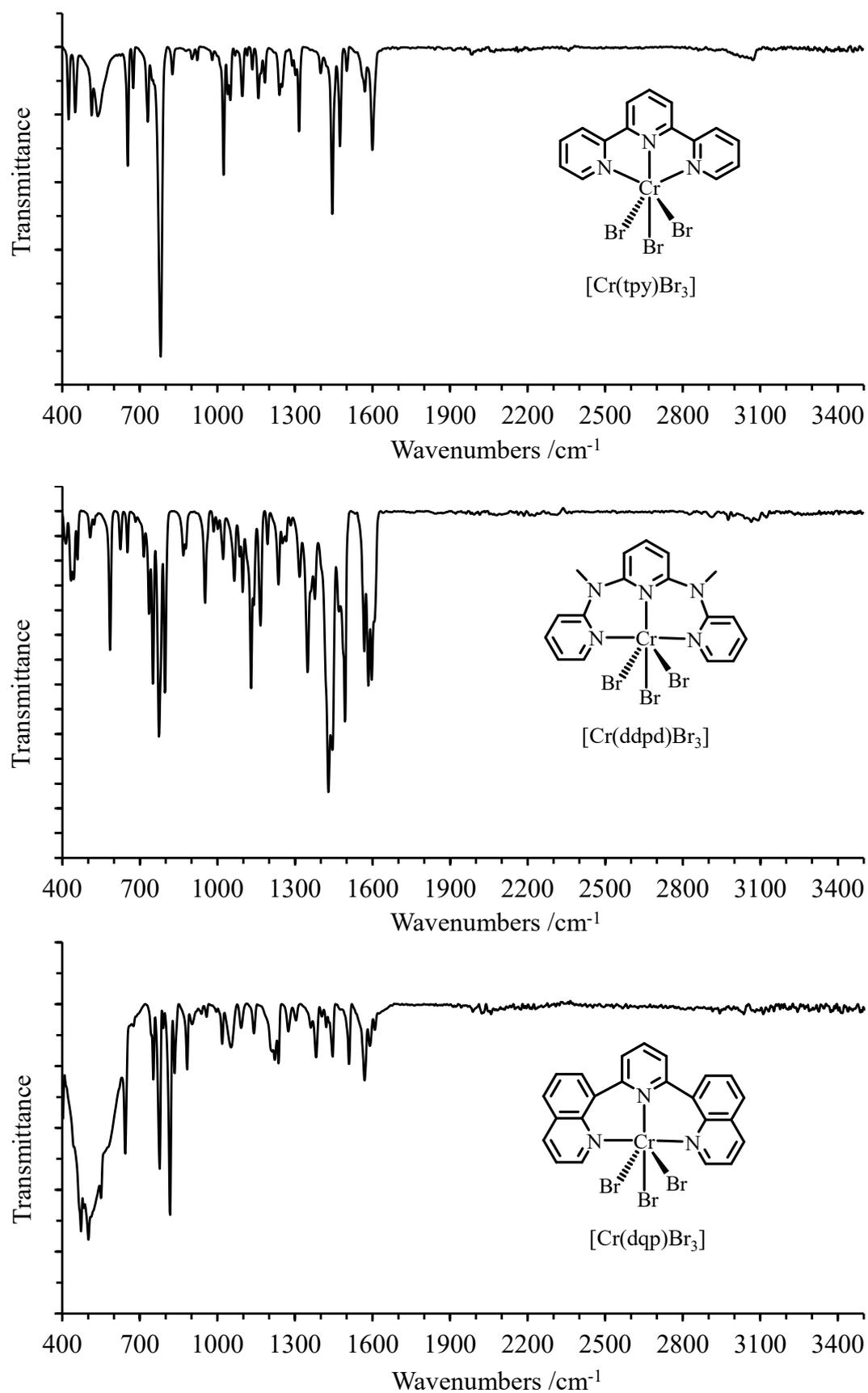[a] The Racah parameters were calculated assuming $C = 4.0B$.

Figure S1 IR spectra of [Cr(**L**)Br₃] (**L** = tpy, ddpd, dqp) recorded in the solid state at 293 K.

Table S2. Elemental analyses found for the heteroleptic Cr^{III} complexes measured as powders.[a]

Compound	Found C, H, N (%)	Calculated C, H, N (%)	Molecular Formula	MW /g.mol^{-1}
[Cr(tpy)Br$_3$]	34.47, 2.45, 7.84	34.32, 2.11, 7.84	C$_{15}$H$_{11}$N$_3$Br$_3$Cr	525.0
[Cr(ddpd)Br$_3$]	35.43, 3.30, 12.01	35.02, 2.94, 12.01	C$_{17}$H$_{17}$N$_5$Br$_3$Cr	583.1
[Cr(dqp)Br$_3$]	43.81, 2.58, 6.51	44.19, 2.42, 6.72	C$_{23}$H$_{15}$N$_3$Br$_3$Cr	625.1
[Cr(tpy)(CN)$_3$]·1.7H$_2$O	54.47, 3.28, 21.22	54.88, 3.68, 21.33	C$_{18}$H$_{11}$N$_6$Cr·1.7H$_2$O	393.9
[Cr(ddpd)(CN)$_3$]·0.85H$_2$O·1.3CH$_2$Cl$_2$	46.90, 4.10, 20.33	46.78, 3.92, 20.48	C$_{20}$H$_{17}$N$_8$Cr·0.85H$_2$O·1.3CH$_2$Cl$_2$	547.1
[Cr(dqp)(CN)$_3$]·1.5H$_2$O·1.7CH$_2$Cl$_2$	52.49, 3.55, 13.10	52.41, 3.40, 13.24	C$_{26}$H$_{15}$N$_6$Cr·1.5H$_2$O·1.7CH$_2$Cl$_2$	634.8

[a] The nature of the solvent molecules are deduced from IR spectroscopies and the solvent contents were obtained by multi-linear least-square fits of the experimental %C, % H, %N data.

Table S3 Crystal data and structure refinement for complex [Ct(tpy)Br$_3$].

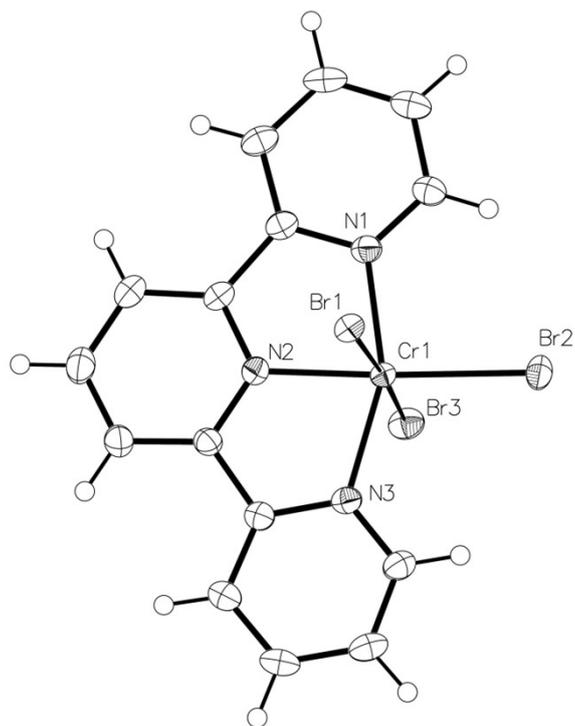|	
CCDC	213357
Empirical formula	C$_{15}$H$_{11}$Br$_3$CrN$_3$
Formula weight	525.00
Temperature	120.00(10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 8.4851(2) Å $\quad$ α = 90°
	b = 14.3395(2) Å $\quad$ β = 106.309(2)°
	c = 13.9396(3) Å $\quad$ γ = 90°
Volume	1627.81(6) Å^3
Z	4
Density (calculated)	2.142 Mg/m^3
Absorption coefficient	14.393 mm^{-1}
F(000)	1004
Crystal size	0.124 x 0.08 x 0.049 mm^3
Theta range for data collection	4.520 to 73.947°.
Index ranges	-10<=h<=10, -12<=k<=17, -17<=l<=17
Reflections collected	29627
Independent reflections	3273 [R(int) = 0.0366]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.820 and 0.390
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3273 / 0 / 199
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0212, wR2 = 0.0548
R indices (all data)	R1 = 0.0218, wR2 = 0.0551
Extinction coefficient	n/a
Largest diff. peak and hole	0.370 and -0.578 e.Å^{-3}

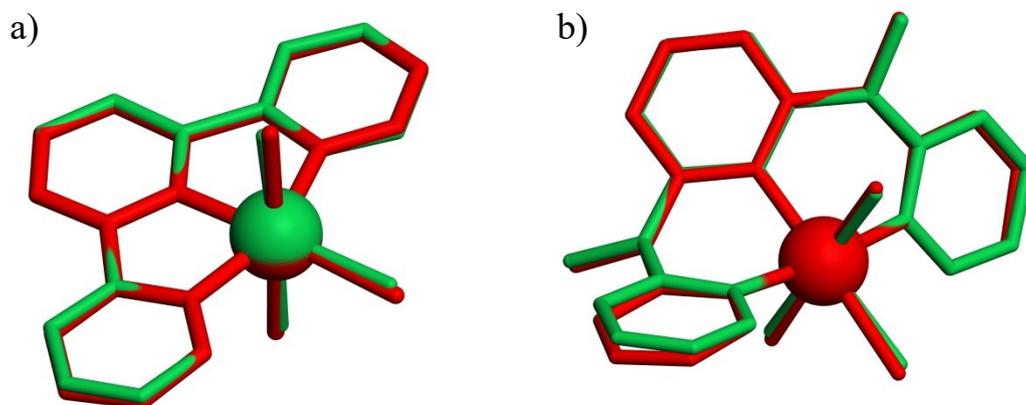**Figure S2** ORTEP view of [Ct(tpy)Br$_3$] at 50% probability level with numbering scheme.

Figure S3 Optimized superimposition of the molecular structures of [Cr(**L**)Cl$_3$] (green) and [Cr(**L**)Br$_3$] (red) with a) **L** = tpy and b) **L** = ddpd.

Table S4 Selected bond distances (Å) and bond angles (°) for complex [Cr(tpy)Br$_3$].

		Bond Distances /Å			
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cr1	2.4995(4)	Cr1	N1	2.0718(19)
Br2	Cr1	2.4532(4)	Cr1	N2	1.9891(19)
Br3	Cr1	2.4667(4)	Cr1	N3	2.0753(19)

	Bond Angles (°)		
Atom	Atom	Atom	Angle /°
Br2	Cr1	Br1	90.600(14)
Br2	Cr1	Br3	93.009(14)
Br3	Cr1	Br1	176.302(17)
N1	Cr1	Br1	90.05(5)
N1	Cr1	Br2	99.81(5)
N1	Cr1	Br3	90.13(5)
N1	Cr1	N3	156.71(8)
N2	Cr1	Br1	85.86(5)
N2	Cr1	Br2	176.02(5)
N2	Cr1	Br3	90.56(5)
N2	Cr1	N1	78.41(7)
N2	Cr1	N3	78.37(7)
N3	Cr1	Br1	90.06(5)
N3	Cr1	Br2	103.47(5)
N3	Cr1	Br3	88.32(5)

Table S5 Selected least-squares planes data for complex [Cr(tpy)Br$_3$].

Plane	mean deviation in Å	max deviation in Å (atom)
Py1: N1 C1 C2 C3 C4 C5	0.017	0.026 (N1)
Py2: N2 C6 C7 C8 C9 C10	0.011	0.018 (N2)
Py3: N3 C11 C12 C13 C14 C15	0.007	0.011 (C11)

Mean and maximum deviation between the atoms of the pyridine rings and their best plane.

Planes	**Py1- Py2**	**Py1- Py3**	**Py2- Py3**
Interplanar angle (°)	7.16(7)	3.57(7)	4.07(7)

Table S6 Crystal data and structure refinement for [Cr(tpy)(CN)$_3$].

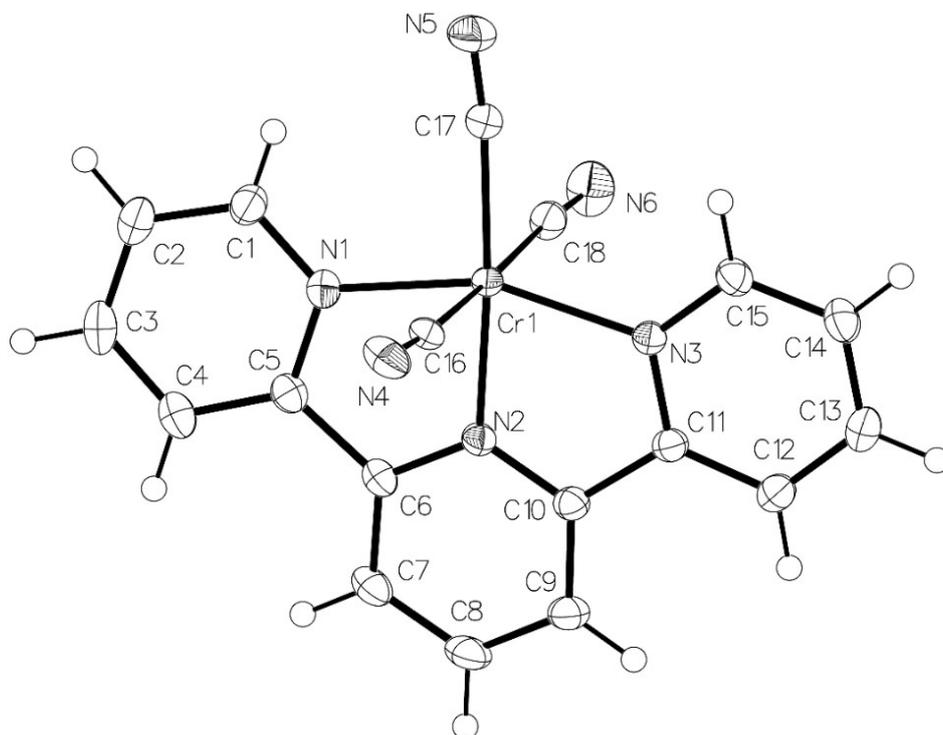|	
CCDC	2133577
Empirical formula	$C_{18}H_{11}CrN_6$
Formula weight	363.33
Temperature	119.99(14) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	$a = 9.09570(10)$ Å $\qquad \alpha = 90°$
	$b = 13.1460(2)$ Å $\qquad \beta = 107.079(2)°$
	$c = 14.3005(2)$ Å $\qquad \gamma = 90°$
Volume	1634.53(4) Å^3
Z	4
Density (calculated)	1.476 Mg/m^3
Absorption coefficient	5.864 mm^{-1}
F(000)	740
Crystal size	0.157 x 0.098 x 0.037 mm^3
Theta range for data collection	4.667 to 73.664°.
Index ranges	-11<=h<=11, -16<=k<=13, -17<=l<=17
Reflections collected	91918
Independent reflections	3295 [R(int) = 0.0468]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.524
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3295 / 0 / 227
Goodness-of-fit on F^2	1.133
Final R indices [I>2sigma(I)]	$R1 = 0.0298$, w$R2 = 0.0882$
R indices (all data)	$R1 = 0.0301$, w$R2 = 0.0884$
Extinction coefficient	0.00046(13)
Largest diff. peak and hole	0.356 and -0.430 e.Å^{-3}

Figure S4 ORTEP view of [Cr(tpy)(CN)$_3$] at 50% probability level with numbering scheme.

Table S7 Selected bond distances (Å) and bond angles (°) for complex [Cr(tpy)(CN)$_3$].

	Bond Distances /Å				
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	N1	2.0636(13)	Cr1	C16	2.0748(15)
Cr1	N2	1.9932(12)	Cr1	C17	2.0593(16)
Cr1	N3	2.0692(13)	Cr1	C18	2.0771(16)

	Bond Angles (°)		
Atom	Atom	Atom	Angle /°
N1	Cr1	N3	156.84(5)
N1	Cr1	C16	87.77(6)
N1	Cr1	C18	92.76(6)
N2	Cr1	N1	78.52(5)
N2	Cr1	N3	78.38(5)
N2	Cr1	C16	89.40(5)
N2	Cr1	C17	175.17(6)
N2	Cr1	C18	93.67(6)
N3	Cr1	C16	93.52(5)
N3	Cr1	C18	87.18(6)
C16	Cr1	C18	176.93(6)
C17	Cr1	N1	98.50(6)
C17	Cr1	N3	104.65(6)
C17	Cr1	C16	86.67(6)
C17	Cr1	C18	90.26(6)

Table S8 Selected least-squares planes data for complex [Cr(tpy)(CN)$_3$].

Plane	mean deviation in Å	max deviation in Å (atom)
Py1: N2 C6 C7 C8 C9 C10	0.011	0.016 (N2, C8)
Py2: N3 C11 C12 C13 C14 C15	0.002	0.003 (C14, C15)
Py3: N1 C1 C2 C3 C4 C5	0.012	0.018 (N1, C5)

Mean and maximum deviation between the atoms of the pyridine rings and their best plane.

Planes	**Py1- Py2**	**Py1- Py3**	**Py2- Py3**
Interplanar angle (°)	1.70	8.60	7.99

Table S9 Crystal data and structure refinement for [Cr(ddpd)(CN)$_3$]·2H$_2$O.

CCDC	2133575
Empirical formula	C$_{20}$H$_{21}$CrN$_8$O$_2$
Formula weight	457.45
Temperature	120(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	C 1 2/c 1
Unit cell dimensions	a = 11.9309(2) Å $\quad$ α = 90°
	b = 13.5078(2) Å $\quad$ β = 102.2381(18)°
	c = 13.8221(3) Å $\quad$ γ = 90°
Volume	2176.94(7) Å^3
Z	4
Density (calculated)	1.396 Mg/m^3
Absorption coefficient	4.613 mm^{-1}
F(000)	948
Crystal size	0.848 x 0.358 x 0.238 mm^3
Theta range for data collection	5.011 to 73.389°.
Index ranges	-14<=h<=14, -14<=k<=16, -17<=l<=17
Reflections collected	20649
Independent reflections	2182 [R(int) = 0.0251]
Completeness to theta = 67.684°	99.9 %
Absorption correction	Analytical
Max. and min. transmission	0.448 and 0.178
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2182 / 0 / 150
Goodness-of-fit on F^2	1.137
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0740
R indices (all data)	R1 = 0.0258, wR2 = 0.0741
Extinction coefficient	n/a
Largest diff. peak and hole	0.233 and -0.370 e.Å^{-3}

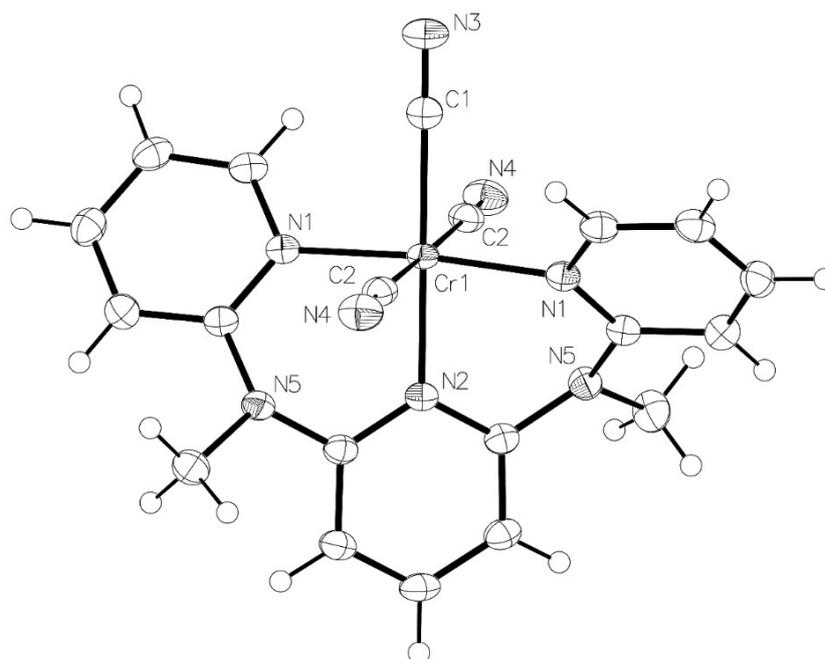**Figure S5** ORTEP view of [Ct(ddpd)(CN)$_3$] at 50% probability level with numbering scheme in the crystal structure of [Cr(ddpd)(CN)$_3$]·2H$_2$O.

Table S10 Selected bond distances (Å) and bond angles (°) for complex [Cr(ddpd)(CN)$_3$]·2H$_2$O.

Bond Distances /Å					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	N1*	2.0556(12)	Cr1	C1	2.080(2)
Cr1	N1	2.0556(12)	Cr1	C2	2.0868(15)
Cr1	N2	2.0408(16)	Cr1	C2*	2.0868(15)

*Symmetry transformations used to generate equivalent atoms:-x+1,y,-z+3/2.

	Bond Angles (°)		
Atom	Atom	Atom	Angle /°
N1*	Cr1	N1	174.59(6)
N1*	Cr1	C1	92.71(3)
N1	Cr1	C1	92.71(3)
N1*	Cr1	C2*	91.72(5)
N1	Cr1	C2	91.72(5)
N1*	Cr1	C2	88.33(5)
N1	Cr1	C2*	88.33(5)
N2	Cr1	N1	87.29(3)
N2	Cr1	N1*	87.29(3)
N2	Cr1	C1	180
N2	Cr1	C2*	90.55(3)
N2	Cr1	C2	90.55(3)
C1	Cr1	C2	89.45(3)
C1	Cr1	C2*	89.45(3)
C2	Cr1	C2*	178.90(7)

*Symmetry transformations used to generate equivalent atoms:-x+1,y,-z+3/2.

Table S11 Selected least-squares planes data for complex [Cr(ddpd)(CN)$_3$]·2H$_2$O.

Plane	mean deviation in Å	max deviation in Å (atom)
Py1: N2 C9 C10 C11 C9* C10*	0.001	0.002 (C9,C10, C9*,C10*)
Py2: N1 C3 C4 C5 C6 C7	0.011	0.021 (N1)
Py2*: N1* C3* C4* C5* C6* C7*	0.011	0.021 (N1*)

Mean and maximum deviation between the atoms of the pyridine rings and their best plane.

Planes	**Py1- Py2**	**Py2- Py2***
Interplanar angle (°)	44.12	73.55

*Symmetry transformations used to generate equivalent atoms:-x+1,y,-z+3/2.

Table S12 Crystal data and structure refinement for $[Cr(dqp)(CN)_3]\cdot 3.28H_2O$.[a]

CCDC	2133576
Empirical formula	$C_{26}H_{21.55}CrN_6O_{3.28}$
Formula weight	522.45
Temperature	120.00(14) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 10.1680(3)$ Å $\quad \alpha = 67.150(2)°$
	$b = 10.6947(2)$ Å $\quad \beta = 76.292(2)°$
	$c = 12.3560(3)$ Å $\quad \gamma = 85.697(2)°$
Volume	1202.71(5) Å^3
Z	2
Density (calculated)	1.443 Mg/m^3
Absorption coefficient	4.271 mm^{-1}
$F(000)$	540
Crystal size	0.139 x 0.119 x 0.08 mm^3
Theta range for data collection	3.986 to 73.872°.
Index ranges	$-12<=h<=12, -12<=k<=13, -11<=l<=15$
Reflections collected	29393
Independent reflections	4749 [R(int) = 0.0354]
Completeness to theta = 67.684°	99.5 %
Absorption correction	Analytical
Max. and min. transmission	0.778 and 0.657
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4749 / 1 / 372
Goodness-of-fit on F^2	1.097
Final R indices [$I>2$sigma(I)]	$R1 = 0.0392$, w$R2 = 0.1151$
R indices (all data)	$R1 = 0.0409$, w$R2 = 0.1164$
Extinction coefficient	n/a
Largest diff. peak and hole	1.025 and -0.406 e.Å^{-3}

[a] The water content is approximative, as the water molecules are strongly disordered. See cif file for more information about the modelling of the water molecules.
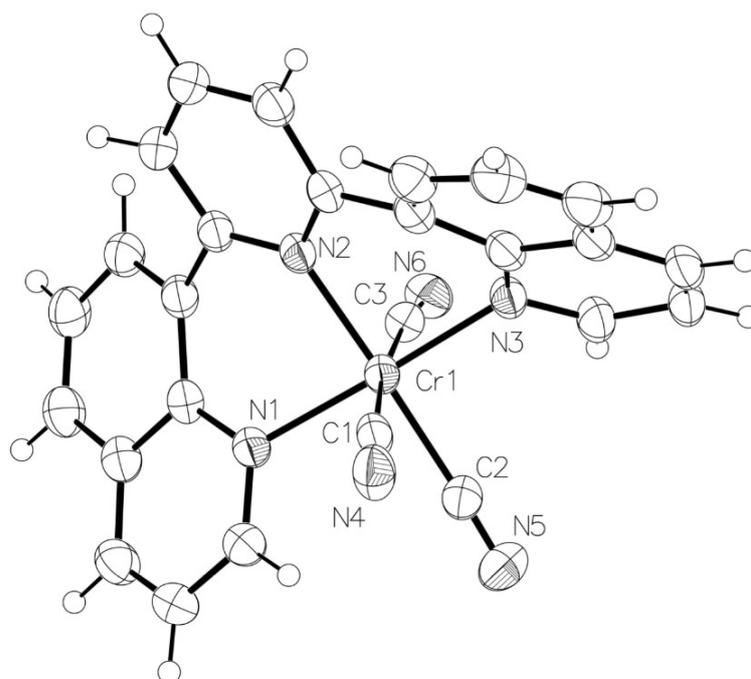
Figure S6 ORTEP view of [Ct(dqp)(CN)$_3$] at 50% probability level with numbering scheme in the crystal structure of [Cr(dqp)(CN)$_3$]·3.28H$_2$O.

Table S13 Selected bond distances (Å) and bond angles (°) for complex [Cr(dqp)(CN)$_3$]·3.28H$_2$O.

Bond Distances /Å					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	N1	2.0726(16)	Cr1	C1	2.085(2)
Cr1	N2	2.0436(17)	Cr1	C2	2.073(2)
Cr1	N3	2.0709(16)	Cr1	C3	2.071(2)

	Bond Angles (°)		
Atom	Atom	Atom	Angle /°
N1	Cr1	C1	89.27(7)
N2	Cr1	N1	88.19(6)
N2	Cr1	N3	89.31(6)
N2	Cr1	C1	94.94(8)
N2	Cr1	C2	175.94(8)
N2	Cr1	C3	90.85(7)
N3	Cr1	N1	176.71(6)
N3	Cr1	C1	88.81(7)
N3	Cr1	C2	93.40(8)
N3	Cr1	C3	88.27(7)
C2	Cr1	N1	89.21(8)
C2	Cr1	C1	88.15(9)
C3	Cr1	N1	93.90(7)
C3	Cr1	C1	173.49(8)
C3	Cr1	C2	86.22(8)

Table S14 Selected least-squares planes data for complex $[Cr(dqp)(CN)_3] \cdot 3.28H_2O$.

Plane	mean deviation in Å	max deviation in Å (atom)
Py1: N2 C13 C14 C15 C16 C17	0.019	0.029 (C14)
Qui1: N3 C18 C19 C20 C21 C22 C23 C24 C25 C26	0.072	0.128 (N3)
Qui2: N1 C4 C5 C6 C7 C8 C9 C10 C11 C12	0.061	0.149 (C11)

Mean and maximum deviation between the atoms of the pyridine rings and their best plane.

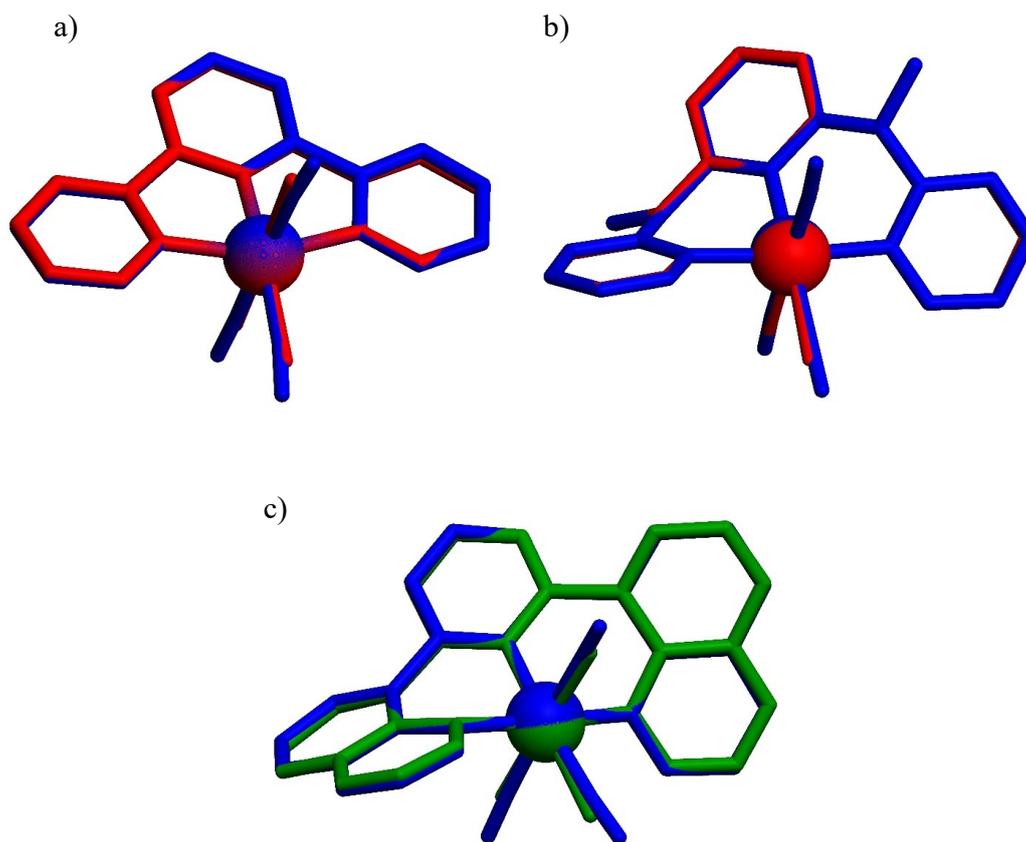| Planes	**Py1- Qui1**	**Py1- Qui2**	**Qui1- Qui2**
Interplanar angle (°)	36.31	38.24	74.55

Figure S7 Optimized superimposition of the molecular structures of a) [Cr(tpy)Br$_3$] (red) with [Cr(tpy)(CN)$_3$] (blue), b) [Cr(ddpd)Br$_3$] (red) with [Cr(ddpd)(CN)$_3$] (blue) and c) [Cr(dqp)Cl$_3$] (green) with [Cr(dqp)(CN)$_3$] (blue). H atoms have been removed for clarity.
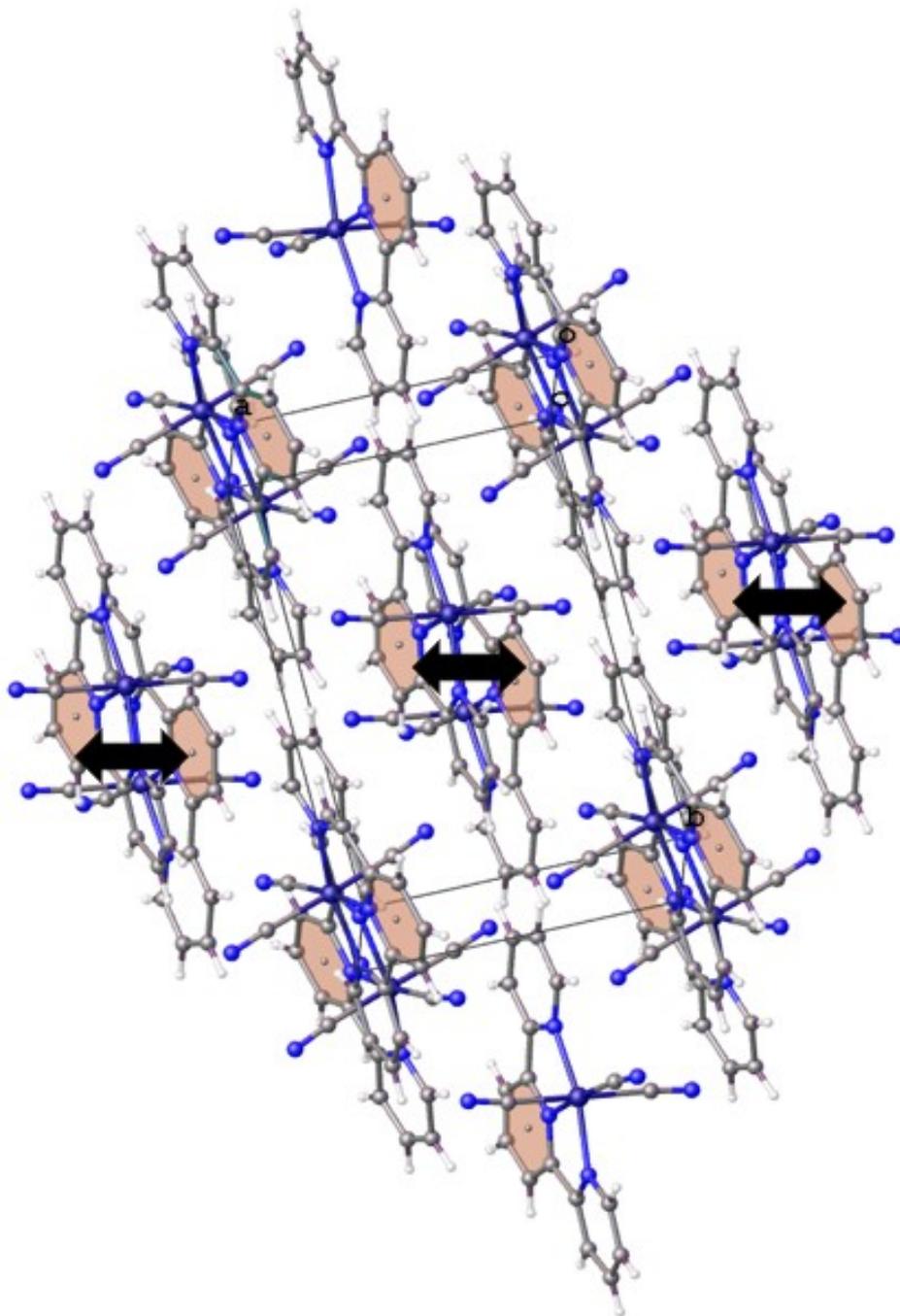
Figure S8 View along the (-1 1 5) direction showing the π- π interactions between the plane N2 C10 C9 C8 C7 C6 and its symmetry equivalent in the crystal structure of [Cr(tpy)(CN)$_3$]. The angle between the planes is 0˚, the centroid-centroid distance is 3.93Å, and there is a shift of 1.7 Å between the projection of one centroid and the other centroid, giving an effective plane-to-plane distance of about 3.5 Å.
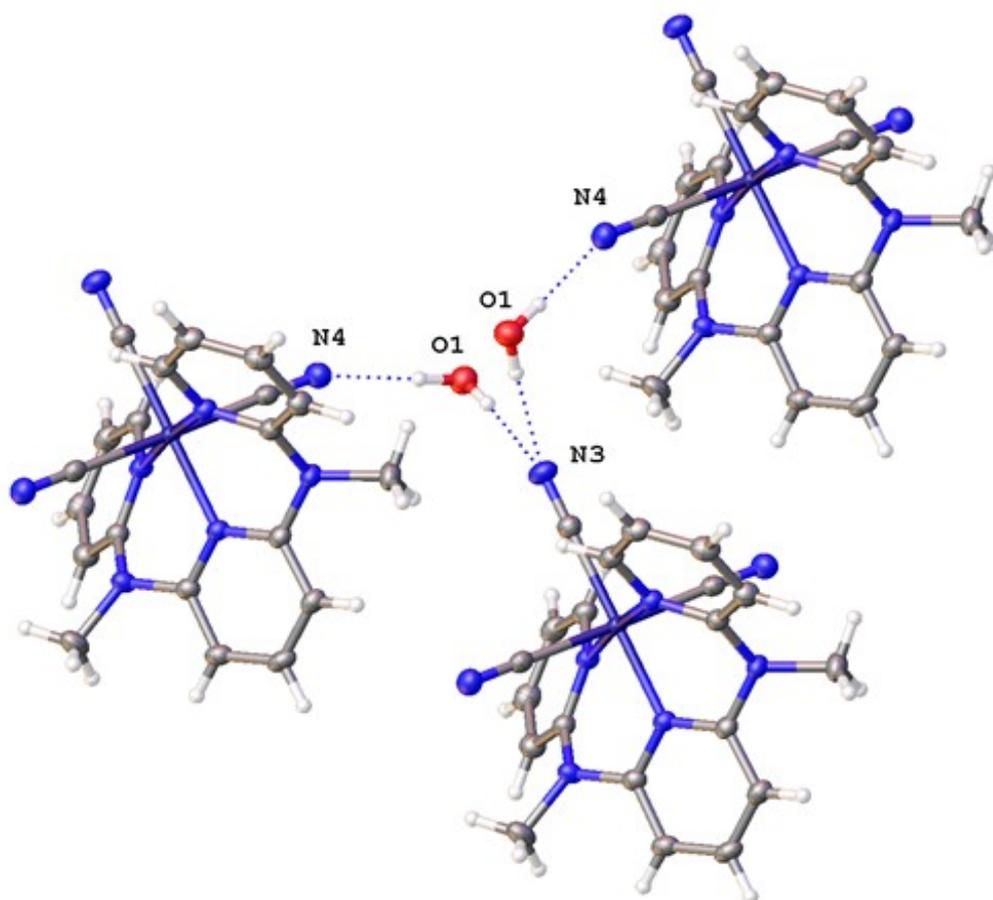
Figure S9 View of the hydrogen-bonds in the crystal structure of [Cr(ddpd)(CN)$_3$]·2H$_2$O. Each hydrogen atoms of the water molecules is bound to the nitrogen atoms N3 and N4 of two adjacent complexes. N4 makes hydrogen bonds to a single water molecule whereas N3 make a hydrogen bond to two adjacent water molecules. This creates a complex path of hydrogen bonds interactions within the crystal, creating layers normal to the *c*-axis where all the complexes interact via hydrogen bonds.

Figure S10 View of the crystal structure of $[Cr(ddpd)(CN)_3] \cdot 2H_2O$ along the (1 0 0) direction displaying three layers of complexes and water molecules interacting via hydrogen bonds (the carbon atoms are depicted in violet, green and grey, respectively). The layers interact with each other via π-π interactions (highlighted with black arrows) through the plane N1 C3 C4 C5 C6 C7 and its symmetrically equivalent plane (angle between the planes is 0˚, the centroid-centroid distance is 3.61Å, and there is a shift of 1.21 Å between the projection of one centroid and the other centroid, giving an effective plane-plane distance of about 3.4 Å).

a)

b)

Figure S11 a) View along the (0 1 0) direction of the crystal structure of $[Cr(dqp)(CN)_3]\cdot3.28H_2O$ showing the stacks made by the complexes and b) view of the π-π interactions (indicated with black arrows) along one of the stacks involving the planes N2 C17 C16 C15 C14 C13 and their symmetry equivalents (angle between the planes is 0˚, the centroid-centroid distance is 3.78Å, and there is a shift of 0.7 Å between the projection of one centroid and the other centroid, giving an effecti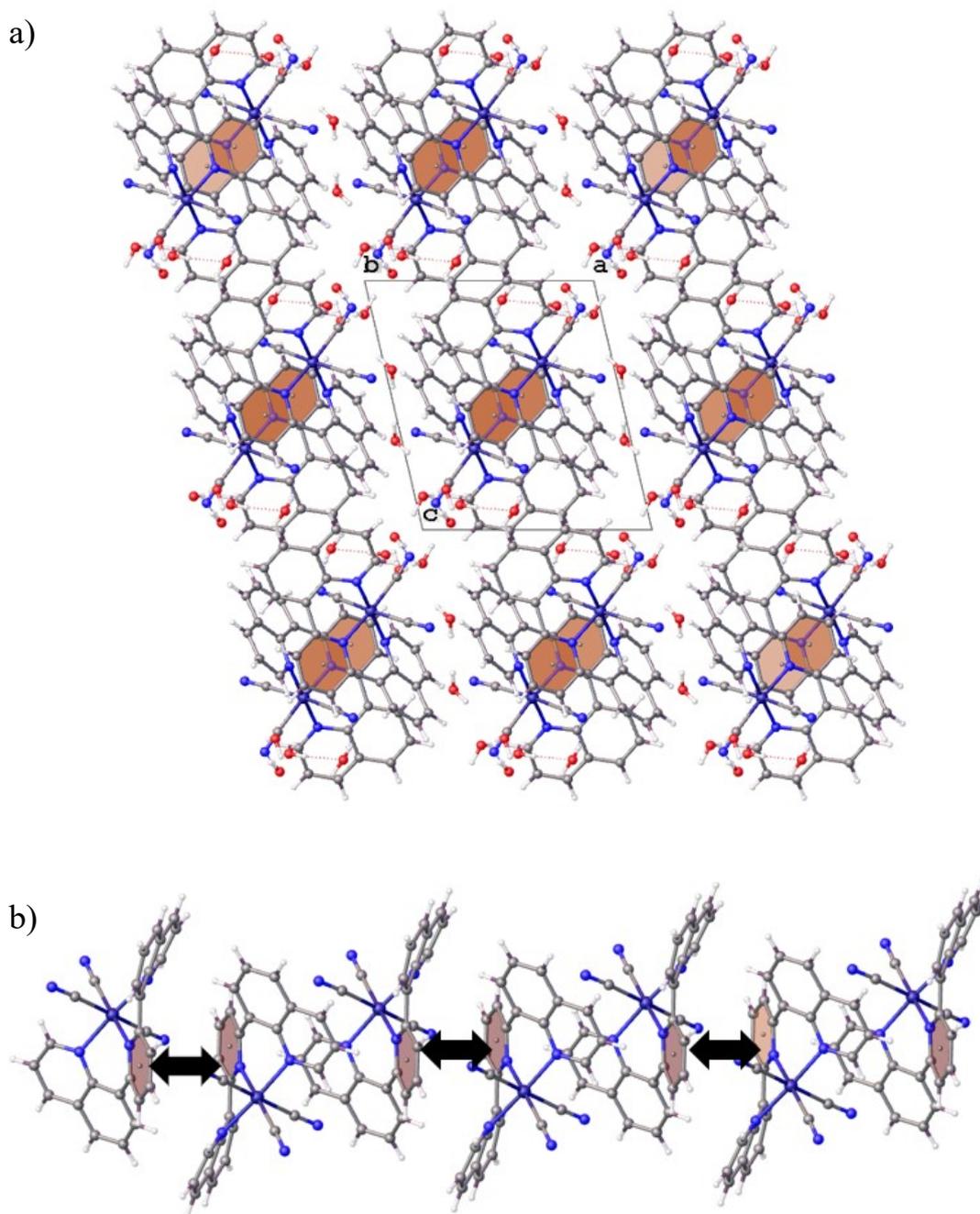ve plane-plane distance of about 3.7 Å). Because of the presence of disordered interstitial water molecules, the hydrogen atoms positions could not be asserted unambiguously and the potential network of hydrogen bonds cannot be described precisely.

Theoretical studies

The Gaussian 16 software package was used to perform structural optimizations of the investigated complexes.[S5] Starting from the X-ray diffraction structures, the ground state, $^4A_2$, structure of the different complexes was obtained from DFT optimizations using the unrestricted version of the Becke three-parameters exchange function in combination with the Lee-Yang-Parr correlation functional (UB3LYP). The basis set used for these optimizations was the 6-31G(d,p) for N, C and H and the LanL2DZ for the metal center. In addition, LANL2 pseudopotential was specified for the core electrons of the Cr atom. Solvent effects were included via the Polarizable Contiunuum Model (PCM) as implemented in Gaussian 16 with the dielectric constant of N,N-dimethylformamide (for $[Cr(tpy)(CN)_3]$) and acetonitrile (for $[Cr(ddpd)(CN)_3]$ and $[Cr(dqp)(CN)_3]$). Optimized geometries were confirmed to be stationary points by analysis of their vibrational frequencies. Orbital and spin density information was extracted from the optimized geometries. The 50 lowest energetic transitions were calculated by TD-DFT, using the unrestricted version of the Coulomb-attenuated B3LYP functional (UCAM-B3LYP), selecting the 6-31++G(d,p) basis set for N, C and H, and the LanL2DZ for the metal center. Same pseudopotential for the Cr atom and solvent effects were selected as for the ground state calculations. Electron Density Difference Maps (EDDM) were computed using GaussSum 3.0[S6] and are represented with an isoval=0.002 using GaussView 6.1.1.[S7]
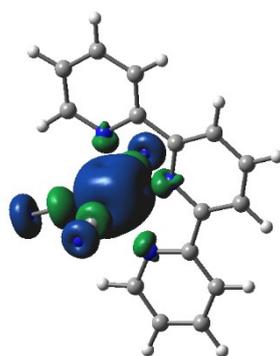

Figure S12 Spin density map for the quartet ground state $^4A_2$ of $[Cr(tpy)(CN)_3]$. (Isovalue = 0.004). Blue: positive spin density; Green: negative spin density.

Table S15. Calculated Mulliken charges and Spin densities of the optimized ground $^4A_2$ state of compound [Cr(tpy)(CN)$_3$].

		$^4A_2$	
		Mulliken charge	Mulliken Spin density
1	Cr	0.425262	3.064047
2	N	-0.545698	-0.039201
3	N	-0.607889	-0.047181
4	N	-0.545698	-0.039201
5	N	-0.461640	0.093646
6	N	-0.451562	0.112876
7	N	-0.461639	0.093647
8	C	0.119159	0.015867
9	H	0.167252	-0.001468
10	C	-0.088560	-0.007400
11	H	0.152400	0.000348
12	C	-0.056960	0.015876
13	H	0.155423	-0.000654
14	C	-0.090502	-0.006424
15	H	0.153286	-0.000159
16	C	0.305177	0.008778
17	C	0.306543	0.017878
18	C	-0.087920	-0.008454
19	H	0.158337	0.000280
20	C	-0.065631	0.021995
21	H	0.159772	-0.000956
22	C	-0.087920	-0.008454
23	H	0.158337	0.000280
24	C	0.306543	0.017878
25	C	0.305177	0.008778
26	C	-0.090502	-0.006424
27	H	0.153286	-0.000159
28	C	-0.056960	0.015876
29	H	0.155423	-0.000654
30	C	-0.088560	-0.007400
31	H	0.152400	0.000348
32	C	0.119159	0.015867
33	H	0.167252	-0.001468
34	C	0.065425	-0.103886
35	C	0.036603	-0.120833
36	C	0.065424	-0.103886
Sum		**0.000000**	**3.000000**

Table S16 Calculated 50 lowest energetic excitation transitions for compound [Cr(tpy)(CN)$_3$] and their energies (in nm) and oscillatory strength (in cgs units). Energies were corrected by –0.15 eV to better fit the experimental results.

Transition number	Wavelength / nm	Osc. Strength /cgs	Transition number	Wavelength / nm	Osc. Strength / cgs
1	462.14	0.0001	26	242.41	0.0001
2	450.96	0.0029	27	242.20	0.0000
3	441.79	0.0000	28	240.86	0.0282
4	418.62	0.0028	29	237.92	0.0000
5	386.78	0.0000	30	237.92	0.0174
6	342.22	0.0004	31	237.75	0.0000
7	336.48	0.0483	32	237.14	0.0093
8	330.95	0.0007	33	236.88	0.0000
9	315.04	0.0103	34	236.06	0.0023
10	312.70	0.2885	35	235.12	0.0000
11	305.11	0.0000	36	234.12	0.0001
12	301.06	0.0014	37	233.67	0.0085
13	300.53	0.0224	38	231.99	0.0799
14	293.31	0.0144	39	231.77	0.0016
15	285.90	0.0034	40	230.92	0.0135
16	284.17	0.0122	41	229.02	0.0002
17	279.76	0.1883	42	228.14	0.0273
18	263.09	0.0971	43	226.74	0.0006
19	257.49	0.0316	44	226.04	0.0561
20	255.76	0.0000	45	224.94	0.0011
21	252.22	0.1063	46	224.87	0.0112
22	248.88	0.0322	47	223.93	0.0000
23	245.80	0.0005	48	221.51	0.0402
24	244.97	0.0029	49	220.93	0.0000
25	243.80	0.0000	50	218.91	0.2332

a)

b)

Figure S13. Oscillatory strength of the 50 first simulated excitation transitions (red) and experimental UV-Vis spectrum of compound [Cr(tpy)(CN)$_3$] at 1.64 × 10^{-5} M in DMF. a) Full view and b) zoom view.

Figure S14 Electron density difference maps (EDDM) for the first 30 transitions of compound [Cr(tpy)(CN)₃]. Purple and blue lobes indicate loss and gain of electron density, respectively.

Figure S15 Spin density map of the quartet ground state $^4A_2$ (Isovalue = 0.004) of [Cr(ddpd)(CN)$_3$]. Blue: positive spin density; Green: negative spin density.

Table S17. Calculated Mulliken charges and Spin densities of the optimized ground $^4A_2$ state of compound [Cr(ddpd)(CN)$_3$].

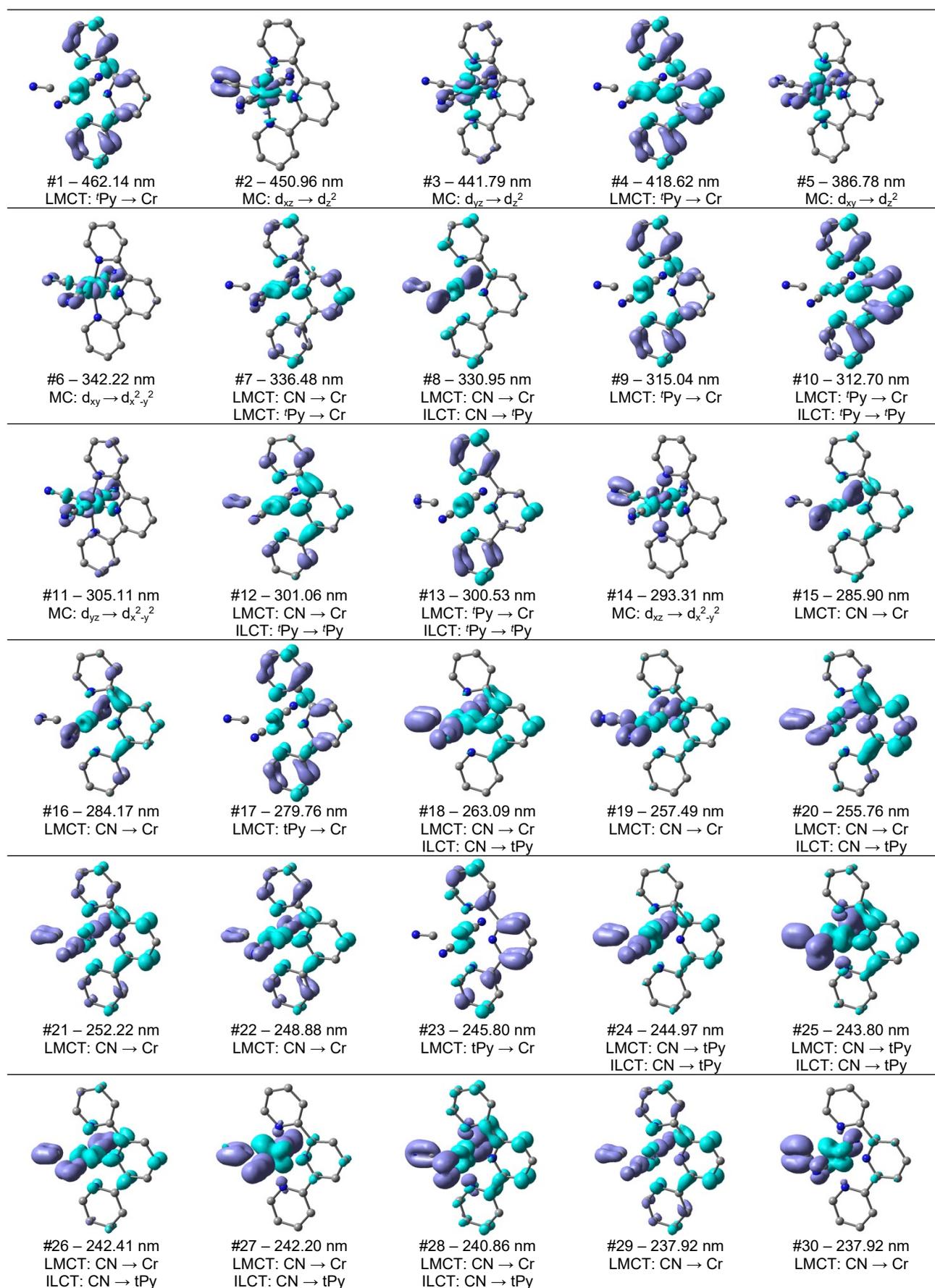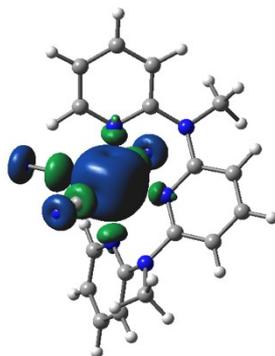|		$^4A_2$	
		Mulliken charge	Mulliken Spin density
1	Cr	0.390201	3.100977
2	N	-0.521802	-0.043791
3	N	-0.558147	-0.035321
4	N	-0.46377	0.095445
5	N	-0.463885	0.089984
6	N	-0.497726	0.005944
7	C	0.038116	-0.117403
8	C	0.051819	-0.102091
9	C	0.127352	0.011712
10	H	0.157114	-0.001351
11	C	-0.108309	-0.007517
12	H	0.139453	0.000219
13	C	-0.059683	0.014723
14	H	0.145305	-0.000586
15	C	-0.109752	-0.008807
16	H	0.143849	0.000051
17	C	0.487855	0.010724
18	C	-0.20655	-0.000297
19	H	0.147571	0.00042
20	H	0.158384	0.000186
21	H	0.157693	0.000191
22	C	0.469114	0.0094
23	C	-0.106536	-0.007435
24	H	0.143777	0.000304
25	C	-0.064368	0.012873
26	H	0.14788	-0.000535
27	N	-0.521803	-0.043791
28	N	-0.497725	0.005944
29	C	0.127352	0.011712
30	H	0.157114	-0.001351
31	C	-0.108309	-0.007517
32	H	0.139453	0.000219
33	C	-0.059683	0.014723
34	H	0.145305	-0.000586
35	C	-0.109752	-0.008807
36	H	0.143849	0.000051
37	C	0.487856	0.010724
38	C	-0.206549	-0.000297
39	H	0.147572	0.00042
40	H	0.158384	0.000186
41	H	0.157694	0.000191
42	C	0.469115	0.0094
43	C	-0.106536	-0.007435
44	H	0.143777	0.000304
45	N	-0.463885	0.089984
46	C	0.051819	-0.102091
Sum		**0.000000**	**3.000000**

Table S18. Calculated 50 lowest energetic excitation transitions for compound $[Cr(ddpd)(CN)_3]$ and their energies (in nm) and oscillatory strength (in cgs units). Energies were corrected by –0.05 eV to better fit the experimental results.

Transition number	Wavelength / nm	Osc. Strength / cgs	Transition number	Wavelength / nm	Osc. Strength / cgs
1	415.90	0.0004	26	246.37	0.0510
2	402.55	0.0000	27	245.24	0.0004
3	369.69	0.0065	28	243.14	0.0100
4	367.72	0.0010	29	241.26	0.0294
5	359.98	0.0003	30	240.46	0.0228
6	351.88	0.0024	31	237.53	0.0198
7	351.26	0.0011	32	236.04	0.0434
8	344.35	0.0014	33	234.15	0.0020
9	341.89	0.0013	34	232.48	0.0000
10	340.56	0.0012	35	232.41	0.0079
11	308.14	0.1578	36	231.48	0.0157
12	306.53	0.0010	37	229.75	0.0031
13	298.06	0.1061	38	228.35	0.1689
14	296.81	0.0014	39	227.92	0.0043
15	285.72	0.0517	40	226.95	0.0356
16	283.61	0.0046	41	226.72	0.0014
17	277.19	0.0232	42	224.95	0.0369
18	270.27	0.0138	43	224.36	0.0053
19	267.61	0.0034	44	223.00	0.0028
20	267.29	0.0019	45	222.04	0.0025
21	265.47	0.0064	46	221.07	0.0007
22	262.47	0.1013	47	220.41	0.0021
23	260.50	0.1037	48	219.08	0.0194
24	249.64	0.0646	49	218.10	0.0120
25	247.86	0.0038	50	217.46	0.0158

a)

b)

Figure S16. Oscillatory strength of the 50 first simulated excitation transitions (red) and experimental UV-Vis spectrum of compound [Cr(ddpd)(CN)$_3$] at 1.75×10^{-5} M in acetonitrile. a) Full view and b) zoom view.

Figure S17 Electron density difference maps (EDDM) for the first 30 transitions of compound [Cr(ddpd)(CN)$_3$]. Purple and blue lobes indicate loss and gain of electron density, respectively.

Figure S18 Spin density map of the quartet ground state $^4A_2$ of $[Cr(dqp)(CN)_3]$ (Isovalue = 0.004). Blue: positive spin density; Green: negative spin density.

Table S19 Calculated Mulliken charges and Spin densities of the optimized ground $^4A_2$ state of compound [Cr(dqp)(CN)$_3$].

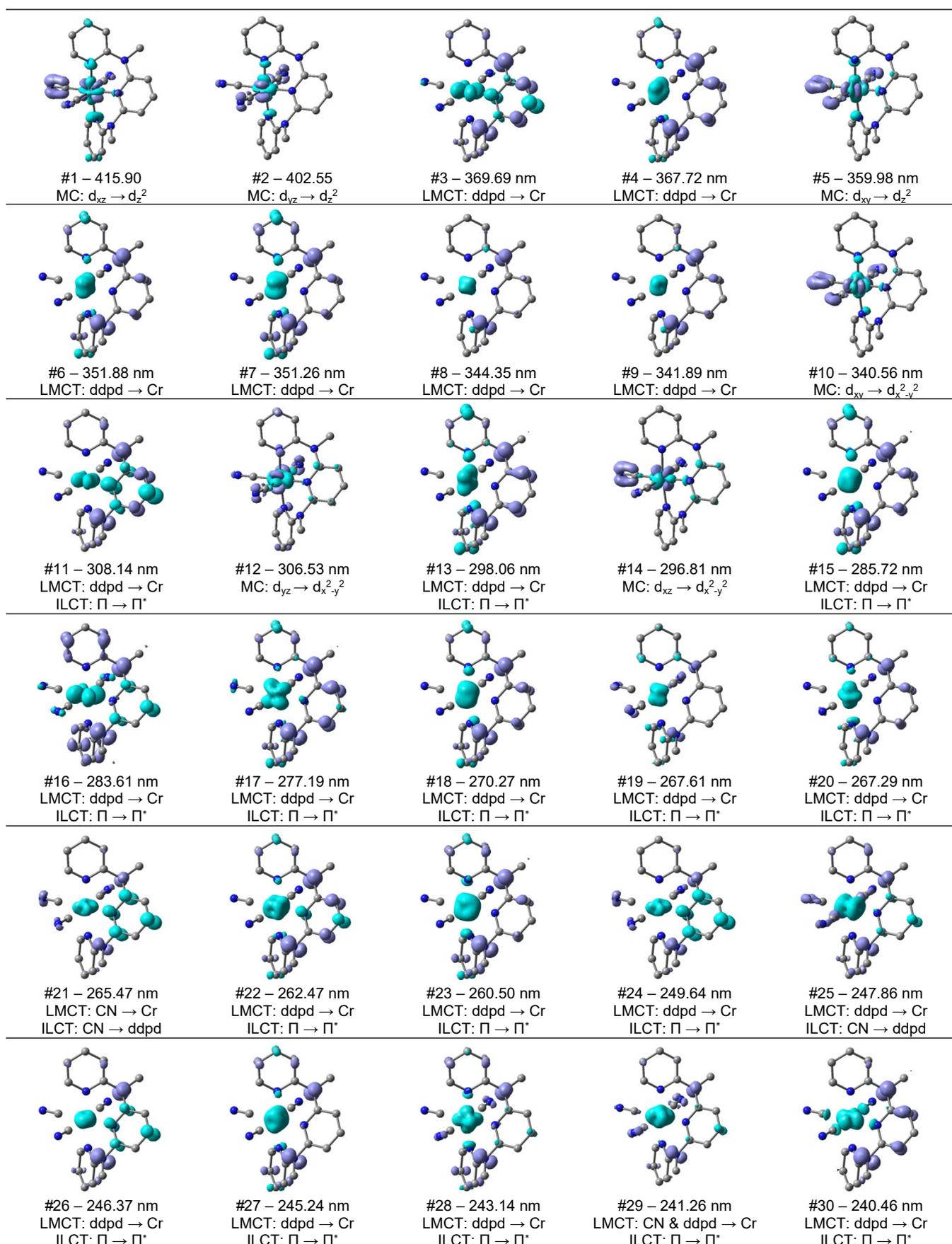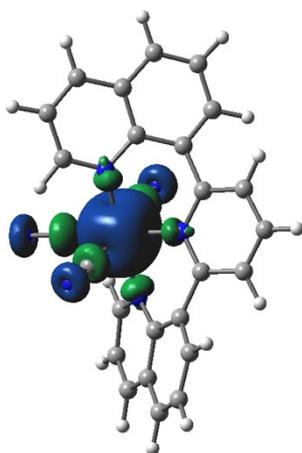|		$^4A_2$	
		Mulliken charge	**Mulliken Spin density**
1	Cr	0.369518	3.109989
2	N	-0.53769	-0.046458
3	N	-0.574462	-0.040885
4	N	-0.53769	-0.046457
5	C	0.140083	0.018117
6	H	0.163102	-0.001703
7	C	-0.110423	-0.009871
8	H	0.146187	0.000218
9	C	-0.075031	0.018704
10	H	0.149964	-0.000809
11	C	0.114678	-0.00822
12	C	-0.122362	0.00762
13	H	0.135596	-0.00043
14	C	-0.089757	-0.005205
15	H	0.131783	0.000197
16	C	-0.145039	0.008004
17	H	0.138771	-0.000362
18	C	0.050744	-0.0065
19	C	0.259673	0.006767
20	C	0.294364	0.01309
21	C	-0.109084	-0.010116
22	H	0.14613	0.000369
23	C	-0.054167	0.015687
24	H	0.149071	-0.00071
25	C	-0.109084	-0.010116
26	H	0.14613	0.000369
27	C	0.294363	0.01309
28	C	0.050745	-0.006499
29	C	-0.145039	0.008003
30	H	0.138771	-0.000362
31	C	-0.089757	-0.005204
32	H	0.131783	0.000197
33	C	-0.122362	0.007619
34	H	0.135596	-0.00043
35	C	0.114678	-0.00822
36	C	0.259673	0.006767
37	C	-0.075031	0.018703
38	H	0.149964	-0.000809
39	C	-0.110423	-0.00987
40	H	0.146187	0.000218
41	C	0.140084	0.018117
42	H	0.163102	-0.001703
43	C	0.043901	-0.100979
44	N	-0.458634	0.088286
45	C	0.038491	-0.11388
46	N	-0.462365	0.088363
47	C	0.043901	-0.100979
48	N	-0.458633	0.088286
Sum		**0.000000**	**3.000000**

Table S20 Calculated 50 lowest energetic excitation transitions for compound $[Cr(dqp)(CN)_3]$ and their energies (in nm) and oscillatory strength (in cgs units).

Transition number	Wavelength / nm	Osc. Strength / cgs	Transition number	Wavelength / nm	Osc. Strength / cgs
1	517.55	0.0000	26	262.05	0.0162
2	509.85	0.0000	27	258.87	0.0069
3	420.44	0.0002	28	257.23	0.0579
4	410.7	0.0000	29	254.7	0.0006
5	368.48	0.0000	30	252.11	0.0061
6	359.25	0.0005	31	249.9	0.0141
7	355.78	0.0044	32	248.96	0.0181
8	349.62	0.0001	33	245.17	0.0472
9	346.15	0.0164	34	244.37	0.0191
10	344.01	0.0013	35	243.54	0.0108
11	321.94	0.5406	36	242.03	0.0203
12	307.26	0.0344	37	239.05	0.0043
13	306.23	0.0000	38	238.64	0.0484
14	304.65	0.0288	39	236.03	0.0006
15	299.97	0.0019	40	235.75	0.0183
16	294.06	0.0013	41	234.46	0.0351
17	288.64	0.0029	42	233.54	0.0066
18	288.4	0.0007	43	233.39	0.0093
19	283.23	0.0313	44	233.23	0.0637
20	282.54	0.0768	45	232.13	0.0172
21	282.17	0.0430	46	229.97	0.0007
22	280.08	0.0112	47	229.89	0.0283
23	277.38	0.0004	48	228.88	0.0212
24	276.96	0.0013	49	228.4	0.0010
25	268.86	0.0046	50	227.66	0.0719

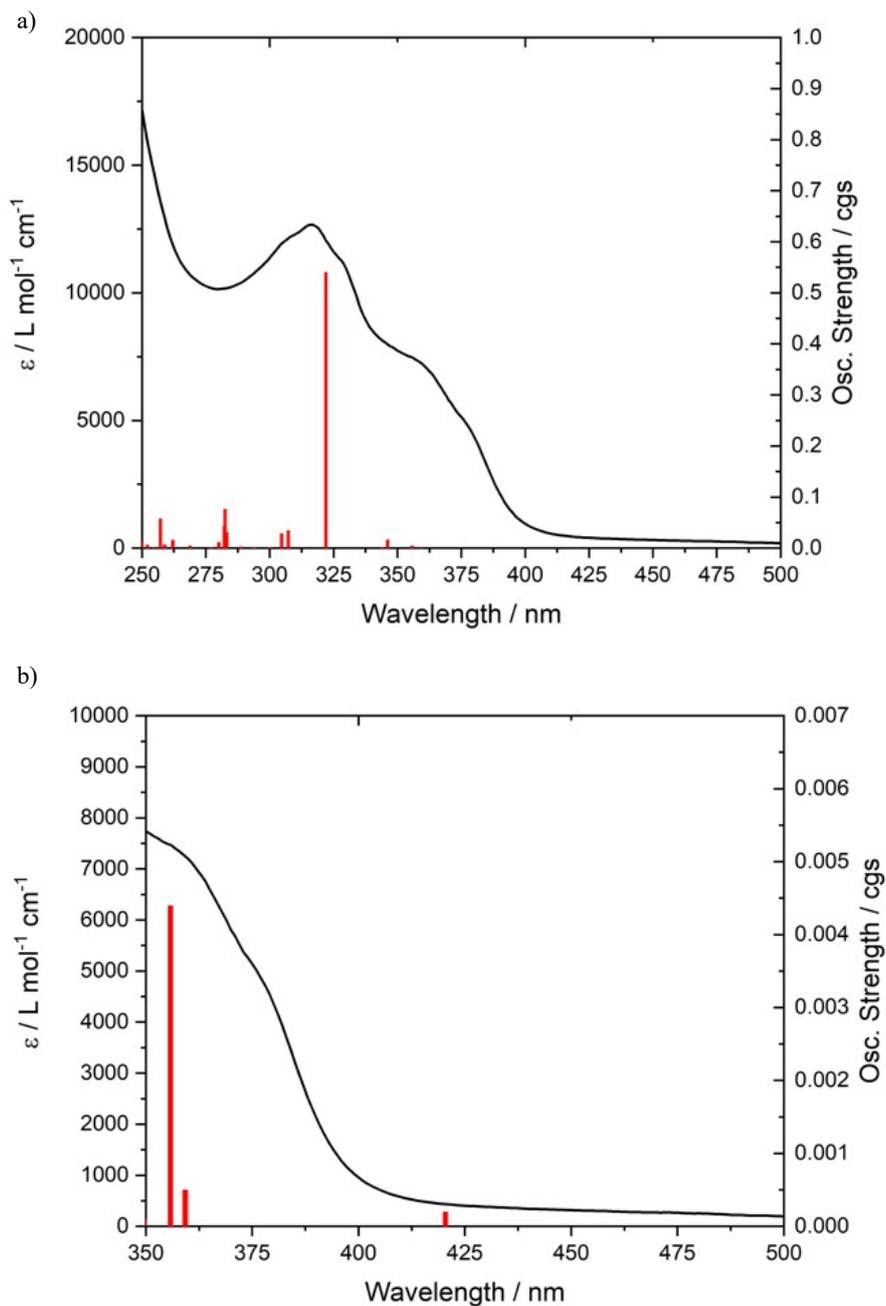**Figure S19** Oscillatory strength of the 50 first simulated excitation transitions (red) and experimental UV-Vis spectrum of compound [Cr(dqp)(CN)$_3$] at 1.94×10^{-5} M in acetonitrile. a) Full view and b) zoom view.

#1 – 517.55 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#2 – 509.85 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#3 – 420.44 nm
MC: $d_{xz} \rightarrow d_z^2$

#4 – 410.70 nm
MC: $d_{yz} \rightarrow d_z^2$

#5 – 368.48 nm
LMCT: dqp → Cr

#6 – 359.25 nm
MC: $d_{xy} \rightarrow d_z^2$

#7 – 355.78 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#8 – 349.62 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#9 – 346.15 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#10 – 344.01 nm
MC: $d_{xy} \rightarrow d_{x^2-y^2}$

#11 – 321.94 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#12 – 307.26 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#13 – 306.23 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#14 – 304.65 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#15 – 299.97 nm
MC: $d_{yz} \rightarrow d_{x^2-y^2}$

#16 – 294.06 nm
MC: $d_{xz} \rightarrow d_{x^2-y^2}$

#17 – 288.64 nm
LMCT: dqp → Cr

#18 – 288.40 nm
LMCT: dqp → Cr

#19 – 283.23 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#20 – 282.54 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#21 – 282.17 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#22 – 280.08 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#23 – 277.38 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#24 – 276.96 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#25 – 268.86 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#26 – 262.05 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#27 – 258.87 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#28 – 257.23 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#29 – 254.70 nm
LMCT: dqp → Cr
ILCT: Π → Π*

#30 – 252.11 nm
LMCT: dqp → Cr
ILCT: Π → Π*

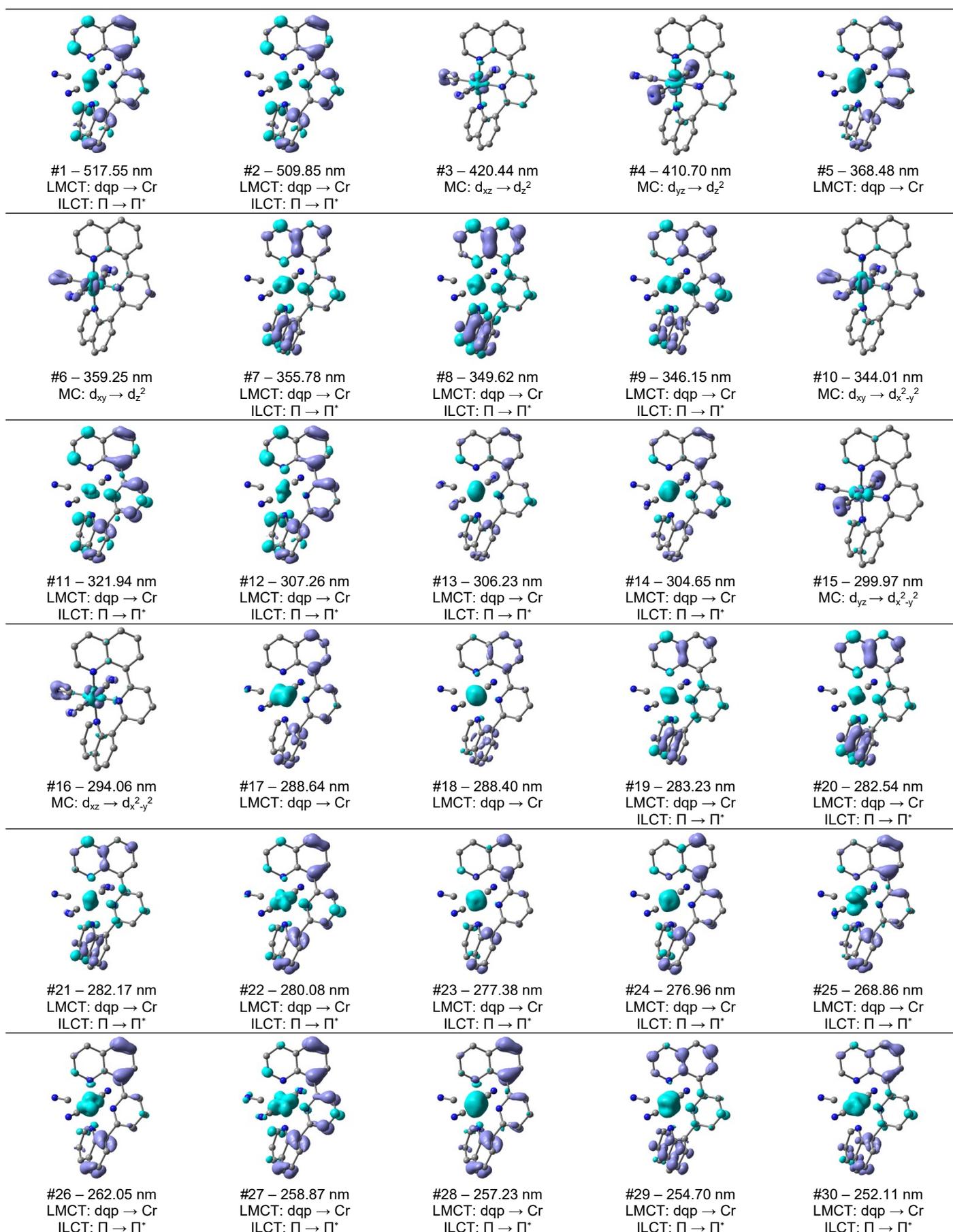**Figure S20** Electron density difference maps (EDDM) for the first 30 transitions of compound [Cr(dqp)(CN)₃]. Purple and blue lobes indicate loss and gain of electron density, respectively.

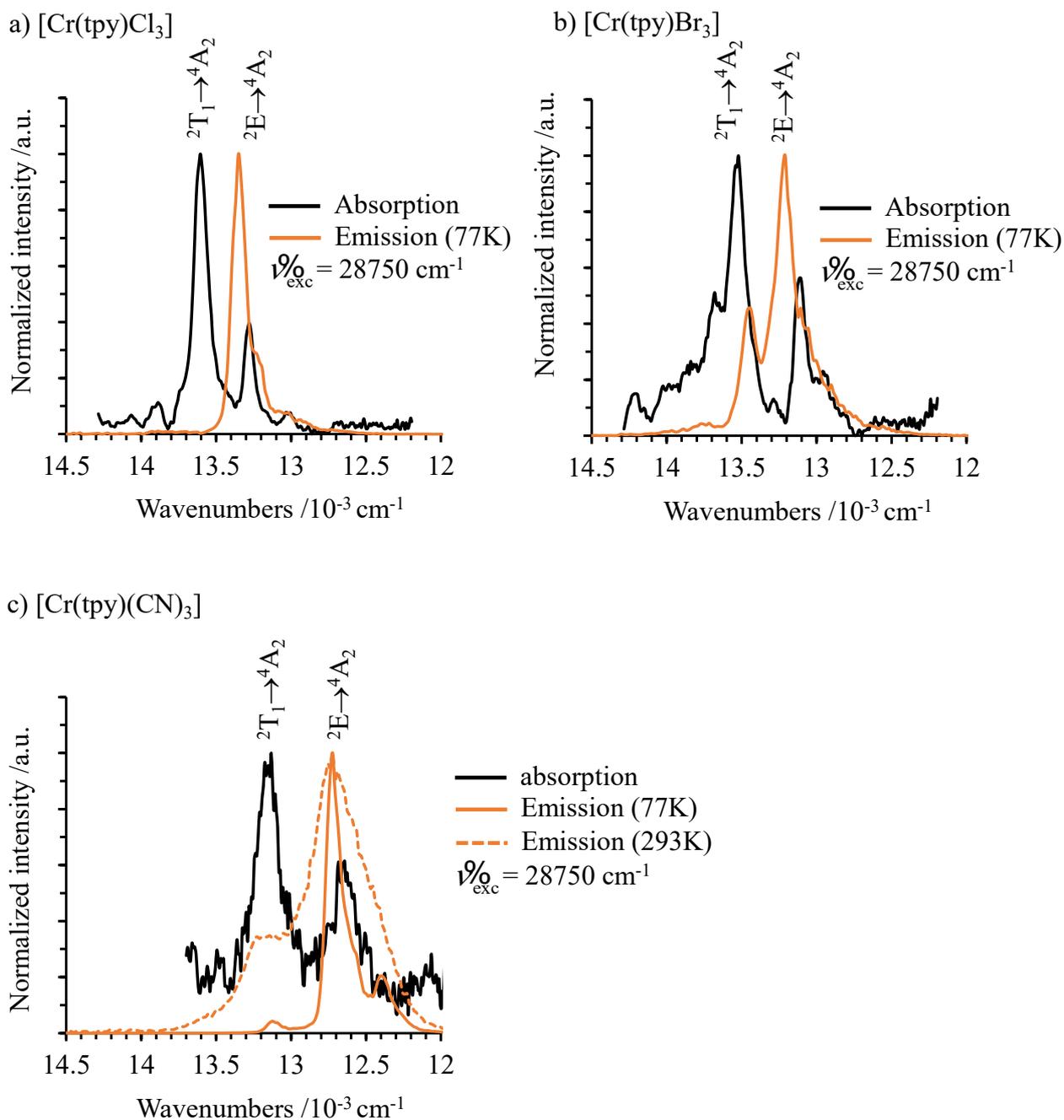a) [Cr(tpy)Cl$_3$]

b) [Cr(tpy)Br$_3$]

c) [Cr(tpy)(CN)$_3$]

Figure S21 Normalized solid state absorption spectra (recorded in transmittance mode, black traces) and solution emission spectra (c =2·10^{-5} M in DMF, $\tilde{\nu}_{exc}$ = 28750 cm^{-1}, λ_{exc} = 350 nm, orange traces) recorded for the heteroleptic complexes [Cr(tpy)X$_3$] (X = Cl, Br, CN).

Figure S22 Normalized solid state absorption spectra (recorded in transmittance mode, black traces) and solution emission spectra (c = 2·10^{-5} M in DMF for X = Cl, Br and in acetonitrile (298 K) or acetonitrile/propionitrile (3:1, 77K) for X = CN, $\tilde{\nu}_{exc}$ = 28750 cm^{-1}, λ_{exc} = 350 nm, orange traces) recorded for the heteroleptic complexes [Cr(ddpd)X$_3$] (X = Cl, Br, CN). * represents the hypothetical OH overtone (see main text).

a) [Cr(dqp)Cl₃]

b) [Cr(dqp)Br₃]

c) [Cr(dqp)(CN)₃]

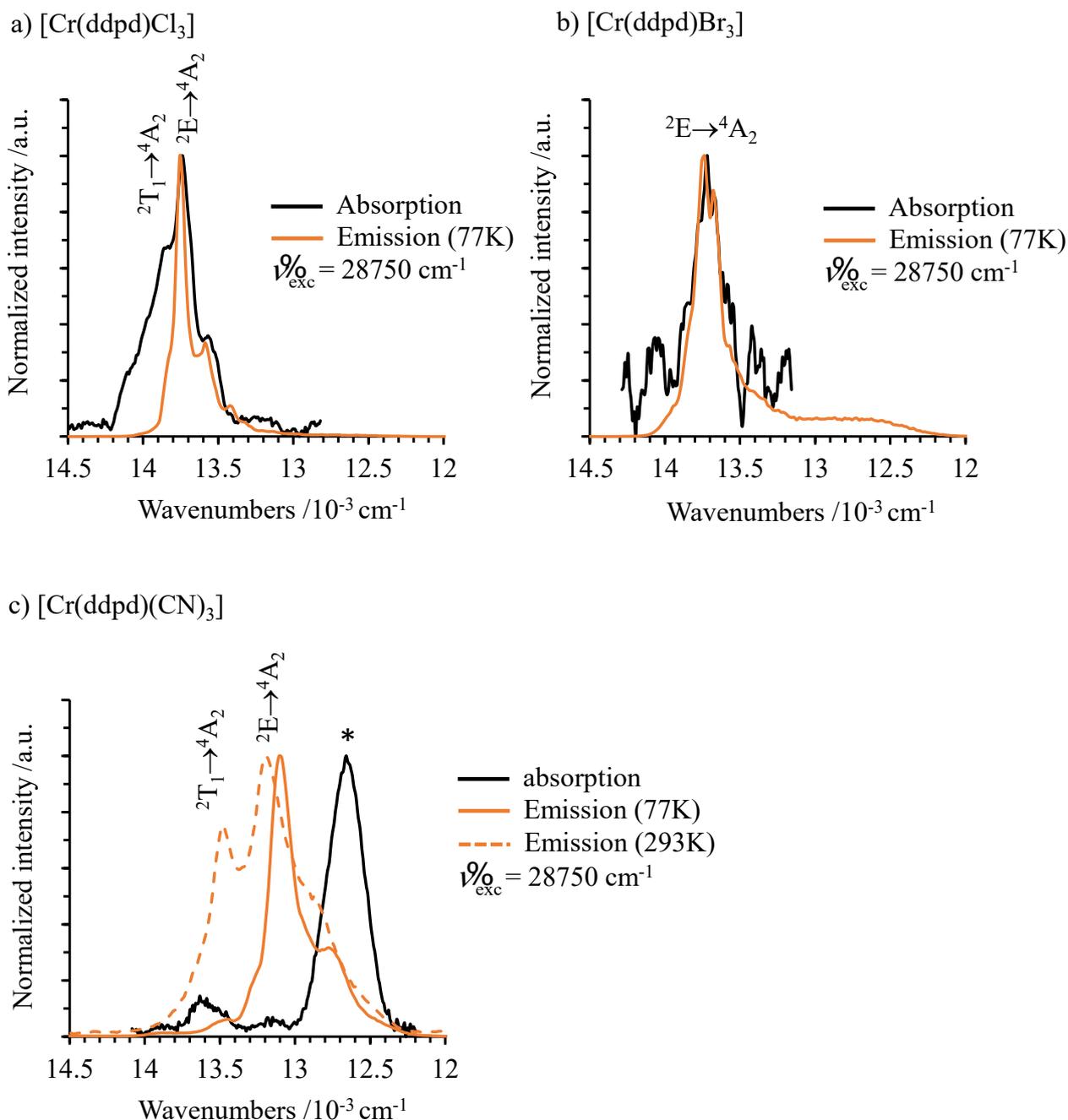**Figure S23** Normalized solid state absorption spectra (recorded in transmittance mode, black traces) and solution emission spectra (c = 2·10⁻⁵ M in DMF for X = Cl, Br, in acetonitrile (298 K) or acetonitrile/propionitrile (3:1, 77K) for X = CN, $\tilde{\nu}_{exc}$ = 28750 cm⁻¹, λ_{exc} = 350 nm, orange traces) recorded for the heteroleptic complexes [Cr(dqp)X₃] (X = Cl, Br, CN). * represents the hypothetical OH overtone (see main text)

Coordinates of the DFT optimized geometries
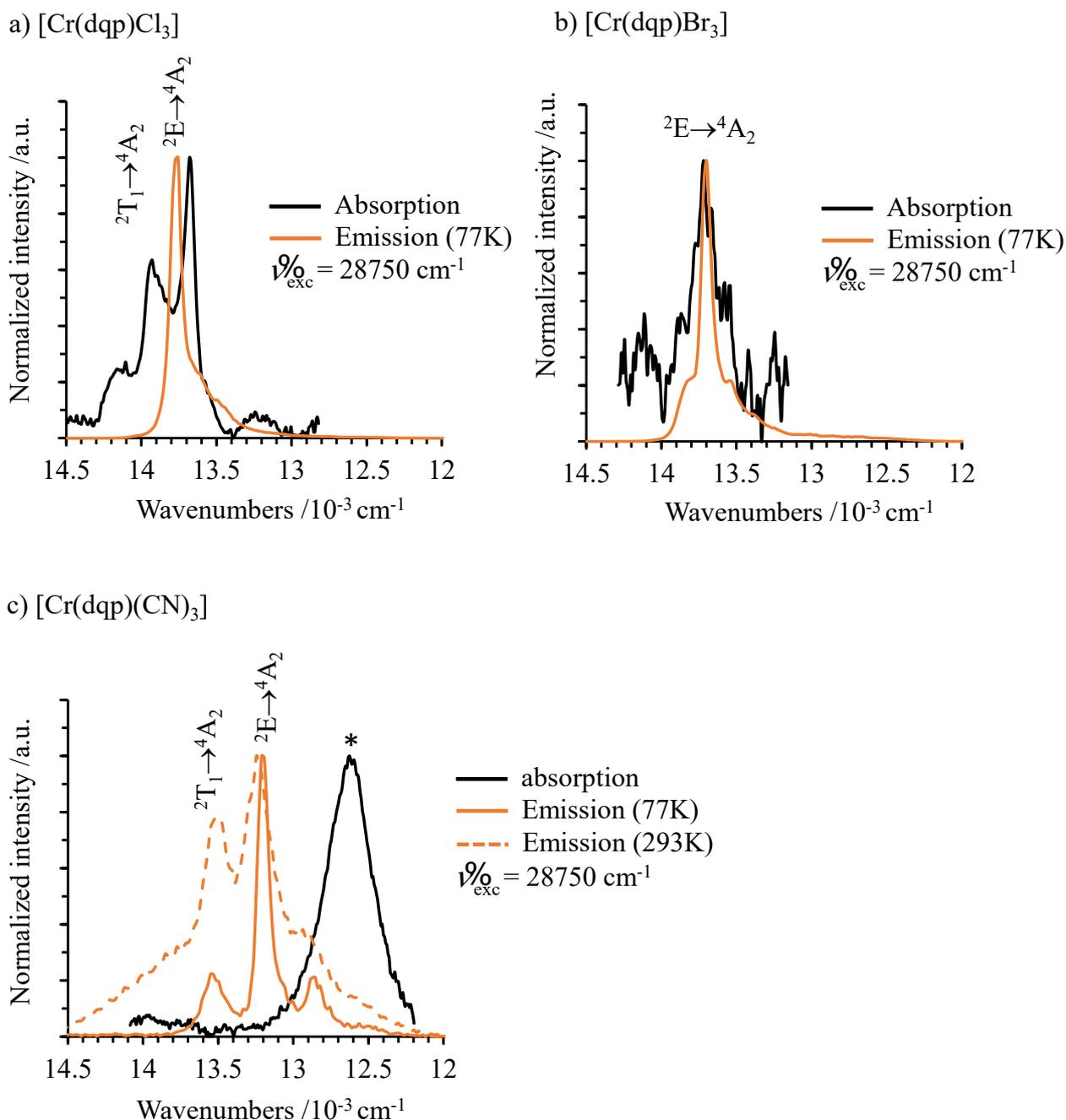
[Cr(tpy)(CN)$_3$]

Cr	0.00000000	0.91096400	-0.00005700
N	2.04721100	0.48002200	-0.00010200
N	0.00000000	-1.10817400	0.00007400
N	-2.04721100	0.48002100	0.00004500
N	-0.00011500	0.95894400	-3.24722300
N	-0.00000200	4.14062500	-0.00028300
N	0.00011900	0.95938500	3.24710300
C	3.03378100	1.38812400	-0.00019500
H	2.72683900	2.42754100	-0.00025300
C	4.37676500	1.01962200	-0.00021700
H	5.14368700	1.78500000	-0.00029400
C	4.69912900	-0.33572600	-0.00013700
H	5.73482200	-0.65760900	-0.00015100
C	3.67455000	-1.28167000	-0.00004000
H	3.90565300	-2.33958200	0.00002300
C	2.35012100	-0.84762700	-0.00002400
C	1.18102900	-1.75262100	0.00007200
C	1.21215000	-3.14883100	0.00015300
H	2.15045900	-3.68878500	0.00015100
C	0.00000000	-3.83986900	0.00023500
H	0.00000000	-4.92424200	0.00029800
C	-1.21215000	-3.14883100	0.00023600
H	-2.15045800	-3.68878600	0.00029900
C	-1.18102900	-1.75262200	0.00015300
C	-2.35012100	-0.84762700	0.00013800
C	-3.67455000	-1.28167100	0.00021100
H	-3.90565400	-2.33958300	0.00028500
C	-4.69912900	-0.33572700	0.00018900
H	-5.73482200	-0.65761000	0.00024600
C	-4.37676500	1.01962100	0.00009500
H	-5.14368700	1.78500000	0.00007500
C	-3.03378100	1.38812300	0.00002400
H	-2.72684000	2.42754000	-0.00005000
C	-0.00007500	0.94582500	-2.07773400
C	-0.00000300	2.97076900	-0.00020300
C	0.00007600	0.94611000	2.07761600

[Cr(ddpd)(CN)₃]

Cr	-0.00000100	0.84577500	-0.00000100
N	2.02544800	0.71955600	0.48040600
N	0.00000100	-1.24238700	-0.00000400
N	-0.00000600	4.07621800	0.00001500
N	0.67669600	1.03311000	-3.17986400
N	2.22116300	-1.21585900	-0.86986300
C	-0.00000500	2.90673200	0.00000900
C	0.45891800	0.93829500	-2.03434400
C	2.58687500	1.66751800	1.26795400
H	1.89549400	2.35217400	1.74024600
C	3.95258300	1.78347400	1.44507900
H	4.35260100	2.56889700	2.07469700
C	4.78153800	0.87000200	0.78688300
H	5.85984900	0.92115200	0.89668300
C	4.21634700	-0.12995800	0.01126800
H	4.84449500	-0.87048700	-0.46383900
C	2.81649100	-0.19811000	-0.11485100
C	3.04068900	-1.85166700	-1.91298600
H	3.75612100	-2.58176300	-1.51816800
H	3.58474300	-1.07290100	-2.44837700
H	2.37656100	-2.35012600	-2.61860900
C	1.09123200	-1.92736200	-0.42519000
C	1.11836300	-3.32561200	-0.43756900
H	2.00853400	-3.85354500	-0.74951900
C	0.00000800	-4.02162700	0.00000000
H	0.00001000	-5.10647300	0.00000200
N	-2.02544700	0.71955000	-0.48040900
N	-2.22116200	-1.21587000	0.86985400
C	-2.58687500	1.66751400	-1.26795500
H	-1.89549400	2.35216800	-1.74024900
C	-3.95258300	1.78347200	-1.44507500
H	-4.35260100	2.56889700	-2.07469100
C	-4.78153800	0.87000200	-0.78687700
H	-5.85984900	0.92115400	-0.89667300
C	-4.21634600	-0.12996000	-0.01126500
H	-4.84449400	-0.87048900	0.46384300
C	-2.81649000	-0.19811600	0.11484900
C	-3.04068600	-1.85167900	1.91297800
H	-3.75611800	-2.58177500	1.51816000
H	-3.58473800	-1.07291400	2.44837200
H	-2.37655600	-2.35013900	2.61859900

C	-1.09122700	-1.92736600	0.42518500
C	-1.11835000	-3.32561600	0.43756800
H	-2.00852000	-3.85355300	0.74951800
N	-0.67671500	1.03308800	3.17986100
C	-0.45892200	0.93827700	2.03434400

[Cr(dqp)(CN)₃]

Cr	0.00000000	-0.81610500	0.00000300
N	1.92334100	-0.74770100	-0.84799500
N	0.00000000	1.27051300	0.00000000
N	-1.92334300	-0.74769900	0.84799600
C	2.32007700	-1.75477400	-1.62466400
H	1.53486900	-2.34135200	-2.08418100
C	3.67023100	-2.09171100	-1.81725700
H	3.92659200	-2.91814700	-2.46907700
C	4.62428600	-1.39832900	-1.10940500
H	5.67322300	-1.67315400	-1.16582300
C	4.24195700	-0.30403500	-0.29508300
C	5.18760100	0.42329800	0.47102100
H	6.22910600	0.11883400	0.44620700
C	4.77330700	1.48612200	1.23811000
H	5.47762500	2.02905300	1.85885700
C	3.43148100	1.91357300	1.18071200
H	3.15022800	2.79146800	1.75074600
C	2.46755900	1.26267200	0.41601000
C	2.85855500	0.05914400	-0.25210400
C	1.16271500	1.94969100	0.19960000
C	1.18298700	3.35180800	0.15714100
H	2.12298300	3.88010000	0.23513800
C	0.00000400	4.05660800	-0.00001000
H	0.00000600	5.14136100	-0.00001400
C	-1.18298000	3.35181000	-0.15715400
H	-2.12297400	3.88010600	-0.23515500
C	-1.16271300	1.94969300	-0.19960400
C	-2.46756000	1.26267700	-0.41600800
C	-3.43148200	1.91358000	-1.18070700
H	-3.15022900	2.79147500	-1.75074000
C	-4.77330900	1.48613200	-1.23810300
H	-5.47762700	2.02906700	-1.85884600
C	-5.18760300	0.42330500	-0.47101900
H	-6.22910800	0.11884200	-0.44620600

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C        -4.24195800    -0.30403300     0.29508000
C        -2.85855600     0.05914700     0.25210400
C        -4.62428700    -1.39833500     1.10939100
H        -5.67322300    -1.67316600     1.16580100
C        -3.67023300    -2.09171900     1.81724300
H        -3.92659500    -2.91816100     2.46905500
C        -2.32008000    -1.75477600     1.62465900
H        -1.53487200    -2.34135200     2.08418000
C         0.79060000    -0.91620400     1.92911200
N         1.17681500    -1.01390600     3.02888100
C         0.00000500    -2.88369800     0.00000800
N         0.00000900    -4.05312100     0.00000900
C        -0.79060500    -0.91622200    -1.92910300
N        -1.17682200    -1.01394500    -3.02886900
```

References

S1   C. K. Jorgensen, *Adv. Chem. Phys.*, **1963**, *5*, 33-146.

S2   J.-R. Jiménez, B. Doistau, C. Besnard and C. Piguet, *Chem. Commun.*, **2018**, *54*, 13228-13231.

S3   S. Otto, M. Dorn, C. Förster, M. Bauer, M. Seitz and K. Heinze, *Coord. Chem. Rev.*, **2018**, *359*, 102-111.

S4   J.-R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campana and C. Piguet, *J. Am. Chem. Soc.*, **2019**, *141*, 13244-13252.

S5   Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

S6   N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comp. Chem.*, **2008**, *29*, 839-845.

S7   GaussView, Version 6.1.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, **2016**.