Cr\textsuperscript{III} as an alternative to Ru\textsuperscript{II} in metallo-supramolecular chemistry†

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Compared to divalent ruthenium coordination complexes, which are widely exploited as parts of multi-component photonic devices, optically active trivalent chromium complexes are under-represented in multi-metallic supramolecular architectures performing energy conversion mainly because of the tricky preparation of stable heteroleptic Cr\textsuperscript{III} building blocks. We herein propose some improvements with the synthesis of a novel family of kinetically inert heteroleptic bis-terdentate mononuclear complexes, which can be incorporated into dinuclear rod-like dyads as a proof-of-concept. The mechanism and magnitude of intermetallic Cr...Cr communication have been unraveled by a combination of magnetic, photophysical and thermodynamic investigations. Alternated aromatic/alkyne connectors provided by Sonogashira coupling reactions emerge as the most efficient wires for long-distance communication between two chromium centres bridged by Janus-type back-to-back bis-terdentate receptors.

Introduction

Since the discovery of chromium by Louis Nicolas Vauquelin in 1798, chromium derivatives, particularly in their most stable oxidation state Cr\textsuperscript{III}, have been widely studied for their catalytic,1–3 hole transfer ability in photo-cathodic solar cells,4,5 magnetic,6–12 and optical properties.13–15 The latter aspect culminated with the building of the first laser in 1960,16 which exploited the stimulated emission of electro-magnetic radiation from the Cr\textsuperscript{III}-centred excited levels found in ruby. Despite its appealing electronic properties, Cr\textsuperscript{III} has been scarcely introduced into polymeric supramolecular architectures working as photonic devices,17,18 whereas hundreds, if not thousands of sophisticated structures built with luminescent divalent ruthenium complexes have been designed and tested so far.19–24 The main reason for this side-lining can be found in the Cr\textsuperscript{III} coordination chemistry, which somehow mirrors that of trivalent cobalt with the formation of kinetically inert complexes as exemplified by the very small rate constants found for ligand exchange (e.g., $k_{\text{H}_2\text{O}} = 2.4 \times 10^{-6}$ s\textsuperscript{-1} for [Cr(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{3+} and for hydrolysis (e.g., $k_{\text{hydrolysis}} = 3.5 \times 10^{-4}$ s\textsuperscript{-1} for cis-[Cr(ethylenediamine)\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+} under acidic conditions).26 Consequently, Cr\textsuperscript{III} cannot be part of sophisticated multi-component self-assembly processes, in which structural self-healing under thermodynamic control is crucial.27 Some rare (but remarkable) exceptions arose with (i) the serendipitous crystallization by Winpenny and coworkers of poly-chromium wheels at high temperatures (210 °C to 400 °C) using thermally resistant ligands28–30 and (ii) the use of preformed chromium complexes working as inert partners for the preparation of hydroxo,31 oxalato,32,33–36 and cyano bridged architectures.7,9,37 In this context, post-modifications were recently shown to open novel pathways for the stepwise building of multi-metallic assemblies including inert ruthenium–poly(pyridine) complexes18–40 or platinum–salen derivatives,41,42 but the manipulation of related Cr\textsuperscript{III}–poly(pyridine) entities remains scarce and elusive.43–45 Moreover, recent demonstration that [Cr(2,2′-6′,2′-terpyridine)\textsubscript{3}]\textsuperscript{3+} (=[Cr(tpy)\textsubscript{3}]\textsuperscript{3+}) complexes rapidly dissociate under slightly alkaline conditions,46 a trend which confirms a previous observation reported for [Cr(2,2′-bipyridine)\textsubscript{3}]\textsuperscript{3+} (=[Cr(bpy)\textsubscript{3}]\textsuperscript{3+}),47 prevents post-treatment of these complexes for the design of organized polynuclear assemblies. To the best of our knowledge, trivalent chromium has thus never been used as a partner for thermodynamic multi-component self-assembly processes occurring in solution, but its labile divalent precursor Cr\textsuperscript{II} was shown to successfully promote the synthesis of heterometallic d-f triple-
stranded helicates under thermodynamic control.\textsuperscript{48,49} Subsequent air oxidation led to inert luminescent Cr\textsuperscript{III} sensitizers, which induced unprecedented lanthanide-centred molecular energy-transfer upconversion.\textsuperscript{50–53} Last but not least, the characterization of Cr\textsuperscript{III} complexes in solution is severely hampered by the broad and poorly interpretable NMR signals produced by the long electronic relaxation times (about 0.5 ns) of their zero-field split Cr(4A2) ground state.\textsuperscript{54} This drawback is overcome for diamagnetic Ru\textsuperscript{II} complexes, which were thus selected for building well-defined photoactive polynuclear architectures useful for water splitting,\textsuperscript{55} light-harvesting and energy conversion.\textsuperscript{56–58} Nevertheless, while trivalent chromium exhibits some shortcomings compared to divalent ruthenium, its photophysical properties in pseudo-octahedral complexes offer some unparalleled attractiveness since the visible window is dominated by a single spin-allowed absorption band corresponding to the Cr(4T2 ← 4A2) transition, the energy of which can be easily tuned by the ligand-field parameter $\Delta$, whereas the near-infrared window is governed by efficient long-lived Cr(2E ← 4A2) phosphorescence, the energy of which is controlled by the nephelauxetic effect tuned by the Racah parameters $B$ and $C$ (Fig. 1).\textsuperscript{13,59,60} It is thus trivial to switch from low-energy absorption combined with high-energy phosphorescence found in CrN\textsubscript{6} chromophores (small values of $\Delta$ and large values of $B$) toward the opposite situation found in CrO\textsubscript{6} chromophores.\textsuperscript{51} Furthermore, the almost spin-only behavior combined with negligible zero-field splitting parameters measured for the degenerate paramagnetic Cr(4A2) ground state (for instance $D = 0.03$ cm$^{-1}$ for [(tpy)CrCl\textsubscript{3}])\textsuperscript{61} offers a simple approach for unravelling electronic intermetallic communications via the estimation of the isotropic exchange coupling constant operating between chromium centres.\textsuperscript{10,12,62}

In diamagnetic polynuclear Ru\textsuperscript{II} architectures, for which the Creutz-Taube complex is the archetype (Fig. 2a),\textsuperscript{63} the magnitude of the intermetallic interaction is deduced from the envelope of the intervalence electronic absorption bands occurring in mixed valence Ru\textsuperscript{II}–Ru\textsuperscript{III} dimers.\textsuperscript{64–68} When applied to back-to-back bis-terpyridine bridging ligands L in [(tpy)Ru(L)Ru(tpy)]\textsuperscript{m+} (Fig. 2b), the associated theories successfully rationalized the exponential decrease of the electronic interaction parameter with increasing intermetallic separations\textsuperscript{69–71} and the magnification of both through-bond electron transfer (Fig. 2c)\textsuperscript{72,73} and energy transfer (Fig. 2d)\textsuperscript{74–78} for short electron-rich aromatic bridges. Unfortunately, one-electron reductions of [Cr(bpy)\textsubscript{3}]\textsuperscript{3+} and [Cr(tpy)\textsubscript{3}]\textsuperscript{3+} occur on the bound ligands\textsuperscript{79,80} and no related approach can be envisioned for unravelling intermetallic coupling in analogous polypyridine Cr\textsuperscript{III} complexes.

![Fig. 1 Low-energy part of the energy level diagram for an octahedral Cr\textsuperscript{III} sensitizer showing the energy levels modeled in terms of the ligand field strength $\Delta$ and the Racah parameters $B$ and $C$.\textsuperscript{59,60} The upward green arrow stands for the lowest-energy spin-allowed absorption transition, while the downward red arrow refers to the lowest-energy phosphorescence.](image-url)

![Fig. 2 (a) Creutz-Taube complex, (b) [(tpy)Ru(L)Ru(tpy)]\textsuperscript{m+} complexes, (c) [(tpy)Ru(L)Co(tpy)]\textsuperscript{m+} complexes displaying directional electron transfer, (d) [(tpy)Ru(L)Os(tpy)]\textsuperscript{m+} complexes displaying directional energy transfer.](image-url)
Results and discussion

Synthesis and characterization of homolectic and heteroleptic mononuclear [CrLCl3], [CrL2](PF6)3 (L = tpy, ebzpy, tppz) and dinuclear [Cl3Cr(L)CrCl3], [(tpy)Cr(L)Cr(tpy)](PF6)6, (L = tppz, bbt, ebbt) complexes

As a first step toward this goal, we used GaIII as a trivalent labile diamagnetic model cation for CrIII for the straightforward formation of a homolectic [Ga(tpy)3]3+ (Table S1, ESI†), which displayed the expected well-resolved $D_{3h}$-symmetrical $^1$H NMR spectrum (6 signals observed for 22 available aromatic protons, Fig. S1, ESI†). The downfield shifts of the aromatic signal ($\Delta \delta = -1.01$ ppm) observed for the hydrogen nuclei located at the ortho-positions of the nitrogen atoms of the distal pyridine rings are diagnostic for an ortho-
gonal arrangement of the two planar tridentate terpyridine ligands around the central cation as found in [Fe(tpy)3]$^{2+}$ ($\Delta \delta = -1.64$ ppm), [Ru(tpy)3]$^{2+}$ ($\Delta \delta = -1.37$ ppm) and [Os(tpy)3]$^{2+}$ ($\Delta \delta = -1.43$ ppm). The crystal structure of [Ga(tpy)3](PF6)2·2CH3CN (1, Fig. 3 left, Fig. S2 and Tables S2, S4 and S5†) confirmed this statement with an interplanar angle of 88.5° between the two tridentate $N_3$ chelates. Combined with the pincer effect brought by the two-fused 5-membered chelate rings in the terpyridine moieties ($N_{\text{distal}}$-Cr–$N_{\text{distal}}$ = 156.6(1)° instead of 180° expected for octahedral geometry, see Fig. 3), the diamagnetic GaN6 core adopts the expected compact and slightly distorted pseudo-octahedral geometry previously reported for other [M(tpy)3]$^{2+}$ ($z = 2, 3$) complexes.86,87 No specific close-packing interactions due to significant $\pi$-$\pi$ aromatic interactions compatible with ‘terpyridine embrace’ supramolecular patterns87 could be identified (the closest inter-aromatic distance amounts to 4.5 Å, far beyond the accepted cutoff of 3.8 Å for $\pi$-stacking interactions; Fig. S3†).88,89 We however note that [Ga(tpy)3][PF6]2·2CH3CN (1) crystallizes in the chiral $P2_12_12$ space group, the origin of which probably arises from packing effects since [Ga(tpy)3]$^{3+}$ cations are essentially achiral. In order to overcome the complications produced by the kinetic inertness of CrIII salts, the related homolectic complex [Cr(tpy)3]$^{3+}$ is obtained by the reaction of the reduced labile precursor Cr(CF3SO3)2·H2O48 with 2,2′,6′,2′-terpyridine (tpy), or with its extended analogue 2,6-bis(1-ethyl-benzimidazol-2-yl)pyridine (ebzpy),90 to give saturated six-coordinated CrIII complexes.80 Subsequent air oxidation (outer sphere mechanism)48 provides [Cr(tpy)3](PF6)2·2.5CH3CN (2, Fig. S4 and Tables S2, S6 and S7, ESI†) and [Cr(ebzpy)3](PF6)2·5.5CH3CN (3, Fig. S5 and Tables S3, S8–S11, ESI†) in 70–80% yields after metathesis with PF6− (Fig. 3).

![Scheme 1 Structures and nomenclature of the investigated dinuclear chromium complexes. tppz = 2,3,5,6-tetra-2-pyridinylpyrazine, bbt = 4,4′-bis(2,2′-6′,2′-terpyridine), and ebbt = 4,4′-(ethynyl)-bis(2,2′-6′,2′-terpyridine). $X_3$ stands for Cl3 or 2.2′-6′,2′-terpyridine.](Image 14x290 to 26x354)

![Fig. 3 Synthesis of the homolectic tricationic [Ga(tpy)3]$^{3+}$ [Cr(tpy)3]$^{3+}$ and [Cripebzpy)3]$^{3+}$ complexes. The molecular structures of the cations are those found in the crystal structures of [Ga(tpy)3](PF6)2·2CH3CN (1), [Cr(tpy)3](PF6)2·2.5CH3CN (2) and [Cripebzpy)3](PF6)2·5.5CH3CN (3). The hydrogen atoms have been omitted for clarity. Color code: C = grey, N = blue, Cr = orange, Ga = green.](Image 309x128 to 544x308)
The molecular structures of the CrN₆ (2 and 3) and GaN₆ (1) moieties are almost superimposable and closely match that previously reported for [Cr(tpy)][(ClO₄)₃]·H₂O.⁹¹,⁹² Again, intermolecular packing interactions are very limited for these chromium complexes (Fig. S6 and S7, ESI†), a trend assigned to the combination of (i) the considerable inter-cation repulsions and (ii) the delicate accommodation of three counter-anions per cationic complex in the crystal structures.⁴⁶ We would like to stress here that the crystal structure of 2, monitored at 180 K in this work, is identical to that previously deposited for 2([Cr(tpy)][(PF₆)₃])·5CH₃CN recorded at 123 K,⁴⁶ an observation which confirms the robustness of the packing process despite the lack of identifiable strong intermolecular interactions in the crystal structures of these [Cr(tpy)₂]X₂ complexes.

Since no high-resolution NMR signals could be recorded for the slow-relaxing CrIII complexes, their magnetic characterization in solution is restricted to the measurement of the effective magnetic moments in acetonitrile for [Cr(tpy)][(PF₆)₃] (μeff = 4.4(4) BM) and [Cr(ebzpy)][(PF₆)₃] (μeff = 4.2(4) BM), which only slightly deviate from the spin-only value (μeff = 3.88 BM). Unfortunately, we were not able to record satisfying ESI-MS spectra for these mononuclear triply-charged complexes in solution, probably because of partial dissociation occurring during the vaporization process.⁴⁶

Higher structural complexity requires the rational synthesis of heteroleptic bis-terdentate CrN₆ chromophores following the strategy originally proposed by Barker et al. for bidentate phenanthroline ligands⁸¹ and adapted for tridentate terpyridines by Housecroft and Constable and coworkers (Fig. 4).⁴⁶,⁹⁴ Beyond [Cr(tpy)Cl₂], the structure of which was previously reported (Fig. 4 top centre),⁶¹,⁹³ we confirm that the three weakly bound THF molecules in CrCl₃(THF)₃ can be displaced by closely related tridentate ligands⁹⁴ to give [Cr(ebzpy)Cl₂]DMF (5, Tables S12–S14 and Fig. S8 and S9†) and [Cr(tppz)Cl₂]DMF (6, Tables S12, S15, and S16 and Fig. S8 and S9†). The three CrN₃ chelate units are almost superimposable showing similar bond distances (Cr–N = 2.05(3) Å) and bond angles (average pincer angle θpincer = 116.5 (5)°). The crystal structure of [Cr(tppz)Cl₂] (6) reveals specific geometric distortions at the metal centre caused by the repulsion of the hydrogen atoms at the 3-position of the bound pyridine rings with the two unbound pyridine units. The result is a twisting of the bound part of the tp pz ligand, in which the dihedral angles between the pyridine and pyrazine rings amount to 19.46°. The reaction of [Cr(L)Cl₂] with concentrated trifluoromethanesulfonic acid (CF₃SO₃H) displaces the three chloride anions to give [Cr(L)(CF₃SO₃)] (L = tpy, tp pz, Table S1†). The slightly more basic ebzpy ligand (compared with tpy and tp pz) did not resist protonation and only [H₂ebzpy][CF₃SO₃] could be isolated (10, Fig. S10 and Tables S17 and S18†). Subsequent mixing of [Cr(L)(CF₃SO₃)] with a second tridentate ligand L’ either restores the homoleptic complexes (L’ = L) or provides (L’ ≠ L) the heteroleptic complexes [Cr(tpy)(ebzpy)][(PF₆)₃] (7, Fig. S11 and Tables S17, S19 and S20†) and [Cr(tpy)(tppz)][(PF₆)₃] (8, Fig. S12 and Tables S21–S25†) in fair to good yields (Fig. 4 bottom). Their molecular structures show CrN₆ units almost superimposable with those found in the homoleptic model cations [Cr(tpy)₂]³⁺ and [Cr(ebzpy)₂]³⁺. Again, no remarkable intermolecular π-stacking interactions could be highlighted (Fig. S13 and S14†) and the structural distortion produced by steric congestion with the coordinated pyridine rings in the tp pz ligand is retained in [Cr(tpy)(tppz)] (the average dihedral angle between the pyridine and pyrazine rings in the tridentate bound unit amounts to 19.46°).

With this strategy at hand, the synthesis of a series of six rod-like heteroleptic dinuclear CrIII complexes with three different bridging ligands (tppz, bbt, and eb b t) and two types of capping entities (Cl₃ or tpy) can be envisioned. Firstly, the reaction of an excess of CrCl₃·6H₂O with the appropriate bridging ligand³⁵ quantitatively yields [Cr₂Cl₆(tppz)] and [Cr₂Cl₆(bbt)], while [Cr₂Cl₆(e b b t)] is obtained with more difficulties because of the low solubility of the free ligand in common organic solvents (left part of Fig. 5 and Table S1†).
activities dedicated to these specific supramolecular architectures. The intermetallic separation is fixed to ca. 10.9 Å by the back-to-back bis(terpyridine) spacer (Fig. 5). The dihedral angle within the bridging 4,4’-bipyrindine motif amounts to 36.5(4)° in [Cr2Cl6(bbt)] and to 83.0(1)° in [Cr2(tpy)2(bbt)][PF6]h. While the smaller angle matches the theoretically computed interplanar angle of 35–40°, which simultaneously minimizes the torsion energy and optimizes orbital overlap in 4,4’-bipyrindine, the almost orthogonal arrangement of the two central pyridine rings found in [Cr2(tpy)2(bbt)][PF6]h is unique for this spacer since the largest value reported so far reached 61(1)° for a dinuclear copper(II) complex. Four PF6− counter-ions are located between the two CrN6 units of the dinuclear complex. They are involved in twelve C–H···F–P hydrogen bonds (2.4 Å to 2.6 Å), which significantly stabilize the orthogonal arrangement of the central back-to-back bis(terpyridine) spacer (Fig. S18†). The crystal structure of [Cr2(tpy)2(ebbt)][PF6]·10CH3CN·(CH3CH2)2O (14, Fig. S19 and Tables S31, S34 and S35) obviously displays not only the longest intramolecular Cr···Cr distance (13.4669(6) Å, Fig. 5), but also the smallest dihedral angle between the two quasi-planar terpyridine units connected by the alkyne bridge (0.1(3)°). To the best of our knowledge, no molecular structure has been previously reported with this extended ebbt ligand. We are now in a position to investigate the nature and magnitude of intramolecular intermetallic interactions operating between pseudo-octahedral CrIII metallic cations incorporated into rod-like heteroleptic dyads possessing variable lengths.

Unravelling intermetallic communication in dinuclear [Cl3Cr(L)CrCl3] † [tpy]Cr(L)Cr(tpy)][PF6]h complexes (L = tppz, bbt, ebbt): magnetic evidence

Two trivalent CrIII centres connected by short oxide bridges usually display strong anti-ferromagnetic interaction (Jex < 0) operating between the two S = 3/2 spin carriers via a super-exchange mechanism. Application of the van Vleck equation to a coupled CrIII pair obeying the Heisenberg–Dirac–van Vleck spin Hamiltonian HVV = −JexԭSB (ԭ and S are the spin operators localized on each metallic centre and Jex is the phenomenological magnetic exchange coupling constant) provides a contribution to the paramagnetic susceptibility \( \chi_{\text{dimer}} \) expressed in eqn (1), where g is the Landé factor, \( N_d = 6.022 \times 10^{23} \) mol−1 is Avogadro’s number, \( \mu_B = 9.274 \times 10^{-24} \) J K−1 is the Bohr magneton and \( k_B = 1.3806 \times 10^{-23} \) J K−1 is the Boltzmann constant.

\[
\chi_{\text{dimer}} = \frac{N_A g^2 \mu_B^2}{k_B T} \left( 2e^{\mu_B/2k_B T} + 10e^{\mu_B/k_B T} + 28e^{\mu_B/4k_B T} - 30e^{\mu_B/6k_B T} + 7e^{\mu_B/8k_B T} \right)
\]  

(1)

Compared with \( \chi_{\text{ex}} \) values expected in the 1–10 cm−1 range for the [X,Cr(L)CrX3] dyes, the weak contribution of the zero-field splitting \( D = 0.03 \) cm−1 for [Cr(tpy)Cl3], \( D = 0.2 \) cm−1 for [Cr(tpy)Cl3](1) and \( D = 0.1 \) cm−1 for [Cr(tpy)Cl3](2) can be neglected and the magnetic susceptibilities recorded in the 2–300 K range for the five dinemic complexes (Fig. 6 plotted as \( \chi T \) vs. \( T \) ) could be satisfyingly fitted to eqn (2), where \( \chi_{\text{dimer}} \) is given in eqn (1), \( \chi_{\text{dia}} \) is the diamag-
the natural magnetic orbitals \((t_{2g})\) for a pseudo-octahedral \(\text{Cr}^{III}\) complex) with respect to that of the HOMO orbital of the bridging ligand. Applying this reasoning to the replacement of three anionic \(\pi\)-donor chloride ligands in \([\text{Cl}_3\text{Cr}\text{bbt}\text{CrCl}_3]\) with three \(\pi\)-acceptor heterocyclic nitrogen atoms in the capping terpyridine units in \([\text{tpy}\text{Cr}\text{bbt}\text{Cr(tpy)}]^+\) is expected to decrease the energy of the \(\text{Cr}\)-centred pseudo-\(t_{2g}\) magnetic orbitals, thus favoring their mixing with the occupied molecular orbitals of the back-to-back bis(terpyridine) bridge. A thorough theoretical approach dealing with Fe\(^{III}\)-Cu\(^{III}\) complexes recently confirmed the prospective dependence of the exchange interaction constant with the nature of the ligand field. Finally, the \emph{a priori} surprising increase of the anti-ferromagnetic interaction accompanying the 24% increase of the intermetallic distance on going from \([\text{tpy}\text{Cr}\text{(bbt)Cr(tpy)}]^+\) (\(\text{Cr} \cdots \text{Cr} = 10.9 \text{ Å}, J_{\text{ex}} = -2.37 \text{ cm}^{-1}\), red trace) to \([\text{tpy}\text{Cr}(\text{ebbt})\text{Cr(tpy)}]^+\) (\(\text{Cr} \cdots \text{Cr} = 13.5 \text{ Å}, J_{\text{ex}} = -2.78 \text{ cm}^{-1}\), violet trace) can be assigned to the beneficial effect of the bridging alkyne unit, which reduces the dihedral angle between the connected pyridine rings from 83.2(3)° in the bbt spacer to 0.1(3)° in the ebbt analog and thus favors the overlap integral leading to detectable intramolecular anti-ferromagnetic interactions on the nanometric scale.

**Unravelling intermetallic communication in dinuclear \([\text{Cl}_3\text{Cr}(\text{L})\text{CrCl}_3]\), \([\text{tpy}\text{Cr}(\text{L})\text{Cr(tpy)}]\)(PF\(_6\))\(_6\) complexes (L = tppz, bbt, ebbt): optical evidence**

The experimental energies of the \(\text{Cr}^{III}\)-centred excited states (with respect to that of the \(\text{Cr}^4\text{A}_2\) ground state) are deduced from the combination of the absorption (Fig. 7a and b and Appendix 1 in the ESI\(^{†}\)) and emission (Fig. 7c and Appendix 2 in the ESI\(^{†}\)) spectra recorded for the dinuclear complexes in solution and in the solid state (Table 1 columns 7–9). At first sight, the energy of these levels can be roughly modeled by using the diagonal elements of the Tanabe–Sugano matrices assuming a pseudo-octahedral geometry for the \(\text{CrN}_3\text{Cl}_4\) and \(\text{CrN}_6\) chromophores found in \([\text{Cl}_3\text{Cr}(\text{L})\text{CrCl}_3]\) (L = tppz, bbt, ebbt) and \([\text{tpy}\text{Cr}(\text{L})\text{Cr(tpy)}]((\text{PF}_6)_6\) (L = bbt, ebbt).\(^{115}\) However, this level of approximation implies that the \(\text{Cr}^2\text{E}\) and \(\text{Cr}^2\text{T}_1\) states are degenerate, which is clearly not the case in these dimeric complexes (Fig. 7 and Table 1).

The additional consideration of configuration interaction between the states of the same multiplicity and symmetry, but from different strong field configurations led Jorgensen\(^{59}\) to introduce second-order corrections \(ab\Delta^2/\Delta\) in eqn (3)–(5), which are derived from the off-diagonal elements of the Tanabe–Sugano matrices.

\[
E^4(\text{T}_2) = \Delta
\]
\[
E^2(\text{T}_1) = 9B + 3C - 24(B^2/\Delta)
\]
\[
E^2(\text{E}) = 9B + 3C - 90(B^2/\Delta)
\]

Although Jorgensen\(^{59}\) fixed \(C/B = 4\) for deriving eqn (3)–(5), there is no obvious reason for this assumption and a systematic and detailed ligand-field analysis of electronic spectra...
recorded for Cr\textsuperscript{III} compounds revealed that $3 \leq C/B \leq 8$.\textsuperscript{115} In his seminal textbook,\textsuperscript{60} Lever replaced eqn (5) with eqn (6).

$$E(2^E) = 9B + 3C - 50(B^2/\Delta)$$

(6)

This transforms the modelling of the $E(2T_1) - E(2^E)$ energy gap, for which Jorgensen’s approach predicts $66B^2/\Delta$ (eqn (5)), to only $26B^2/\Delta$ (eqn (6)). Compared with the theoretical set of exact energies computed by Ferguson by means of full Eisenstein’s matrices with $B = 680$ cm\textsuperscript{-1} and $C = 2720$ cm\textsuperscript{-1} ($C/\Delta = 4.0$),\textsuperscript{116,117} the exact computed $E(2^T_1) - E(2^E)$ energy gap amounts to 630 cm\textsuperscript{-1} for $\Delta = 19940$ cm\textsuperscript{-1} in fair to good agreement with the prediction of the second-order correction $26B^2/\Delta = 603$ cm\textsuperscript{-1} (eqn (6)), but rather far from 1531 cm\textsuperscript{-1} obtained with eqn (5). We conclude that only a complete ligand-field treatment is capable of extracting reliable Racah parameters $B$ and $C$ for Cr\textsuperscript{III} complexes,\textsuperscript{119} but eqn (6) seems superior to eqn (5) when a rough modeling of the energy of the lowest spin-flip $^4E$ excited state is foreseen. We therefore used eqn (3), (4) and (6) for estimating the ligand-field strength $\Delta$ and the Racah parameters $B$ and $C$ for each dimeric and monomeric complex (Table 1 and Fig. 8, Table S37 and Fig. S20 in the ESI†) together with eqn (7) and (8) for predicting the energy of the missing Cr\textsuperscript{II} to Cr\textsuperscript{II} levels.

$$E(2^T_2) = 15B + 5C - 176(B^2/\Delta)$$

(7)

$$E(4^T_1) = 1.5\Delta + 7.5B - 0.5\sqrt{225B^2 + \Delta^2 - 18B\Delta}$$

(8)

In agreement with both the spectrochemical and the nephelauxetic series,\textsuperscript{118} the ligand-field parameters in mononuclear complexes increase on going from CrN\textsubscript{6}Cl\textsubscript{3} ($16300 \leq \Delta \leq 17000$ cm\textsuperscript{-1}) to CrN\textsubscript{6} ($18750 \leq \Delta \leq 19120$ cm\textsuperscript{-1}), whereas the Racah parameters $B = 682(19)$ cm\textsuperscript{-1} are comparable for both types of chromophores. A narrow distribution of these complexes around $\Delta/B \approx 25$ results in the d\textsuperscript{1} Tanabe-Sugano diagram (Fig. S21†). The latter $\Delta/B$ values are significantly smaller than $\Delta/B = 31.2$ reported for the well-known [Cr(bpy)]\textsubscript{3} (PF\textsubscript{6})\textsubscript{3} complex ($\Delta = 23400$ cm\textsuperscript{-1}, $B = 730$ cm\textsuperscript{-1} and $C = 2730$ cm\textsuperscript{-1}, $C/B = 3.7$)\textsuperscript{119} because the pincer effect produced by 5-membered chelate rings operates four times in [Cr(L)]\textsubscript{3} (L = tpy, ebzpy) and only three times in [Cr(bpy)]\textsubscript{3}\textsuperscript{3+}. This deleterious effect is not a fatality for tridentate ligands and it can be overcome by the use of six-membered chelate rings as found in [Cr(ddpd)]\textsubscript{3} (15) (Fig. S22 and S23 and Tables S38–S40 in the ESI†) and in [Cr(ddpd)]\textsubscript{2}(BF\textsubscript{4})\textsubscript{3} complexes (ddpd = N,N-dimethyl-N,N’-dipyridin-2-ylpyridine-2,6-diamine).\textsuperscript{120} The larger N\textsubscript{distal}–Cr–N\textsubscript{distal} angle of 172.0(9)° observed in [Cr(ddpd)]\textsubscript{3} (compared with 156.5(5)° in [Cr(tpy)]\textsubscript{3}\textsuperscript{3+}) indeed restores a large ligand field strength in bis-terdentate pseudo-octahedral complexes ($\Delta = 22990$ cm\textsuperscript{-1}, Table S37†). Focusing now on the through-bridge effect produced by the connection of a second neutral CrCl\textsubscript{3} unit which transforms [Cr(tpz)Cl\textsubscript{3}] into its dinuclear [Cl\textsubscript{2}Cr(tpz)CrCl\textsubscript{3}] analogue [Cr⋯Cr = 6.66 Å], we observe that $\Delta$ decreases by almost 500 cm\textsuperscript{-1} (Fig. 8). This effect can be taken as an assessment of the mutual polarization (i.e. electronic communication) produced by the two Cr\textsuperscript{II} centres connected to the bridging back-to-back bis-terdentate ligand. Taking now [Cr(tpy)Cl\textsubscript{3}] as the mononuclear reference, the same trend is monitored for [Cl\textsubscript{2}Cr(bbt) CrCl\textsubscript{3}] ($\Delta$ decreases by 300 cm\textsuperscript{-1} for Cr⋯Cr = 10.93 Å) and [Cl\textsubscript{2}Cr(ebbt)CrCl\textsubscript{3}] ($\Delta$ decreases by 200 cm\textsuperscript{-1} for Cr⋯Cr $\geq$ 13 Å), but with an expected attenuation for longer intermetallic distances. For the charged [CrN\textsubscript{6}]\textsuperscript{3+} chromophore found in the mononuclear [Cr(tpy)]\textsubscript{3}\textsuperscript{3+} reference complex ($\Delta = 18750$ cm\textsuperscript{-1}, Table 1), the latter effect is drastically amplified leading to a ca. 2000 cm\textsuperscript{-1} reduction of the ligand-field parameter $\Delta$ in the
Table 1. Ligand-field energy $\Delta$ and Racah parameters (B and C) deduced with eqn (3), (4) and (6) by using the experimental energy of the excited \( \text{Cr}(E) \), \( \text{Cr}(T_2) \) and \( \text{Cr}(T_1) \) levels observed for the dinuclear \([\text{Cl}_3\text{Cr}(L)\text{CrCl}_3]\) and \([\text{tpy}Cr(L)\text{Cr}(tpy)]\langle\text{PF}_6\rangle_6\) complexes \((L = \text{tppz}, \text{tpy}, \text{ebbt})\) and for their mononuclear analogues \([\text{Cl}_3\text{Cr}(L)] \) \((L = \text{tpy}, \text{tpy})\) and \([\text{Cr}(tpy)_2]\langle\text{PF}_6\rangle_3\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta$/cm$^{-1}$</th>
<th>$B$/cm$^{-1}$</th>
<th>$C$/cm$^{-1}$</th>
<th>$\Delta/B$</th>
<th>$E$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cl}_3\text{Cr}(\text{tpy})])</td>
<td>16 000</td>
<td>708</td>
<td>2564</td>
<td>23</td>
<td>3.6</td>
</tr>
<tr>
<td>([\text{Cl}_3\text{Cr}(\text{bbt})])</td>
<td>16 393</td>
<td>648</td>
<td>2785</td>
<td>25</td>
<td>4.3</td>
</tr>
<tr>
<td>([\text{Cl}_3\text{Cr}(\text{ebbt})])</td>
<td>16 502</td>
<td>604</td>
<td>2863</td>
<td>27</td>
<td>4.7</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2][\text{PF}_6])_6</td>
<td>16 722</td>
<td>720</td>
<td>2636</td>
<td>23</td>
<td>3.7</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2][\text{ebbt}][\text{PF}_6])_6</td>
<td>16 474</td>
<td>668</td>
<td>2672</td>
<td>25</td>
<td>4.0</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2][\text{Cl}])_3</td>
<td>16 474</td>
<td>693</td>
<td>2770</td>
<td>24</td>
<td>4.0</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2][\text{PF}_6])_3</td>
<td>18 750</td>
<td>675</td>
<td>2698</td>
<td>28</td>
<td>4.0</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2]\langle\text{PF}_6\rangle_3)</td>
<td>21 980</td>
<td>675</td>
<td>2698</td>
<td>28</td>
<td>4.0</td>
</tr>
</tbody>
</table>

* Energies are given with respect to that of the ground \( \text{Cr}(A_2) \) level. $b$ Computed with eqn (7). $c$ Computed with eqn (8). $d$ The Cr($T_2$) $\sim$ A$_2$ transition could not be unambiguously assigned and the associated Racah parameters were calculated assuming \( C = 4B \). The energy of the Cr($T_1$) level was computed using eqn (4).

Fig. 8 Low-energy part of the energy level diagrams obtained for the dinuclear \([\text{Cl}_3\text{Cr}(L)\text{CrCl}_3]\) and \([\text{tpy}Cr(L)\text{Cr}(tpy)]\langle\text{PF}_6\rangle_6\) complexes \((L = \text{tpy}, \text{bbt}, \text{ebbt}, \text{normal font})\) and for their mononuclear analogues \([\text{Cl}_3\text{Cr}(L)] \) \((L = \text{tpy}, \text{tpy})\) and \([\text{Cr}(tpy)_2]\langle\text{PF}_6\rangle_3\). The ligand-field $\Delta$ parameter is highlighted. Full traces are used for experimentally observed excited levels, whereas dotted traces correspond to calculated levels.

Table 2. Experimental lifetimes found for the dinuclear \([\text{Cl}_3\text{Cr}(L)\text{CrCl}_3]\) and \([\text{tpy}Cr(L)\text{Cr}(tpy)]\langle\text{PF}_6\rangle_6\) complexes \((L = \text{tpy}, \text{bbt}, \text{ebbt})\) and intermetallic energy transfer rate constants \(W_{A\rightarrow D}\) estimated with eqn (9).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\tau$/ns</th>
<th>$\tau$/s</th>
<th>$W_{D\rightarrow A}$/s$^{-1}$</th>
<th>$\text{Cr} \cdots \text{Cr}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cl}_3\text{Cr}(\text{tpy})])</td>
<td>5</td>
<td>3.6(1)</td>
<td>8.2(2) $\times 10^5$</td>
<td>6.660(2)</td>
</tr>
<tr>
<td>([\text{Cl}_3\text{Cr}(\text{bbt})])</td>
<td>5</td>
<td>21(1)</td>
<td>—</td>
<td>10.926(1)</td>
</tr>
<tr>
<td>([\text{Cl}_3\text{Cr}(\text{ebbt})])</td>
<td>3.5</td>
<td>3.6(1)</td>
<td>0.4(1)</td>
<td>2.2(4) $\times 10^{-4}$</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2][\text{bbt}]\langle\text{CF}_3\text{SO}_4\rangle_6)</td>
<td>5</td>
<td>40.3(1)</td>
<td>2.3(3)</td>
<td>4.1(8) $\times 10^7$</td>
</tr>
<tr>
<td>([\text{Cr}(\text{tpy})_2][\text{ebbt}]\langle\text{PF}_6\rangle_3)</td>
<td>3.5</td>
<td>0.24(1)</td>
<td>0.04(1)</td>
<td>2.1(4) $\times 10^{-10}$</td>
</tr>
</tbody>
</table>

$^a$ Intermetallic distance measured in the crystal structures. $^b$ Mono-exponential decay.
Fig. 9  (a) Energy level diagram and (b) kinetic matrix equations for the relaxation of the Cr(2E) excited states in a dinuclear chromium complex with non-equivalent metallic sites (CrD·CrA). \( k_A \) and \( k_D \) are the first-order de-excitation rate constants (sum of radiative and non-radiative processes), whereas \( W_{D\rightarrow A} \) and \( W_{A\rightarrow D} \) are the intramolecular energy transfer rate constants.

exponential decay observed in solid samples of [Cr(urea)\( \text{Cl}_3 \)]\( \text{Cl}_3 \) chromophores.\(^{124} \) It is further supported by the time-resolved luminescence spectra recorded for \([(tpy)Cr(bbt)Cr(tpy)]X_6 \) (X = PF\(_6\) in Fig. 7c and X = CF\(_3\)SO\(_3\) in Fig. A2-13 in Appendix 2\(^{†}\)), which show a faster decay of the high energy part of the emission band (corresponding to the lifetime of CrD(2E)) followed by a longer decay for the low energy part (corresponding to the lifetime of CrA(2E)).

Although the time evolution of the population densities of the three states (\( N^{(i)} \), \( i = 0, 1, 2 \)) can be obtained by numerically solving the kinetic matrix equation shown in Fig. 9b with the help of projection operators and Lagrange-Sylvester formula,\(^{125} \) reasonable approximations assume that (i) the back energy transfer is negligible \((W_{A\rightarrow D} \approx 0)\) for time-resolved measurements performed below 5 K, (ii) the long-lived component \( \tau_1 \) of the bi-exponential decay kinetic trace (Table 2, column 3) reflects the sum of radiative and non-radiative relaxation rate constants of the acceptor \((k_A \approx \tau_1^{-1})\) in Fig. 9 and (iii) \( \tau_1 \) can also be taken as an acceptable estimation for the relaxation rate constant of the donor in the absence of acceptor \((k_D \approx k_A \approx \tau_1^{-1})\) in Fig. 9. With this in mind, the short-lived component \( \tau_2 \) observed in the dinuclear complexes (Table 2, column 4) stands for the sum of the relaxation pathways affecting CrD(2E) (eqn (9) left), from which the intramolecular intermetallic energy transfer rate constants \( W_{D\rightarrow A} \) can be easily deduced (eqn (9) and Table 2 column 5).

\[
\frac{1}{\tau_2} = k_D + W_{D\rightarrow A} \Rightarrow W_{D\rightarrow A} = \frac{1}{\tau_2} - \frac{1}{\tau_1}
\]  

The first striking results concern the rather short characteristic lifetimes 0.2 ≤ \( \tau_1 \) ≤ 40 μs measured for the Cr(2E) levels in the dinuclear complexes in the absence of energy transfer \((\tau_1 = (k_A)^{-1} \approx (k_D)^{-1})\), Table 2, column 3. The reduction by one to two orders of magnitude compared with related data recorded for the mononuclear analogues under the same experimental conditions (solid state, cryogenic temperatures, Table S37\(^{†}\)) are reminiscent of the well-documented\(^{4, 127} \) effect of the reduction in ligand-field strength on the relaxation pathways affecting the Cr(2E) level. For a given chromophore \([\text{CrN}_3\text{Cl}_3] \) in \([\text{Cl}_3\text{Cr}(L)\text{CrCl}_3] \) or Cr\(_6\) in \([[(tpy)\text{Cr}(L)\text{Cr}(tpy)](PF_6)_6] \), we additionally detect a surprising counter-intuitive increase of the intermetallic energy transfer rate constant for larger intramolecular Cr–Cr distances (Table 2). According to the Fermi’s golden rule summarized in eqn (10), the rate of resonant intermetallic energy transfer depends on (i) the spectral overlap integral \( \Omega_{DA} \) between the absorption spectrum of the acceptor A, and the emission spectrum of the donor D and (ii) the perturbation operator \( H_p \) usually modelling the magnitude of through-space (multipolar electrostatic) and/or through-bond (double electronic exchange) communication.\(^{75, 126} \)

\[
W_{D\rightarrow A} \propto (2\pi/\hbar)|\langle DA^\dagger H_p D^\dagger A \rangle|^2 \Omega_{DA}
\]  

Unravelling intermetallic communication in dinuclear \([\text{Cl}_3\text{Cr}(L)\text{CrCl}_3] \), \([(tpy)\text{Cr}(L)\text{Cr}(tpy)](PF_6)_6] \) complexes (\( L = \text{tppz, bbt}, \text{ebbt} \)): thermodynamic evidence

The failure to isolate the dinuclear \([(tpy)\text{Cr(tppz)Cr(tpy)](PF_6)_6}] \) complex from the reaction of \([(tpy)\text{Cr(CF}_3\text{SO}_3)_6] \) with tppz (Fig. 5) suggests the operation of a strong anti-cooperative protocol for the successive binding of two [Cr(tpy)]\(^{2+} \) to the bridging tppz ligand. The spectrophotometric titrations of \([(tpy)\text{Cr}(tppz)]^{2+} \) with \( \text{Er}^{3+} \) in acetonitrile \( \text{Er}^{3+} \) stands for a labile and non-hydrolysable substitute of \([\text{Cr(tpy)}]^{3+} \) confirms the lack of affinity of the available tridentate site of tppz in \([(tpy)\text{Cr}(tppz)]^{3+} \) for a second trivalent cation \( \beta_{11}\text{Cr(tppz)Er}^{3+} \) ≪ 50 in equilibrium (11), Fig. 10.\(^{129} \) A quantitative assessment of the
Table 3 (entries 1 to 5) together with macroscopic formation constants gathered in the stoichiometry of two-dimensional and three-dimensional polymers. The resulting changes in the absorption spectra are characterized by smooth end points occurring at Eu : L = 1 : 3, Eu : L = 1 : 2, Eu : L = 1 : 1 (Fig. 11a and b for L = tppz and Fig. S24a for L = bbt in the ESI†). Factor analysis (Fig. 11c and Fig. S24c†) followed by non-linear least square fits† to equilibria (12)–(15) leads to eqn (16)–(19) for the titration of [(tpy)Cr(tppz)]3+ (2 × 10−4 M) with Er(CF3SO3)3 in acetonitrile (298 K).

Monitoring these titrations using light-scattering techniques did not reveal any sign of aggregation due to the formation of a bis-terdentate ligand and a back-to-back bis-terdentate ligand. Application of the site binding model (eqn (16)) involving a back-to-back bis-terdentate ligand and a back-to-back bis-terdentate ligand with the successive binding of ligands to the same site taken separately. As expected, the successive binding of products (Appendix 3 in the ESI†) provides satisfying reconstructed thermodynamic descriptors collected in Table 3 (entries 1–4).

The intrinsic affinity of the tridentate N3 binding units for the entering trivalent Er3+ cation in the bridging bbt ligand Er(N3)3.bbt = −2.303 · RT log(fEr3+ tppz)/fEr3+ bbt = −40(2) kJ mol−1 perfectly matches the one previously reported for the monomeric precursor terpyridine (tpy) ligand under similar conditions (acetonitrile, 298 K).135 This implies that, beyond an obvious statistical factor of 2, the connection of a second tridentate binding unit in the back of the original terpyridine units to give bbt has little effect on the binding properties of the tridentate N3 site taken separately. As expected, the successive binding of several tridentate N3 units to the same trivalent Er3+ centre is accompanied by some minor anti-cooperative processes (ΔL18Er = 9(2) kJ mol−1 for bbt and 6(2) kJ mol−1 for tpy) resulting from the stepwise neutralization of the positive metallic charge by an increasing number of bound nitrogen donors.135

With this in mind, it appears logical that the much less basic bridging pyrazine ring found in tppz (pKα = 0.37),136 compared with the 4,4′-bipyridine bridge in bbt (pKα = 4.8),137 leads to both a reduced affinity for Er3+ (ΔGEr3+ tppz = −32(2) kJ mol−1) and a smaller ligand–ligand interaction (ΔfEr3+ tppz = 5(3).

![Fig. 10](image-url) (a) Variation of absorption spectra, (b) corresponding variation of molar extinctions and (c) proposed modeling (ψEr3+ Cr(tppz) ≪ 50) for the titration of [(tpy)Cr(tppz)]3+ (2 × 10−4 M) with Er(CF3SO3)3 in acetonitrile (298 K).
kJ mol\(^{-1}\)). However, the most noteworthy thermodynamic result concerns the considerable anti-cooperative mechanism accompanying the successive fixation of two Er\(^{3+}\) cations onto the bridging ligand, which are diagnostic for the operation of intermetallic electrostatic communication on the nanometric scale in these polyaromatic dyads. The large value \(\Delta G_{\text{Er-Er}}^{\text{tppz}} = 18(5)\) kJ mol\(^{-1}\) found for the short-bridging tppz ligand combined with its limited intrinsic affinity \(\Delta G_{\text{N3-tppz}}^{\text{Er}}\) explains the difficulties in isolating dinuclear \([\text{X}_3\text{Cr(tppz)CrX}_3]\) complexes. The smaller anti-cooperative effect observed for bbt (\(\Delta G_{\text{bbt-Er}}^{\text{Er}} = 12(5)\) kJ mol\(^{-1}\)) restores sufficient affinity for the formation of dinuclear \([\text{X}_3\text{Cr(bbt)CrX}_3]\) complexes.

Fig. 11 (a) Variation of absorption spectra and (b) corresponding variation of observed molar extinctions at different wavelengths observed for the spectrophotometric titration of tppz with Er\((\text{CF}_3\text{SO}_3)\)\(_3\) (total ligand concentration: \(8 \times 10^{-5}\) mol dm\(^{-3}\) in CH\(_3\)CN : CHCl\(_3\) = 65 : 35, 298 K). (c) Evolving factor analysis using five absorbing eigenvectors\(^{130}\) (d) re-constructed individual electronic absorption spectra\(^{131}\) and (e) proposed thermodynamic model.
and orbital overlap, which are optimized when two CrN₆
magnetic coupling constants. For the [Cl₃Cr(L)CrCl₃] and 
field low-spin d₆ electronic configuration), the photophysical 
[(L)Cr(L]
character of CrIII centres o 
get mixed-valence systems, the paramagnetic and spin-only 
with the Janus-type bis-terdentate receptors L 
opening large avenues for the selective introduction of tri-

Table 3  Experimental stability constants (log(β₉₁₃₁)) and microscopic
thermodynamic parameters fitted with eqn (17)-(20) for the reaction of 
ppz or bbt with Er(CF₃SO₃)₃ in acetonitrile/chloroform (65 : 35) at 298 K

<table>
<thead>
<tr>
<th>Ligand</th>
<th>log(β₉₁₃₁)</th>
<th>log(β₉₁₃₁)</th>
<th>log(β₉₁₃₁)</th>
<th>log(β₉₁₃₁)</th>
<th>log(β₉₁₃₁)</th>
</tr>
</thead>
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<td>tpz</td>
<td>6.42(2)</td>
<td>8.19(16)</td>
<td>12.03(3)</td>
<td>13.76(32)</td>
<td>15.89(4)</td>
</tr>
<tr>
<td>bbt</td>
<td>9.80(3)</td>
<td>13.63(16)</td>
<td>16.16(50)</td>
<td>18.16(50)</td>
<td>18.16(50)</td>
</tr>
</tbody>
</table>

Δccoli₉/Δ coli₉ in kJ mol⁻¹

Δcoli₉ = −2.303RT log(βcoli₉)

Δcoli₉ = −2.303RT log(βcoli₉)

Δcoli₉ = −2.303RT log(ucoli₉)

AF⁰ = \frac{\sum_{m,n} (\log(\beta_{m,n,exp}) - \log(\beta_{m,n,cald}))²}{\sum_{m,n} (\log(\beta_{m,n,exp}))²}

AF = \frac{\sum_{m,n} (\log(\beta_{m,n,exp}) - \log(\beta_{m,n,cald}))²}{\sum_{m,n} (\log(\beta_{m,n,exp}))²}

Conclusion

The synthetic method developed by Housecroft and Constable⁴⁶ for the preparation of a semi-labile [[tpy] 
Cr(OTf₂)₃]₃ precursor can be successfully applied for [[tppz] 
Cr(OTf₂)₃]₃, but failed for the slightly more basic bis-benz-
imidazole derivative ebzpy, which is decomplexed from CrIII in 
trifluoromethanesulfonic acid. A subsequent reaction of 
(L)Cr(O₃SCF₃)₃ (L = tpy, tpz) with a second tridentate 
immidazole derivative ebzpy, which is decomplexed from CrIII in 

EF₉/EF₉ in kJ mol⁻¹

Δcoli₉ = −2.303RT log(βcoli₉)

Δcoli₉ = −2.303RT log(βcoli₉)

Δcoli₉ = −2.303RT log(ucoli₉)

AF⁰ = \frac{\sum_{m,n} (\log(\beta_{m,n,exp}) - \log(\beta_{m,n,cald}))²}{\sum_{m,n} (\log(\beta_{m,n,exp}))²}

AF = \frac{\sum_{m,n} (\log(\beta_{m,n,exp}) - \log(\beta_{m,n,cald}))²}{\sum_{m,n} (\log(\beta_{m,n,exp}))²}

Experimental section

Solvents and starting materials

2,2’;6’,2’”-Terpyridine (tpy) and the Janus-type bridging ligand 
tetra-2-pyridinylpyrazine (tppz) are commercially available. 
2,6-Bis(1-ethyl-1H-benz[d]imidazol-2-yl) pyridine (ebzpy),⁹⁰ N,N-
dimethyl-N,N’-dipyridin-2-ylpyridine-2,6-diamine (ddpd)¹¹² and 
6,6’-di(dipyridin-2-yl)-2,2’;4’;2’”-quaterpyridine (bbt)¹¹² 
were synthesized according to the published procedures. The 
synthesis of 4’;4”-([ethyl]bis(2,2’;6’,2’”-terpyridine) (ebbt) was 
adapted from the literature (Appendix 4).¹⁰⁹ Reagent 
g grade acetonitrile (ACN) and chloroform were distilled from CaH₂ 
when needed. All other chemicals were purchased from com-
mmercial suppliers and used without further purification. Silica-
gel plates (Merck, 60 F₂₅₄) were used for thin-layer chromatog-
raphy. Preparative column chromatography was performed 
using either neutral alumina gel from Fluka (Typ 507 C) 
100–125 mesh or SiliaFlash® silica gel P60 (0.04–0.063 mm).

Synthesis of gallium and chromium complexes

All complexes were characterized by IR spectroscopy (Tables 
S41–S44†) and gave satisfying elemental analyses (Table S1†).

[Ga(tpy)₂][PF₆]₃. A solution of Ga(CF₃SO₃)₃ (60.5 mg, 
0.117 mmol, 1 eq.) in degassed acetonitrile was added into a 
solution of terypyridine (54.8 mg, 0.235 mmol, 2.01 eq.) in 
distilled acetonitrile (20 mL). The color of the mixture 
slightly turned yellow. After being stirred at 50 °C overnight, 
acetonitrile was evaporated and the resulting solid was re-solu-
bilized in methanol (5–8 mL). A solution of saturated 
(nBu₄)NPF₆ (2.5 mL, C = 90–100 mg mL⁻¹) was added and the 
resulting pale yellow precipitate was filtered, washed with 
dichloromethane (2 × 5 mL) and diethyl ether (2 × 5 mL) 
dried under vacuum to obtain [Ga(tpy)₂][PF₆]₃ as a yellow 
powder (98 mg, 0.101 mmol, yield 86%). Slow diffusion of 
diethyl ether into a solution of the complex in acetonitrile gave 
pale yellow single crystals of [Ga(tpy)₂][PF₆]₃·2CH₃CN (1) suitable 
for X-ray diffraction studies.¹¹ H NMR of [Ga(tpy)₂][PF₆]₃, 
(CD₃CN, 400 MHz, δ/ppm): 9.10 (6H, m), 8.80 (4H, d, 3J = 
8 Hz), 8.43 (4H, td, 3J = 8 Hz, 4J = 0.8 Hz), 7.74 (4H, d, 3J = 8 Hz),
nitrile (20 mL). The blue color of the Cr(II) solution turned into a solution of terypyridine (209 mg, 0.895 mmol, 1.99 eq.) in degassed acetonitrile (20 mL). The color of the mixture immediately turned deep dark green. After being stirred at 45 °C for 4 hours, a solution of (n-Bu)4NCF3SO3 (177 mg, 0.450 mmol, 1 eq.) in degassed acetonitrile (2 mL) was added. The Schlenk tube was transferred into the lab and Cr(II) was oxidized by bubbling dioxygen. The colour of the solution changed to red-orange. After being stirred for 1 hour at RT, acetonitrile was evaporated and the resulting solid was solubilized in hot methanol (20 mL). A solution of saturated (n-Bu)4NF6 in methanol (4 mL, C = 100 mg mL⁻¹) was added into the solution in order to precipitate a red-orange complex, which was filtered, washed with dichloromethane (3 × 15 mL) and diethyl ether (3 × 10 mL) and dried under vacuum to obtain a red-orange powder [Cr(tpy)(ebzpy)][PF6]3 (326 mg, 0.342 mmol, yield 76%). Slow diffusion of diethyl ether into a solution of the complex in acetonitrile gave red-orange single crystals of [Cr(tpy)(ebzpy)][PF6]3·2.CH3CN (2) suitable for X-ray diffraction studies.

[Cr(ebzpy)]3[PF6]2. In a glovebox, a sky blue solution of [Cr(CF3SO3)2]·H2O (155 mg, 0.420 mmol, 1 eq.) in degassed acetonitrile was introduced into a 50 mL Schlenk tube containing a solution of 2,6-bis(1-ethyl-1H-benzo[d]imidazol-2-yl)pyridine (ebzpy, 307 mg, 0.833 mmol, 1.99 eq.) in degassed acetonitrile (20 mL). The blue color of the Cr(II) solution turned immediately dark green. After being stirred at 45 °C for 4 hours, a solution of (n-Bu)4NCF3SO3 (165 mg, 0.420 mmol, 1 eq.) in degassed acetonitrile (2 mL) was added. The Schlenk tube was transferred into the lab and the Cr(II) was oxidized by bubbling dioxygen. The colour of the solution changed to red-orange to give [Cr(ebzpy)]3[CF3SO3]3. The red-orange acetonitrile solution of [Cr(ebzpy)]3[CF3SO3]3 was evaporated and the resulting solid was solubilized in hot methanol (20 mL). Anion metathesis was performed by adding 4 mL of a saturated solution of (n-Bu)4NF6 in methanol (100 mg mL⁻¹). The red-orange precipitate was filtered, washed with dichloromethane (3 × 15 mL) and diethyl ether (3 × 10 mL) and dried under vacuum to give [Cr(ebzpy)]3[PF6]3 as a red-orange powder (385 mg, 0.315 mmol, yield 75%). Slow diffusion of diethyl ether into a solution of the complex in acetonitrile gave red-orange single crystals of [Cr(ebzpy)]3[CF3SO3]3·5.5CH3CN (3) suitable for X-ray diffraction studies. Slow diffusion of diethyl ether into a solution of the intermediate [Cr(ebzpy)]3[CF3SO3]3 complex in acetonitrile gave red-orange single crystals of [Cr(ebzpy)]3[CF3SO3]3·2CH3CN (4) suitable for X-ray diffraction studies as well.

[Cr(ebzpy)]Cl3. A solution of 2,6-bis(1-ethyl-1H-benzo[d]imidazol-2-yl)pyridine (182 mg, 0.495 mmol, 1.01 eq.) in dry dichloromethane (5 mL) was dropwise added into a solution of [CrCl3(THP)]3 (184 mg, 0.490 mmol, 1 eq.) in dry dichloromethane (30 mL). The color of the mixture changed from purple to green. After being stirred at room temperature for 24 hours, the mixture was filtered and the solid was washed with dichloromethane (3 × 15 mL) and diethyl ether (3 × 10 mL), and dried under vacuum to give [Cr(ebzpy)]Cl3 (253 mg, 0.47 mmol, yield 98%). Slow diffusion of diethyl ether into a solution of a complex in DMF gave dark green single crystals of [Cr(ebzpy)Cl3]·DMF (5) suitable for X-ray diffraction studies. The complex was characterized by elemental analysis (Table S1†).

[Cr(tppy)]2Cl2. Tetra-2-pyridylpyrazine (tppz) (170 mg, 0.438 mmol, 2 eq.) was suspended in a distilled mixture of acetonitrile and ethanol (25 mL: 25 mL) and heated under reflux. A solution of [CrCl3(THF)]3 in acetonitrile (82 mg, 0.219 mmol, 1 eq.) was added dropwise to the tppz solution mixture, the colour of which immediately turned from purple to green. After being stirred and refluxed for 24 hours under an inert N2 atmosphere, the insoluble product was filtered (micro-filtering), then washed with a hot solution of acetonitrile and ethanol (1:1) for removing the excess ligand. The resulting solid was washed with diethyl ether (3 × 7 mL) and dried under vacuum to give Cr(tppz)Cl1 (114 mg, 0.208 mmol, yield 95%). Slow diffusion of diethyl ether into a solution of the complex in DMF gave dark green single crystals of [Cr(tppz)Cl2]·2DMF (6) suitable for X-ray diffraction studies.

[Cr(tppz)(SO3CF3)]3. Cr(tppz)Cl1 (140 mg, 0.256 mmol, 1 eq.) and triflic acid (300 μL, 3.4 mmol, 13 eq.) were loaded into a 50 mL Schlenk tube under a N2 atmosphere. The green colour of the complex turned to dark red immediately together with gas escape of HCl (confirmed by precipitation of AgCl when bubbling into an aqueous solution of AgNO3). After being stirred at room temperature for 3 hours, the dark red complex of [Cr(tppz)(SO3CF3)]3 was precipitated by the addition of 25 mL of diethyl ether. The complex was filtered, washed with diethyl ether (3 × 6 mL) and dried under vacuum to give Cr(tppz)(SO3CF3)3 (204 mg, 0.230 mmol, yield 90%).

[Cr(ebzpy)(tpy)][PF6]3. A dark red solution of [Cr(tpy)]3[CF3SO3]3 (168 mg, 0.230 mmol, 1 eq.) in distilled acetonitrile was loaded into a 50 mL Schlenk tube under an inert N2 atmosphere. A solution of 2,6-bis(1-ethyl-1H-benzo[d]imidazol-2-yl)pyridine (85 mg, 0.230 mmol, 1 eq.) in acetonitrile (8–10 mL) was added to the Schlenk tube. The mixture was refluxed under N2 for 3 hours, then the solution was evaporated to dryness and the residual solid solubilized in distilled acetonitrile (3 mL). Slow diffusion of diethyl ether into the concentrated solution of the complex in acetonitrile gave [Cr(tpy)(ebzpy)][CF3SO3]3 as red crystals (126 mg, 0.115 mmol, yield 50%). [Cr(tpy)(ebzpy)][CF3SO3]3 was solubilized in MeOH, then anion metathesis was initiated by adding 4 mL of a saturated solution of tetrabutylammonium hexafluorophosphate [(n-Bu)4NF6] in methanol (100 mg mL⁻¹). The resulting red-orange precipitate was filtered, washed with diethyl ether and dried under vacuum to give [Cr(tpy)(ebzpy)][PF6]3. Slow diffusion of diethyl ether in a concentrated solution of the complex in acetonitrile (3 mL) produced red single crystals of [Cr(tpy)(ebzpy)][PF6]3·2CH3CN (7) suitable for X-ray diffraction studies.

[Cr(tppz)(tpy)][PF6]3. A solution of Cr(tppz)[CF3SO3]3 (177.5 mg, 0.2 mmol, 1 eq.) in distilled acetonitrile was drop-
wise added into a concentrated solution of terpyridine in acetonitrile (58 mg, 0.25 mmol in 8 mL). The solution became warm during the addition and was then refluxed for 3 hours. The resulting mixture was cooled, filtered, and the remaining dark-red solution was evaporated to dryness. Slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile (3 mL) produced yellow single crystals of [Cr(tppz)(tpy)][CF3SO3]6 suitable for X-ray diffraction studies in approximately 40–50% yields. [Cr(tppz)(tpy)][CF3SO3]6 was solubilized in MeOH, then anion metathesis was initiated by adding 4 mL of a saturated solution of tetrabutylammonium hexafluorophosphate [(n-Bu)4NPF6] in methanol (100 mg mL−1). The resulting red-orange precipitate was filtered, washed with diethyl ether and dried under vacuum to give [Cr(tppz)(tpy)][PF6]6 (104 mg, 0.094 mmol, yield 47%). Slow diffusion of diethyl ether in a concentrated solution of the complex in acetonitrile (3 mL) produced red single crystals of [Cr(tppy)(tppz)][PF6]3·3CH3CN (8) suitable for X-ray diffraction studies.

[CrCl6(tppz)]. Tetra-pyridinylpyrazine (220 mg, 0.566 mmol, 1 eq.), CrCl3, 6H2O (440 mg, 1.65 mmol, 2.9 eq.), and EtOH (12 mL) were introduced into a round bottom flask. After complete dissolution of CrCl3, acetonitrile (24 mL) was added to the resulting green solution, and the mixture was refluxed for 24 hours. The brown greenish precipitate was filtered, washed with boiling EtOH (4 times), and dried with diethyl ether to give [CrCl6(tppz)] as a brown greenish solid (390 mg, 0.555 mmol, yield 98%). Slow diffusion of diethyl ether in a concentrated solution of the complex in acetonitrile (3 mL) produced red single crystals of [CrCl6(bbt)] (PF6)6·8CH3CN·(CH3CH2)2O (13) suitable for X-ray diffraction studies. ESI-MS m/z: [Cr2(tppy)2(bbt); SO3CF3]+ calc: 1779.0, found: 1780.3; [Cr2(tppy)2(bbt); 4SO3CF3]2+ calc: 815.0, found: 814.3; [Cr2(tppy)2(bbt); 3SO3CF3]3+ calc: 493.7, found: 493.6.

[Cr2(tppy)2(ebbt)][PF6]6. 4′,4′″-(Ethynyl)bis(2,2′,6′,2″-terpyridine) (ebbt, 40 mg, 0.082 mmol, 1 eq.), and distillated CHCl3 (15 mL) were introduced into a Schlenk tube under argon. After complete ligand dissolution, a solution of [Cr(tppy)(SO3CF3)6] (180 mg, 0.246 mmol, 3 eq.) dissolved in distilled acetonitrile (5 mL) was added. The mixture was stirred at 70 °C for 15 hours. The orange precipitate was filtered, washed with dichloromethane and dried with diethyl ether. The resulting orange solid was recrystallized from EtOH and dried with diethyl ether to give [Cr2(tppy)2(ebbt)][PF6]6 (130 mg, 0.066 mmol, yield 81%) as an orange solid. [Cr2(tppy)2(ebbt)][PF6]6 was dissolved in MeOH, and a saturated solution of TBAPF6 in MeOH was slowly added until complete precipitation of the yellow compound. The precipitate was filtered, washed with a few drops of MeOH, and dried with diethyl ether to give [Cr2(tppy)2(ebbt)][PF6]6·8CH3CN·(CH3CH2)2O (13) suitable for X-ray diffraction studies. ESI-MS m/z: [Cr2(tppy)2(ebbt); 5SO3CF3]+ calc: 1779.0, found: 1780.3; [Cr2(tppy)2(ebbt); 4SO3CF3]2+ calc: 827.0, found: 827.8; [Cr2(tppy)2(ebbt); 3SO3CF3]3+ calc: 501.7, found: 501.8; [Cr2(tppy)2(ebbt); 2SO3CF3]4+ calc: 339.0, found: 339.7; [Cr2(tppy2)(ebbt); 1SO3CF3]+ calc: 241.4, found: 241.8; [Cr2(tppy2)(ebbt)]6+ calc: 176.4, found: 176.9.

[CrCl6(ddpd)]. N,N,N′-Dimethyl-N,N′-dipyridin-2-ylpyridine-2,6-diamine (ddpd) (80 mg, 0.274 mmol, 1 eq.), CrCl3, 6H2O (95 mg, 0.357 mmol, 1.3 eq.), and EtOH (20 mL) were introduced into a round bottom flask. After refluxing for 15 hours, a green precipitate formed was filtered and dried with diethyl ether to give [CrCl6(ddpd)] (75 mg, 0.167 mmol, yield 61%) as a green solid. Slow diffusion of diethyl ether into a concentrated solution of [CrCl6(ddpd)] in DMF provided green crystals of [CrCl6(ddpd)] (15) suitable for X-ray diffraction studies.

Spectroscopic and analytical measurements

H and 1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer equipped with a variable temperature
unit. Chemical shifts are given in ppm with respect to tetramethylsilane Si(CH$_3$)$_4$. Pneumatically-assisted electrospray (ESI) mass spectra were recorded from $10^{-5}$ M solutions on an Applied Biosystems API 150EX LC/MS System equipped with a Turbo Ionspray source®. Elemental analyses were performed by K. L. Buchwalder from the Microchemical Laboratory of the University of Geneva. Spectrophotometric titrations were performed with a J&M diode array spectrometer (Tidas series) connected to an external computer. In a typical experiment, 50 cm$^3$ of ligand in acetonitrile : chloroform (65 : 35) ($8 \times 10^{-5}$ mol dm$^{-3}$) were titrated at 298 K with a solution of Er(CF$_3$SO$_3$)$_3$ ($2 \times 10^{-3}$ mol dm$^{-3}$) in the same solvent under an inert atmosphere. After each addition of 0.10 mL, the absorbance was recorded using a Hellma optrode (optical path length 0.1 cm) immersed in the thermostatted titration vessel and connected to the spectrometer. Mathematical treatment of the spectrophotometric titrations was performed with factor analysis and with the SPECFIT program.$^{131}$ Absorption spectra in solution were recorded using a Cary 5000 Varian spectrometer (quartz cell path length 1 mm, 200–800 nm domain). Absorption spectra in the solid state were recorded on a Lambda 900 PerkinElmer spectrometer equipped with an integration sphere (background recorded on MgO). Emission spectra were recorded upon excitation at 400 nm from powder samples at various temperatures from 3 K to 295 K with a Fluorolog-3-22 (Horiba Jobin–Yvon), equipped with a peltier-cooled photo multiplier tube (Hamamatsu R2658P), and corrected for the spectral response of the system. Excitation at 355 nm was obtained with the third harmonic of a pulsed Nd:YAG laser (Quantel Brilliant). The emitted light was collected with a telescope and focused onto a light-guide with a fibre bundle connected to a monochromator (Spex 270 M). Full spectra were recorded with a CCD (Spex Spectrum One), decay curves with a photomultiplier (Hamamatsu R928) and a digital oscilloscope (Tektronix TDS540B) or a multichannel scaler (Stanford Research SR430). For the latter the spectral bandwidth of the monochromator was set to 20 nm, thus giving the decay of the integral signal. Low temperatures were achieved with a closed cycle cryosystem (Janis, SHI-950) with the sample sitting in exchange gas for efficient cooling. Microcrystalline samples were mounted on copper plates with rubber cement. The copper plates were attached to the sample holder. Magnetization was measured using a Quantum Design VSM system (Department of Quantum Matter Physics, University of Geneva) in the range of 2–300 K. Solid samples of Cr$_2$Cl$_6$(tppz) (15.8 mg), Cr$_2$Cl$_6$(bbt) (16.0 mg), Cr$_2$Cl$_6$(ebbt) (4.7 mg), [Cr$_2$(tpy)$_2$(bbt)][PF$_6$]$_6$ (8.1 mg) and [Cr$_2$(tpy)$_2$(ebbt)][PF$_6$]$_6$ (14.9 mg) were immobilized in capsules, which were locked in an inert atmosphere of helium.

X-Ray crystallography

A summary of crystal data, intensity measurements and structure refinements for compounds (1) to (15) is collected in Tables S2, S3, S12, S17, S21, S26, S31 and S38 (ESI†). The crystals were mounted on MiTeGen raptor cryoloops with protective oil. X-ray data collections were performed with an Agilent SuperNova Dual diffractometer equipped with a CCD Atlas detector (Cu[Kα] radiation). The structures were solved by using direct methods.$^{140}$ Full-matrix least-squares refinements on $\chi^2$ were performed with SHELX97.$^{141}$

Specific refinement details. [Cr(ebzpy)$_2$(CF$_3$SO$_3$)$_3$]·2CH$_3$CN (4): One triflate (of the 3 which are required for electroneutrality) and 0.5 CH$_3$CN molecules were extremely disordered. Because of the lack of well-defined features in the electron density map, several attempts to model this disorder didn’t give satisfactory refinement. We thus performed SQUEEZE after exclusion of these disordered molecules (using Platon)$^{142}$ and found 8 voids of 123 Å$^3$ containing 75 electrons (corresponding to one CF$_3$SO$_3$) and 4 voids of 71 Å$^3$ containing 20 electrons (leading to 0.5 CH$_3$CN per formula unit).

Cr$_2$Cl$_6$(tppz):3C$_2$H$_5$NO (11): The crystal was twinned. The twinned operation was a two-fold rotation along the c axis producing apparent Laue symmetry 6/m. The twin law [−1 0 0; 0 −1 0; 0 0 1] was applied in SHELXL,$^{141}$ including racemic twinning (four components). The twin fraction was 0.405(5) and the corresponding racemizing twinning fractions were close to zero. Reflections $hk0l$ were weak. There was almost translational symmetry with vector c/2. Indeed, the structure could be solved and refined in the smaller unit-cell with one complex and three solvent molecules, one of them disordered over two positions. The packing of this molecule produced the superstructure.

Cr$_2$Cl$_6$(bbt) (12): A very large hole (around 1700 Å$^3$) was present in the structure. The squeeze/bypass procedure as implemented in Platon$^{142}$ was used to take care of the disordered solvent present in this hole (which could not be modelled otherwise). Around 505 electrons were found in each hole, which corresponded to about 4 acetone molecules per formula unit ($Z = 4$). These molecules were not added to the formula so that the density and absorption coefficients were somehow underestimated. $R$ factors before squeezing: $R_I = 0.0788$ and w$R_I = 0.22756$ (all data).

CCDC 1542315–1542329† contain the supplementary crystallographic data.

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References
