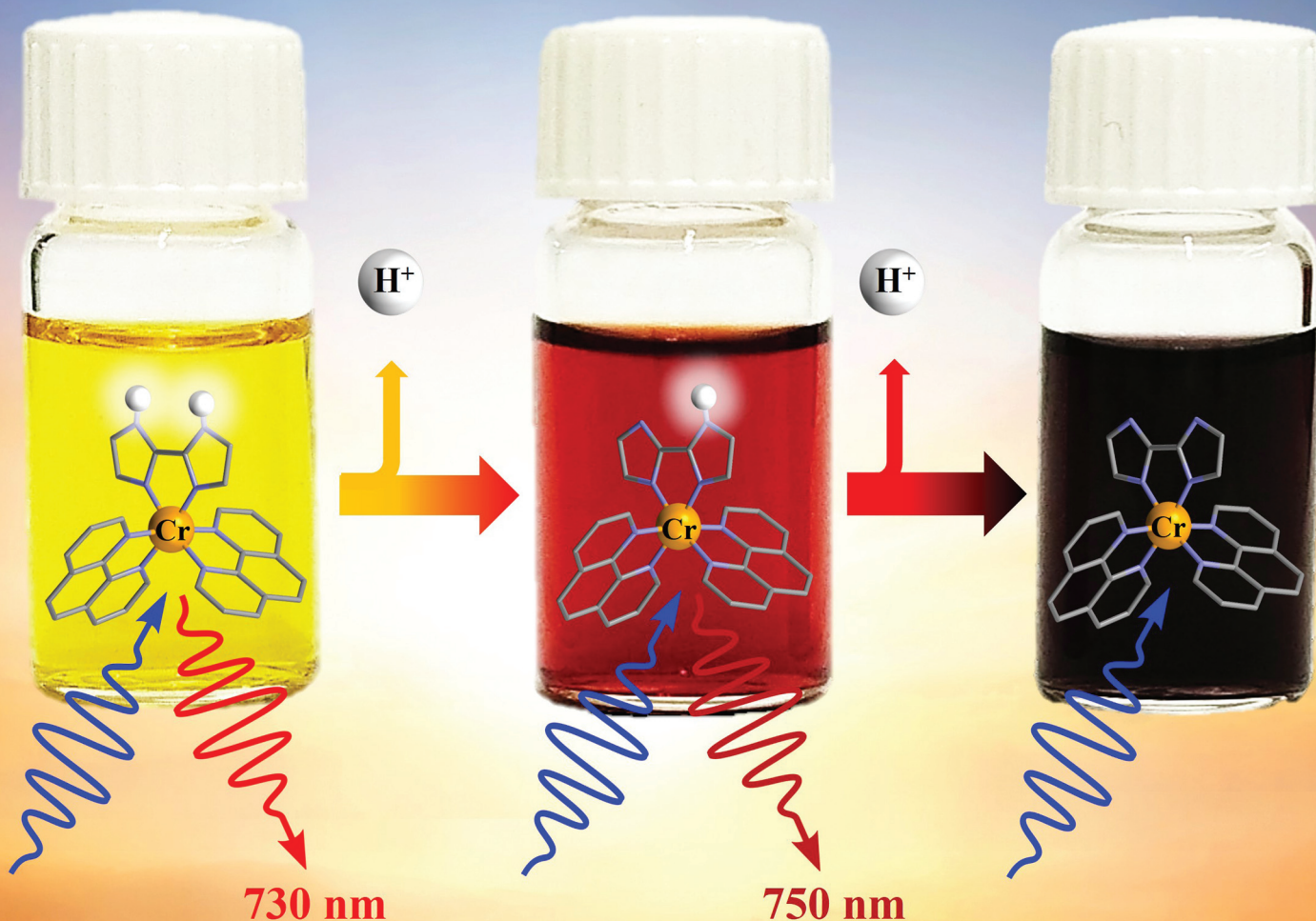


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15801Taming 2,2'-biimidazole ligands in trivalent
chromium complexes†Julien Chong,^a Amina Benchohra,^{a,b} Céline Besnard,^c Laure Guénée,^c
Arnulf Rosspeintner,^d Carlos M. Cruz,^e Juan-Ramón Jiménez^f and
Claude Piguet^{*,a}

Complete or partial replacement of well-known five-membered chelating 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) ligands with analogous didentate 2,2'-biimidazole (H₂biim) provides novel perspectives for exploiting the latter pH-tuneable bridging unit for connecting inert trivalent chromium with cationic partners. The most simple homoleptic complex [Cr(H₂biim)₃]³⁺ and its stepwise deprotonated analogues are only poorly soluble in most solvents and their characterization is limited to some solid-state structures, in which the pseudo-octahedral [CrN₆] units are found to be intermolecularly connected via peripheral N–H...X hydrogen bonds. Moreover, the associated high-energy stretching N–H vibrations drastically quench the targeted near infrared (NIR) Cr^{III}-based phosphorescence, which makes these homoleptic building blocks incompatible with the design of molecular-based luminescent assemblies. Restricting the number of bound 2,2'-biimidazole ligands to a single unit in the challenging heteroleptic [Cr(phen)₂(H_xbiim)]^{(1+x)+} (x = 2–0) complexes overcomes the latter limitations and allows (i) the synthesis and characterization of these [CrN₆] chromophores in the solid state and in solution, (ii) the stepwise and controlled deprotonation of the bound 2,2'-biimidazole ligand and (iii) the implementation of Cr-centered phosphorescence with energies, lifetimes and quantum yields adapted for using the latter chromophores as sensitizers in promising 'complex-as-ligand' strategies.

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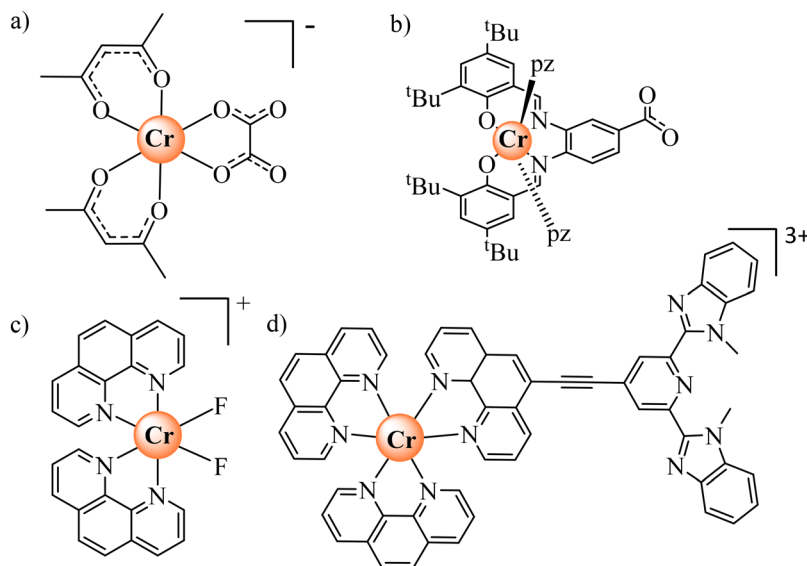
Introduction

The lack of first-order orbital momentum in pseudo-octahedral trivalent chromium complexes makes isotropic and spin-only [CrX₆] units ideal partners for programming, tuning and rationalizing magnetic coupling with neighbouring paramagnetic d-block^{1–5} and f-block^{6–10} cations. In this context, many of the chromium-containing heterometallic assemblies exploit the

kinetically inert [Cr(CN)₆]^{3–} synthon, which behaves as a 'complex-as-ligand' connecting cationic metals *via* cyanide bridges in solid state materials.^{1–10} The realization that, beyond magnetic properties, both lanthanide-based light downshifting^{11,12} and light upconversion^{13,14} can be boosted by close Cr(III) sensitizers/emitters resulted in some active search for novel synthetic strategies, leading to Cr^{III}–Ln^{III} molecular pairs (Ln(III) is a trivalent lanthanide cation) beyond serendipitous co-crystallization processes.¹⁵ One approach involves self-assembly processes with segmental multisite ligands where labile Cr^{II} precursors are selectively recognized by didentate binding units while Ln^{III} is caught by adjacent tridentate sites. The subsequent Cr^{II} to Cr^{III} oxidation provides kinetically inert heterometallic triple-stranded Cr^{III}–Ln^{III} and Cr^{III}–Ln^{III}–Cr^{III} helicates with remarkable photophysical properties,^{16,17} among which is the programming of the first molecular-based energy transfer light-upconversion (ETU) process.¹³

A more versatile synthetic strategy for incorporating open-shell [CrX₆] chromophores as tuneable and operable sensitizers in multimetallic (supra)molecular architectures involves extending the 'complex-as-ligand' strategy, originally used for introducing [Cr(CN)₆]^{3–} into multimetallic coordination polymers.^{1–10,18} Taking advantage of kinetically-controlled ligand exchange processes around inert Cr(III), a few heterolep-

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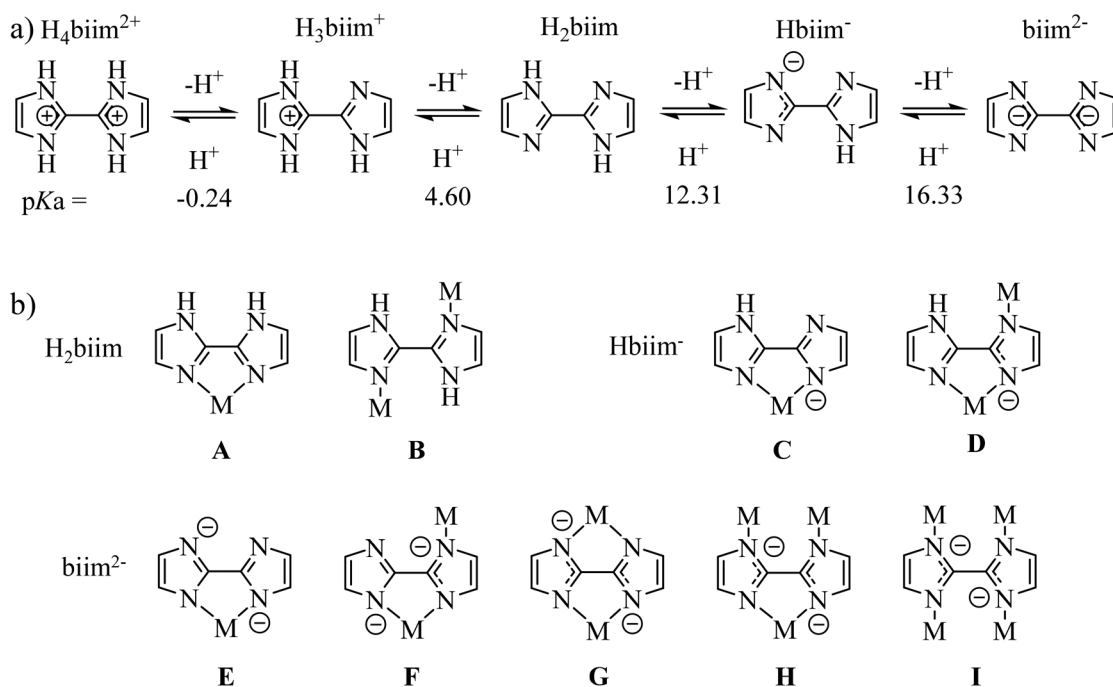


Scheme 1 Kinetically-inert heteroleptic six-coordinate Cr^{III} complexes used as complex-as-ligand when preparing multimetallic assemblies.^{12,18–21}

tic six-coordinate complexes could be prepared, in which an oxalate (Scheme 1a),¹² a phenyl-carboxylate (Scheme 1b),¹⁹ a difluoride (Scheme 1c)²⁰ or an extended ethyne-bis(benzimidazole)pyridine (Scheme 1d)²¹ acted as a bridging unit between the Cr(III)-based complex-as-ligand unit and some adjacent d-block or f-block partners. However, the molecular aspects of their association processes in solution remain elusive and only solid-state crystal data support the physicochemical analyses. Considering the recent recognition that strong-field [CrN₆]

chromophores are ideal for maximizing phosphorescence quantum yields, emission lifetimes and sensitization in ‘molecular rubies’,^{22–24} there is clearly a need for the design of novel [CrN₆] analogues working as complex-as-ligand, but using more accessible and reliable bridging units.

With this in mind, the 2,2′-biimidazole ligand (H₂biim, Scheme 2a)²⁵ is famous for working as a versatile bridging ligand after its binding to a metallic cation (Scheme 2b). In its protonated form, it can either form hydrogen bonds for



Scheme 2 a) Successive acid–base equilibria of fully protonated 2,2′-biimidazole (H₄biim²⁺) with pK_a values measured in DMF : H₂O = 7 : 3 (*I* = 0.1 M).²⁵ (b) Different coordination modes encountered in the literature for H₂biim (A^{26,27} and B²⁸), Hbiim[−] (C and D)³⁰ and biim^{2−} (E–I).^{31–34}



sensing anions (mode A in Scheme 2b)^{26,27} or connect other cations in a linear way (mode B in Scheme 2b).²⁸ More often,²⁹ multimetallic assemblies are obtained after stepwise deprotonation of the bound 2,2'-biimidazole ligand to give bridging Hbiim[−] (modes C and D in Scheme 2b)³⁰ and biim^{2−} scaffolds (modes E–I in Scheme 2b).^{31–34} Surprisingly, the studies dealing with the complexation of inert Cr^{III} centers by potentially bridging 2,2'-biimidazole are undervalued, probably due to the synthetic difficulties associated with the synthesis of these poorly soluble and pH-sensitive complexes.^{35–38} To the best of our knowledge, only the molecular structures of [Cr(H₂biim)₃]³⁺,³⁶ [Cr(H₂biim)₂(Hbiim)]²⁺ (ref. 37) and [Cr(Hbiim)₃]³⁶ have been characterized in the solid state following poorly reproducible and serendipitous crystallization from intricate mixtures of ligands and metals in the presence of various amounts of counter-anions and/or solvent molecules. A recent synthetic improvement, which used anhydrous THF under microwave heating, gave [Cr(H₂biim)₃](NO₃)₃ in 94% yield (Fig. 1).³⁵

Beyond the detailed descriptions of (i) sophisticated hydrogen-bonding networks in which the latter homoleptic complexes are a part and (ii) some expected axial flattening produced by didentate five-membered chelating 2,2'-biimidazole bound to Cr^{III},^{36–38} no effort has been focused on the thermodynamic deprotonation processes and the associated control of the photophysical properties. Moreover, to the best of our knowledge, no attempt to prepare heteroleptic [L₂Cr(H₂biim)]³⁺ has been made, while related systems with inert 4d and 5d metal ions have been designed regularly to access the two crucial pK_a values for their use as complex-as-ligand (Table S1 in the ESI†).^{25,39–47} In order to provide new perspectives for exploiting 2,2'-biimidazole as a bridging ligand between photo-physically-active Cr^{III} and promising open-shell lanthanides, we

report here on the molecular structures and photophysical properties of the accessible and isolable homoleptic complexes [Cr(H₂biim)₃]³⁺, [Cr(Hbiim)₃] and [Cr(Hbiim)₂(biim)][−] in solution and in the solid state. The second part proposes the synthesis of the unprecedented heteroleptic [(phen)₂Cr(H₂biim)]³⁺ complex with its detailed acid–base and photophysical properties, which become accessible in the solid state and in solution.

Results and discussion

Preparation and structures of the homoleptic [Cr(Me₂biim)₃]³⁺, [Cr(H₂biim)₃]³⁺, [Cr(Hbiim)₃] and [Cr(Hbiim)₂(biim)][−] complexes

2,2'-Biimidazole (H₂biim) was synthesized from ammonium acetate and glyoxal under aqueous conditions with moderate yield.⁴⁸ Its methyl derivative 1,1'-dimethyl-2,2'-bi-1*H*-imidazole (Me₂biim) could be obtained by deprotonation, followed by methylation with methyl iodide (Fig. 2, top).⁴⁹

The original literature synthesis of [Cr(H₂biim)₃](NO₃)₃ involved the reaction of CrCl₃·3THF with [Ag(H₂biim)]NO₃ in MeOH³⁶ or in THF³⁵ (Fig. 1) because the formation of highly insoluble AgCl drove the reaction to completion. To simplify the procedure, the intermediate [Ag(H₂biim)]NO₃ was not isolated in this work, but was formed *in situ* by mixing AgNO₃

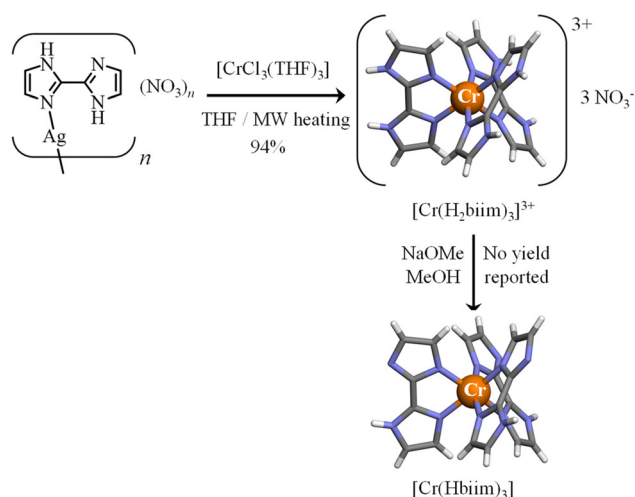


Fig. 1 Synthesis of [Cr(H₂biim)₃]³⁺ (ref. 35) and [Cr(Hbiim)₃].³⁶ The molecular structures of the complexes are those found in the crystal structures of [Cr(H₂biim)₃](NO₃)₃ (CCDC-603707) and [Cr(Hbiim)₃]₂·C₆H₆·2H₂O (CCDC-603730).³⁶ Color code: C = grey, N = blue, H = white, and Cr = orange.

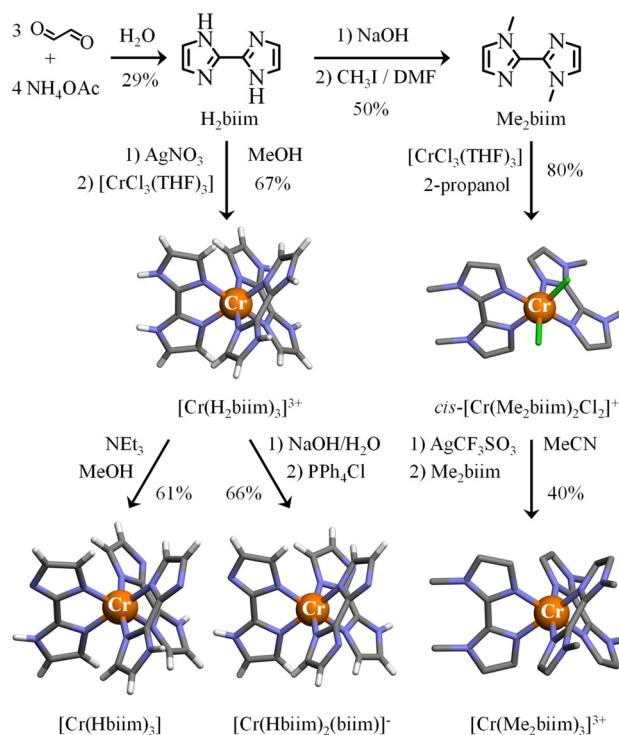


Fig. 2 Synthesis of ligands 2,2'-biimidazole (H₂biim) and 1,1'-dimethyl-2,2'-bi-1*H*-imidazole (Me₂biim) and their homoleptic [Cr(H₂biim)₃]³⁺, [Cr(Hbiim)₃], [Cr(Hbiim)₂(biim)][−] and [Cr(Me₂biim)₃]³⁺ complexes. The molecular structures of the metallic complexes are those found in the associated crystal structures. Color code: C = grey, N = blue, H = white, and Cr = orange. The counter-ions and hydrogen atoms (for Me₂biim ligands) are omitted for clarity.

and H₂biim in MeOH. Then CrCl₃·3THF was added into the resulting solution of [Ag(H₂biim)]NO₃. The purification method was identical to that used in ref. 35 and [Cr(H₂biim)₃](NO₃)₃ was isolated in good yield (Fig. 2). Recrystallization by vapor diffusion of Et₂O into a methanolic solution provided crystals suitable for X-ray diffraction, the structural resolution of which at 120 K confirmed the crystal structure previously reported for [Cr(H₂biim)₃](NO₃)₃ at 290 K (Fig. 2, Tables S2–S3 and Fig. S1†).³⁶ The synthesis of [Cr(Hbiim)₃] was first described by Gruia *et al.*,³⁶ where they used a stoichiometric amount of NaOMe to deprotonate [Cr(H₂biim)₃]³⁺ in MeOH. However, the complete insolubility of the formed neutral [Cr(Hbiim)₃] complex did not allow any reproducible recrystallization techniques. To overcome this problem, a methanolic solution of [Cr(H₂biim)₃]³⁺ was treated in this work with vapor diffusion of an excess of volatile triethylamine, the limited pK_a of which (10.74)⁵⁰ prevented any double deprotonation of the bound Hbiim ligand and finally gave crystals of [Cr(Hbiim)₃] with good yield (61%) and in a reproducible way (Fig. 2, Tables S4–S6 and Fig. S2†). Further deprotonation of [Cr(Hbiim)₃] could not be obtained by Gruia *et al.*,³⁶ but some partial reports of analogs of [Cr(biim)₃]^{3–}, *i.e.* Ba_{1.5}[Co(biim)₃]⁴¹ and K₃[Ru(biim)₃]⁵¹ that were obtained using harsh basic conditions (aqueous NaOH 2 M/BaCl₂ and ^tBuOK 1.2 M in MeOH, respectively) have been noted. Consequently, [Cr(Hbiim)₃] was dissolved in an excess of aqueous NaOH (0.5 M) until a clear yellow solution was formed. The addition of a concentrated solution of PPh₄Cl immediately resulted in the formation of an orange precipitate. Recrystallization from MeOH by vapor diffusion of ^tBuOMe provided block-shaped crystals of [Cr(Hbiim)₂(biim)]PPh₄(CH₃OH) suitable for X-ray diffraction analysis in a good yield (66%) (Fig. 2, Tables S7–S9 and Fig. S3†). A detailed geometrical analysis of these homoleptic complexes (Appendix 2 in the ESI†) concludes that the [Cr(H_xbiim)₃]ⁿ⁺ units display standard pseudo-octahedral arrangements of the six bound nitrogen donor atoms, with a compression along the pseudo-C₃ axis due to the 79.6–80.4° ligand bite angles (Table A2-1 in Appendix 2†), which is characteristic of five-membered chelating polyaromatic ligands²³ as reported for related [Cr(bipy)₃]³⁺ (bipy = 2,2′-bipyridine, 79.1°)⁵² and [Cr(phen)₃]³⁺ (phen = 1,10-phenanthroline, 81.0°) complexes.⁵³ The Cr–N distances in [Cr(H_xbiim)₃]ⁿ⁺ do not vary drastically (2.028–2.037 Å, compared with averages of 2.042 Å for [Cr(bipy)₃]³⁺ and 2.051 Å for [Cr(phen)₃]³⁺) and do not show obvious correlations with the degree of deprotonation of the bound ligand. Due to the chelation of semi-rigid didentate polyaromatic ligands, some standard trigonal distortions characterize all these complexes (Table A2-1 in Appendix 2†).

The main difference between [Cr(bipy)₃]³⁺ and [Cr(phen)₃]³⁺ on one hand, and the family of [Cr(H_xbiim)₃]ⁿ⁺ complexes, is associated with the bound didentate 2,2′-biimidazole ligands which may act as N–H hydrogen-bond donors when they are protonated and as N[–] hydrogen-bond acceptors when they are deprotonated. For the fully protonated [Cr(H₂biim)₃](NO₃)₃ complex, the weak N–H...O hydrogen bonds observed between

the bound ligand and the nitrate counter-anion (Fig. A2-2†) are responsible for the *circa* 400 cm^{–1} decreases of the N–H stretching frequency in the vibrational spectrum with respect to the free ligand ($\nu(\text{NH}) \approx 3000 \text{ cm}^{-1}$ in Fig. S14 and S18-top, Table S29†). The formation of strong intermolecular N–H...N hydrogen bonds observed in the deprotonated complexes [Cr(Hbiim)₃] (Fig. A2-4†) and [Cr(Hbiim)₂(biim)]PPh₄ (Fig. A2-6†) further weakens the N–H bond force constants and step-wise shifts the associated stretching frequency toward $\nu(\text{NH}) \approx 2400 \text{ cm}^{-1}$ (Fig. S15 and S18 center, Table S30†) and $\nu(\text{NH}) \approx 2300 \text{ cm}^{-1}$ (Fig. S16 and S18 bottom, Table S31†), respectively. In this context, the replacement of hydrogen atoms with methyl groups to give [Cr(Me₂biim)₃](CF₃SO₃)₃ *via* the Kane-Maguire synthetic strategy (Fig. 2) maintains the pseudo-octahedral structure of the [CrN₆] core (Tables S16–S17 and Fig. S7†),⁵⁴ but it limits intermolecular hydrogen bonds in the crystal structure (Fig. A2-10 in Appendix 2†).

The spectroscopic properties of the ligands H₂biim and Me₂biim and the chromium complexes [Cr(H₂biim)₃](NO₃)₃, [Cr(Hbiim)₂(biim)]PPh₄ and [Cr(Me₂biim)₃](CF₃SO₃)₃ could be recorded in methanol or in acetonitrile. Unfortunately, the neutral complex [Cr(Hbiim)₃] is not soluble enough in common organic solvents to perform reliable measurements in solution. The electrospray ionization mass spectrometry (ESI-MS) spectra (Fig. S19–S38 and Tables S33–S35†) show complicated mixtures in the gas phase containing various amounts of intact 1 : 3 complexes with variable degrees of deprotonation ([Cr(H_xbiim)₃]ⁿ⁺) together with (i) partial ligand dissociation to give 1 : 2 complexes ([Cr(H_xbiim)₂]ⁿ⁺ + H₂biim) and (ii) metal reduction into Cr(II)-based systems. All peaks could be identified from high-resolution MS spectra with a special emphasis on the detection of the ‘full’ deprotonated [Cr(Hbiim)₂(biim)][–] anion (negative mode) for [Cr(Hbiim)₂(biim)]PPh₄ (Fig. S25 and Table S34†). It is concluded that these deprotonatable complexes suffer from the ionization process and exist as fragmented mixtures in the gas phase.

Photophysical properties of the homoleptic [Cr(Me₂biim)₃]³⁺, [Cr(H₂biim)₃]³⁺, [Cr(Hbiim)₃] and [Cr(Hbiim)₂(biim)][–] complexes

The absorption (Fig. 3 and 4a) and emission (Fig. 4b and S39†) spectra of the ligands H₂biim and Me₂biim and the complexes [Cr(H₂biim)₃](NO₃)₃, [Cr(Hbiim)₂(biim)]PPh₄ and [Cr(Me₂biim)₃](CF₃SO₃)₃ could be recorded in MeOH. Unfortunately, the neutral complex [Cr(Hbiim)₃] is not soluble enough to perform spectroscopy except for solid-state investigations (Fig. S40†). The UV parts of the absorption spectra are dominated by intraligand-centered $\pi^* \leftarrow \pi$ transitions (ILCT), which are split and red-shifted upon coordination to Cr³⁺ in the associated complexes. Additional LMCT (Ligand-to-Metal Charge Transfer) transitions are known to also contribute within the 330–400 nm range for these [CrN₆] chromophores (Fig. 3).^{29,55–57} The spin-allowed, but parity forbidden ligand-field Cr(⁴T₂ ← ⁴A₂) transition (intensity $10 < \epsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$, highlighted in Fig. 3b) can be detected as a minor contribution to the low-energy tail of the charge transfer bands.^{58–63} Careful spectral deconvolutions are required (Fig. S41–S43 and Tables



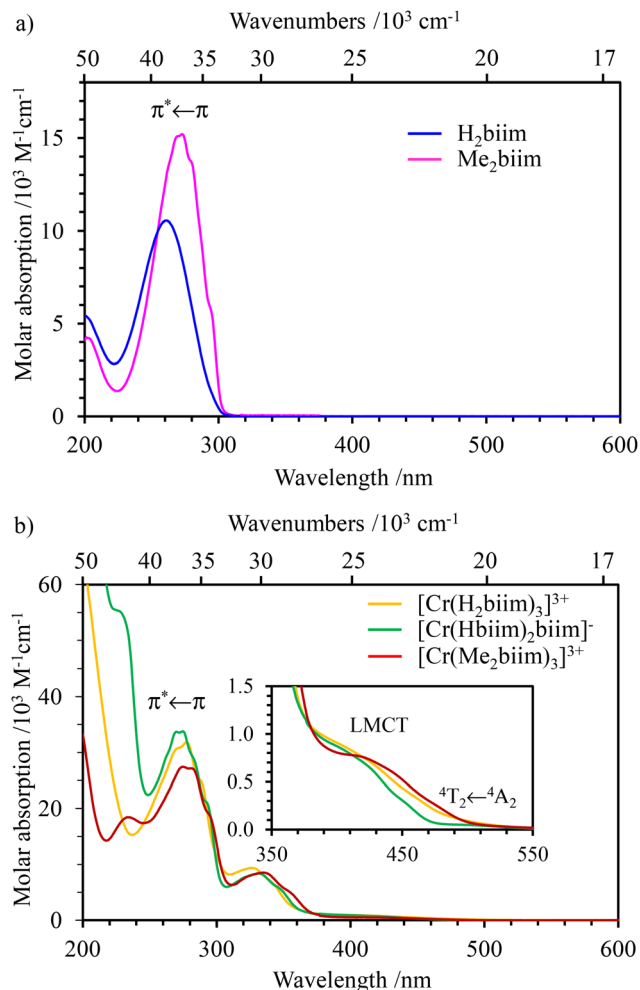


Fig. 3 UV-visible absorption spectra of (a) non-coordinated ligands H₂biim (purple) and Me₂biim (dark blue) and (b) complexes [Cr(H₂biim)₃]³⁺ (NO₃)₃ (orange), [Cr(Hbiim)₂(biim)][−]PPH₄ (green) and [Cr(Me₂biim)₃]³⁺ (CF₃SO₃)₃ (red) in MeOH at 293 K.

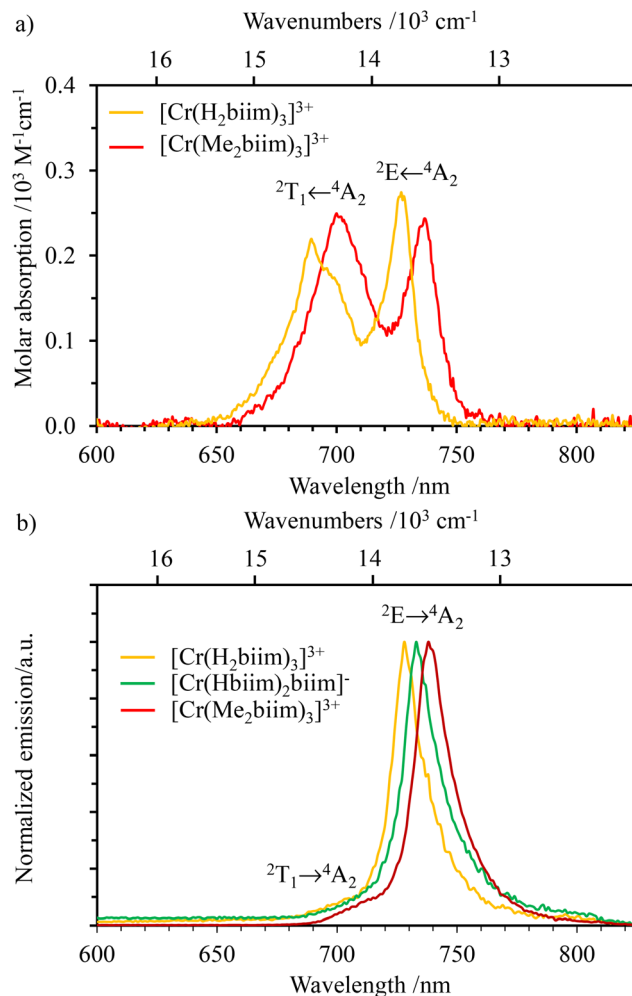


Fig. 4 NIR (a) absorption spectra of [Cr(H₂biim)₃](NO₃)₃ (water) and [Cr(Me₂biim)₃](CF₃SO₃)₃ (acetonitrile) and (b) emission ($\lambda_{\text{exc}} = 330$ nm) spectra of complexes [Cr(H₂biim)₃](NO₃)₃ (orange), [Cr(Hbiim)₂(biim)][−]PPH₄ (green) and [Cr(Me₂biim)₃](CF₃SO₃)₃ (red) in MeOH at 293 K.

S36–S39†) to safely assign $E(^4T_2)$, *i.e.*, the energy of the Cr(⁴T₂) excited level with respect to the ground state $E(^4A_2) = 0$ (Table 1, column 2).

Interestingly, for pseudo-octahedral d³ complexes, $E(^4T_2)$ provides a straightforward estimation of the ligand-field splitting (eqn (1)),^{64,65} which covers a narrow $19\,956 \leq \Delta \leq 21\,026$ cm^{−1} range for [Cr(H₂biim)₃]³⁺, [Cr(Hbiim)₂(biim)][−] and [Cr(Me₂biim)₃]³⁺ in solution (Table 1).

$$\Delta = E(^4T_2) - E(^4A_2) \quad (1)$$

As established for the programming of spin crossover processes while tuning the ligand-field strength,⁶⁶ the replacement of didentate 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), made of two connected 6-membered heterocyclic rings, with 2,2′-biimidazole (H₂biim), made of two connected five-membered heterocyclic rings, is accompanied by an increase of the trigonal distortion in their pseudo-octahedral complexes. This is measured by a stepwise increase in the θ angular distor-

tion ($\theta[\text{Cr}(\text{phen})_3]^{3+} = 47.5^\circ < \theta[\text{Cr}(\text{bpy})_3]^{3+} = 63.6^\circ < \theta[\text{Cr}(\text{Me}_2\text{biim})_3]^{3+} = 80.4^\circ$ computed with eqn (A2-2) and gathered in Table A2-1, see Appendix 2†), which results in a concomitant stepwise reduction of the ligand-field strength $\Delta[\text{Cr}(\text{bpy})_3]^{3+} \approx \Delta[\text{Cr}(\text{phen})_3]^{3+} \approx 22\,500$ cm^{−1} > $\Delta[\text{Cr}(\text{Me}_2\text{biim})_3]^{3+} \approx 20\,500$ cm^{−1} > $\Delta[\text{Cr}(\text{tpy})_2]^{3+} = 18\,750$ cm^{−1} (Table 1).

The interelectronic repulsion is estimated using the Racah parameters B (eqn (2)) and C (eqn (3)), which requires the energy of the lowest doublet levels $E(^2E)$ and $E(^2T_1)$ to be accessible (Fig. 5).^{64,65}

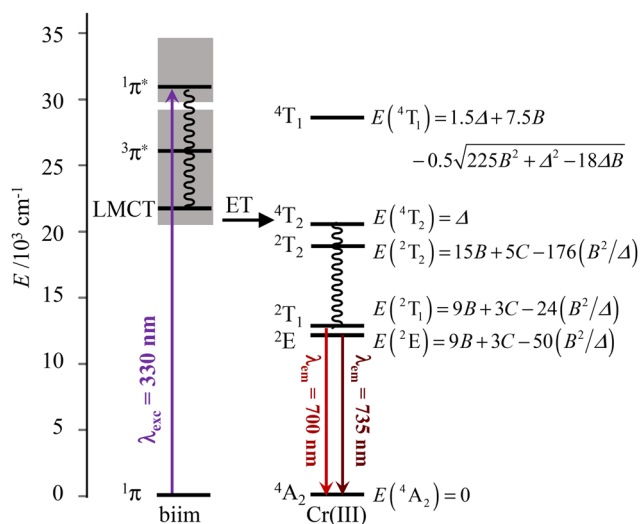
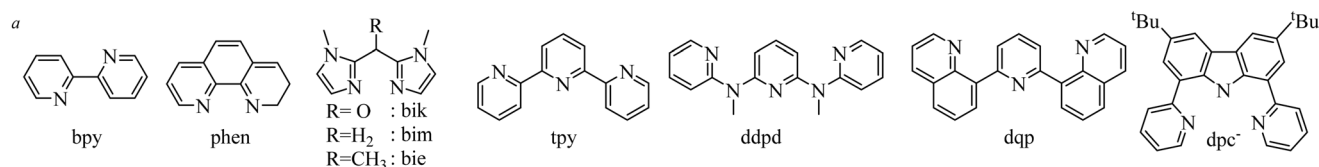
$$B = \sqrt{\frac{[E(^2T_1) - E(^2E)] \cdot \Delta}{26}} \quad (2)$$

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

Assuming an O_h symmetry, the ground state absorption bands Cr(²E ← ⁴A₂) and Cr(²T₁ ← ⁴A₂) have very weak intensities ($0.05 < \epsilon < 1$ M^{−1} cm^{−1}) due to the breaking of both parity



Complex	$E(^4T_2)/\text{cm}^{-1}$	$E(^2T_1)/\text{cm}^{-1}$	$E(^2E)/\text{cm}^{-1}$	Δ/cm^{-1}	B/cm^{-1}	C/cm^{-1}	$E(^4T_2) - E(^2E)/\text{cm}^{-1}$	Δ/B	C/B	Ref.
$[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$	20 268	14 376	13 717	20 268	717	2845	6551	28.3	4.0	This work
$[\text{Cr}(\text{Hbiim})_3]$	—	14 263	13 670	—	—	—	—	—	—	This work
$[\text{Cr}(\text{Hbiim})_2(\text{biim})]^-$	19 956	14 096	13 482	19 956	686	2828	6474	29.1	4.1	This work
$[\text{Cr}(\text{Me}_2\text{biim})_3]^{3+}$	21 026	14 164	13 538	21 026	712	2779	7488	29.6	3.9	This work
$[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$	23 202	14 381	13 723	23 202	766	2697	9479	30.3	3.5	This work
$[\text{Cr}(\text{bpy})_3]^{3+}$	23 400	14 450	13 800	23 400	765	2730	9600	30.6	3.6	60
$[\text{Cr}(\text{phen})_3]^{3+}$	22 075	14 451	13 736	22 075	779	2700	8339	28.3	3.5	53
$[\text{Cr}(\text{tpy})_2]^{3+}$	18 750	13 584	12 953	18 750	790	2512	5797	23.7	3.2	61
$[\text{Cr}(\text{ddpd})_2]^{3+}$	22 990	13 550	12 903	22 990	756	2419	10 087	30.4	3.2	23
$[\text{Cr}(\text{dqp})_2]^{3+}$	24 937	13 864	13 405	24 937	656	2791	11 532	38.0	4.3	24
$[\text{Cr}(\text{dpc})_2]^+$	19 200	—	9370	19 200	470	1880	9830	40.9	4.0	62
$[\text{Cr}(\text{CN})_6]^{3-}$	26 600	—	12 400	26 600	480	2800	14 200	55.4	5.8	63
$[\text{Cr}(\text{bik})_3]^{3+}$	23 094	14 771	14 044	23 094	804	2737	9050	28.7	3.4	57
$[\text{Cr}(\text{bim})_3]^{3+}$	21 008	14 859	14 104	21 008	781	2842	6904	26.9	3.6	57
$[\text{Cr}(\text{bie})_3]^{3+}$	20 747	14 837	14 124	20 747	754	2902	6623	27.5	3.8	57



and spin conservation rules. These transitions could be detected in the NIR domain of the solid-state absorption spectra of the four investigated complexes (Fig. S40†), while related solution data could be recorded only for the most soluble $[\text{Cr}(\text{H}_2\text{biim})_3](\text{NO}_3)_3$ ($c \geq 10^{-2}$ M in water) and $[\text{Cr}(\text{Me}_2\text{biim})_3](\text{CF}_3\text{SO}_3)_3$ ($c \geq 10^{-2}$ M in acetonitrile) complexes (Fig. 4a). Introducing $E(^4\text{T}_2)$, $E(^2\text{E})$ and $E(^2\text{T}_1)$ into eqn (1)–(3) provides the Racah parameters B and C collected in Table 1. Interestingly, $686 \leq B \leq 717 \text{ cm}^{-1}$

For absorption spectra recorded in solution (Fig. 4a), it is possible to calculate the radiative rate constant of the emissive levels ^2E and $^2\text{T}_1$ using the Strickler–Berg eqn (4)^{67,68}, which is derived from Einstein’s relationship for spontaneous emission (Table 2, column 2 and Table S40†).⁶⁹

$$k_{\text{rad}} = 2303 \times \frac{8\pi c n^2 \tilde{\nu} g_{\text{GS}}}{N_{\text{A}} g_{\text{FS}}} \int \varepsilon(\tilde{\nu}) d\tilde{\nu} \quad (4)$$

Here c is the speed of light in vacuum (cm s^{-1}), n is the refractive index of the solvent, N_{A} is the Avogadro number (mol^{-1}), g_{GS} is the degeneracy of the ground state ($g(^4\text{A}_2) = 4$), g_{ES} is the degeneracy of the excited state ($g(^2\text{T}_1) = 6$ and $g(^2\text{E}) = 4$), $\tilde{\nu}$ is the barycenter of the transition in the wavenumber (cm^{-1}) and $\int \varepsilon(\tilde{\nu})d\tilde{\nu}$ is the area under the absorption spectrum of each transition ($\text{M}^{-1} \text{cm}^{-2}$, Fig. S44 and S45†). The radiative rate constants of the emissive $\text{Cr}(^2\text{E})$ excited level estimated for $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$ ($k_{\text{rad}} = 75(4) \text{ s}^{-1}$) and $[\text{Cr}(\text{Me}_2\text{biim})_3]$ ($k_{\text{rad}} = 73(4) \text{ s}^{-1}$) are smaller than those reported for $[\text{Cr}(\text{bpy})_3]^{3+}$ ($k_{\text{rad}} = 182 \text{ s}^{-1}$) and $[\text{Cr}(\text{phen})_3]^{3+}$ ($k_{\text{rad}} = 319 \text{ s}^{-1}$, Table 2),^{58,69–73} but fall within the expected range for pseudo-octahedral $[\text{CrN}_6]$ chromophores (Table S40†).^{70–77} Upon room-temperature ligand-based excitation at 330 nm in solution, the complexes $[\text{Cr}(\text{H}_2\text{biim})_3](\text{NO}_3)_3$, $[\text{Cr}(\text{Hbiim})_2(\text{biim})]\text{PPh}_4$ and $[\text{Cr}(\text{Me}_2\text{biim})_3](\text{CF}_3\text{SO}_3)_3$ show the expected down-

Table 2 Experimental Cr^{2+} lifetimes (τ) and radiative (k_{rad}) and non-radiative ($k_{\text{non-rad}}$) relaxation rate constants and intrinsic quantum yields ($\phi_{\text{intrinsic, Complex}}$) of chromium complexes

Complex	$k_{\text{rad}}/\text{s}^{-1}$	$\tau^{293\text{ K, air}} a/\mu\text{s}$	$k_{\text{non-rad}}^{293\text{ K, air}}/10^3\text{ s}^{-1}$	$\phi_{\text{complex}}^{\text{intrinsic } 293\text{ K, air}}$	$\tau^{293\text{ K, air}} b/\mu\text{s}$	$k_{\text{non-rad}}^{293\text{ K, air}}/10^3\text{ s}^{-1}$	$\phi_{\text{complex}}^{\text{intrinsic } 293\text{ K, air}}$	$\tau^{77\text{ K}} c/\mu\text{s}$	$k_{\text{non-rad}}^{77\text{ K}}/\text{s}^{-1}$	$\phi_{\text{complex}}^{\text{intrinsic } 77\text{ K}}$	Ref.
$[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$	75(4)	0.47(2) ^d	2120(106)	$3(1) \times 10^{-5}$	0.44(2) ^d	2260(113)	$3(1) \times 10^{-5}$	2950(150) ^e	263(13)	$2.0(6) \times 10^{-1}$	This work
$[\text{Cr}(\text{Hbiim})_2(\text{biim})]^-$	—	0.178(9) ^d	—	—	0.141(7) ^d	—	—	2780(140) ^e	—	—	This work
$[\text{Cr}(\text{Me}_2\text{biim})_3]^{3+}$	73(4)	0.48(4) ^d	234(12)	$3(1) \times 10^{-4}$	3.31(9) ^d	302(1)	$2.4(8) \times 10^{-4}$	3005(150) ^e	260(13)	$2.2(7) \times 10^{-1}$	This work
$[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$	65(3)	38(1) ^f	26(7)	$2.5(8) \times 10^{-3}$	14(1) ^f	71(7)	$9(3) \times 10^{-4}$	2940(140) ^g	—	$1.9(6) \times 10^{-1}$	This work
$[\text{Cr}(\text{bpy})_3]^{3+}$	182	74 ^h	13.3	$1.4(4) \times 10^{-2}$	52 ^h	19	$9(3) \times 10^{-3}$	5000 ⁱ	18	$9(3) \times 10^{-1}$	54, 58 and 70-72
		39 ^d	25.5	$7(2) \times 10^{-3}$	29 ^d	34	$5(2) \times 10^{-3}$	6500 ^j	≈ 0	≈ 1	
	319	356 ^h	2.49	$1.1(4) \times 10^{-1}$	74 ^h	13	$2.4(7) \times 10^{-2}$	2100 ^g	157	$6.7(2) \times 10^{-1}$	53, 54, 58 and 70-73
		34 ^d	29.1	$1.1(3) \times 10^{-2}$	22 ^d	45	$7(2) \times 10^{-3}$	5300 ^j	≈ 0	≈ 1	
		224 ^f	4.15	$7(2) \times 10^{-2}$	37 ^f	27	$1.2(3) \times 10^{-2}$	—	—	—	
		270 ^k	3.38	$9(3) \times 10^{-2}$	—	—	—	—	—	—	
$[\text{Cr}(\text{tpy})_2]^{3+}$	—	—	—	—	0.14 ^f	—	—	540 ⁱ	—	—	61, 74 and 75
		—	—	—	—	—	—	670 ^g	—	—	
$[\text{Cr}(\text{dqp})_2]^{3+}$	30	1270 ^h	0.76	$4(1) \times 10^{-2}$	83 ^h	12	$2.5(8) \times 10^{-3}$	3070 ⁱ	296	$9(3) \times 10^{-2}$	24
		2140 ^f	0.44	$6(2) \times 10^{-2}$	31 ^f	32	$9(3) \times 10^{-4}$	—	296	$9(3) \times 10^{-2}$	
$[\text{Cr}(\text{CN})_6]^{3-}$	97	—	—	—	0.12 ⁱ	8330	$1.2(4) \times 10^{-5}$	3950 ⁱ	156	$4(1) \times 10^{-1}$	72
$[\text{Cr}(\text{bik})_3]^{3+}$	31	209 ^f	4.75	$7(2) \times 10^{-3}$	128 ^f	7.8	$4(1) \times 10^{-3}$	8220 ^g	91	$2.6(8) \times 10^{-1}$	57
$[\text{Cr}(\text{biim})_3]^{3+}$	37	131 ^f	7.60	$5(2) \times 10^{-3}$	73 ^f	14	$2.7(8) \times 10^{-3}$	6750 ^g	111	$2.5(8) \times 10^{-1}$	57
$[\text{Cr}(\text{bie})_3]^{3+}$	60	7 ^f	143	$4(1) \times 10^{-4}$	8 ^f	125	$5(2) \times 10^{-4}$	5250 ^g	130	$3(1) \times 10^{-1}$	57

^a Recorded in degassed solution at room temperature. ^b Recorded in air-equilibrated solution at room temperature. ^c Recorded in a frozen solvent mixture at 77 K. ^d In MeOH. ^e In MeOH/H₂O. ^f In CH₃CN. ^g In CH₃CN/C₂H₅CN. ^h In H₂O. ⁱ In H₂O/DMSO. ^j In aq. HClO₄/MeOH. ^k In aq. HCl.

shifted NIR spin-flip $\text{Cr}^2\text{E} \rightarrow {}^4\text{A}_2$) phosphorescence at 730–740 nm together with weak shoulders corresponding to $\text{Cr}^2\text{T}_1 \rightarrow {}^4\text{A}_2$ within the 700–710 nm domain (Fig. 4b and 5). The latter dual emission disappears at 77 K (Fig. S39†) as a result of the depopulation of the high-energy Cr^2T_1 level, and a single band $\text{Cr}^2\text{E} \rightarrow {}^4\text{A}_2$ contributes to phosphorescence. Very similar results are observed in the solid state upon 330 nm excitation for the four complexes $[\text{Cr}(\text{H}_2\text{biim})_3](\text{NO}_3)_3$, $[\text{Cr}(\text{Hbiim})_3]$, $[\text{Cr}(\text{Hbiim})_2(\text{biim})]\text{PPh}_4$ and $[\text{Cr}(\text{Me}_2\text{biim})_3](\text{CF}_3\text{SO}_3)_3$ (Fig. S40b†), which ultimately demonstrate (i) the expected negligible Stokes shifts affecting the spin-flip $\text{Cr}^2\text{T}_1, {}^2\text{E} \leftrightarrow {}^4\text{A}_2$ transitions (Fig. S46†) and (ii) the efficient sensitization of the spin-flip phosphorescence by all the accessible ligand-based excited states (Fig. S47†).

Upon pulsed laser excitation at 355 nm at 77 K in frozen MeOH/H₂O solutions, the characteristic lifetime of the emissive Cr(²E) levels for [Cr(H₂biim)₃](NO₃)₃ ($\tau^{77\text{ K}} = 3.0(1)\text{ ms}$), [Cr(Hbiim)₂(biim)]PPh₄ ($\tau^{77\text{ K}} = 2.7(1)\text{ ms}$) and [Cr(Me₂biim)₃](CF₃SO₃)₃ ($\tau^{77\text{ K}} = 3.0(1)\text{ ms}$) tends toward the radiative lifetime $\tau_{\text{rad}} = 13.4(7)\text{ ms}$, in agreement with minor non-radiative vibrational quenching constants at this temperature for rigid triple-helical units, as similarly reported for [Cr(bpy)₃]³⁺ and [Cr(phen)₃]³⁺ (Table 2 column 8). At room temperature, the Cr(²E) lifetimes drastically drop below the microsecond range for [Cr(H₂biim)₃](NO₃)₃ and [Cr(Hbiim)₂(biim)]PPh₄, which possess high-energy N–H oscillators, while the decrease of the lifetime for the methylated analogue [Cr(Me₂biim)₃](CF₃SO₃)₃ ($\tau^{293\text{ K, Ar}} = 4.28(4)\text{ }\mu\text{s}$) is less dramatic and mirrors those reported for [Cr(bpy)₃]³⁺ and [Cr(phen)₃]³⁺ (Table 2 and Fig. S48–S56†). Consequently, the non-radiative rate constant $k_{\text{non-rad}}^{293\text{ K, Ar}} = 1/\tau^{293\text{ K, Ar}} - k_{\text{rad}} = 2.1(1) \times 10^6\text{ s}^{-1}$ measured for [Cr(H₂biim)₃](NO₃)₃ in MeOH corresponds to the largest vibrational quenching process along the series of [Cr(NⁱN)₃]³⁺ chromophores collected in Table 2. Finally, the presence of ³O₂ in solution has only a minor effect on the lifetime, indicating that quenching by oxygen is not a major contributor to energy relaxation in these systems ($\tau^{293\text{ K, air}}$ in Table 2, column 6).

Acid–base properties of homoleptic $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$, $[\text{Cr}(\text{Hbiim})_3]$ and $[\text{Cr}(\text{Hbiim})_2(\text{biim})]^-$ complexes

In order to extract the acid–base thermodynamic constants connecting $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$ with its successive deprotonated forms $[\text{Cr}(\text{H}_2\text{biim})_2(\text{Hbiim})]^{2+}$ (K_{a1}), $[\text{Cr}(\text{H}_2\text{biim})(\text{Hbiim})_2]^{+}$ (K_{a2}), $[\text{Cr}(\text{Hbiim})_3]$ (K_{a3}) and $[\text{Cr}(\text{Hbiim})_2(\text{biim})]^{-}$ (K_{a4}), we performed two successive pH-metric titrations of aqueous solutions of $[\text{Cr}(\text{H}_2\text{biim})_3](\text{NO}_3)_3$ using NaOH as the titrant. An initial addition of 0.2 equivalents of HNO_3 ensured that the complex exists initially in its fully protonated form $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$ (Fig. 6). The pH curve profile is different from the standard pH-metric titration expected for a weak polyacid with a strong base due to the concomitant precipitation of insoluble $[\text{Cr}(\text{Hbiim})_3]$ (Fig. 6). It is therefore not possible to extract the searched $\text{p}K_a$ values and one can only estimate qualitatively $\text{p}K_{a1}$, $\text{p}K_{a2} < 7$. Moreover, the preservation of $[\text{Cr}(\text{Hbiim})_3]$ as a precipitate in the presence of a large excess

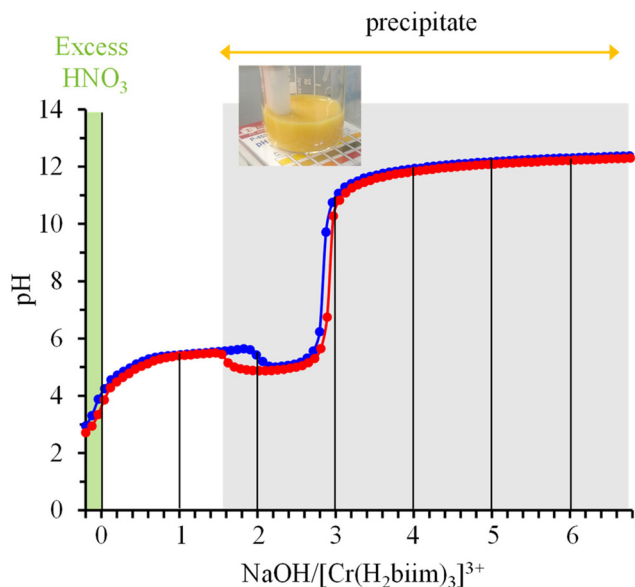


Fig. 6 Reproducible acid–base titrations (blue trace for titration 1 and red trace for titration 2) of a solution of $[\text{Cr}(\text{H}_2\text{biim})_3](\text{NO}_3)_3 + 0.2$ eq. HNO_3 with NaOH (water, 293 K) highlighting the formation of an insoluble yellow precipitate.

of base indicates its negligible deprotonation for $\text{pH} \leq 12$ in water and $\text{p}K_{\text{a}4} > 12$.

Preparation and structures of the heteroleptic $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$ ($x = 2-0$) complexes

In order to limit the number of bound deprotonatable ligands and the concomitant formation of insoluble neutral complexes, we followed the Kane-Maguire synthetic strategy for preparing inert heteroleptic $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ (Fig. 7).⁵⁴ Taking advantage of the *trans* influence,⁷⁸ the complexation of 2.0 eq. of 1,10-phenanthroline (phen) to CrCl_3 yields almost quantitatively $\text{cis-}[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ under reducing conditions for catalyzing $\text{Cr}(\text{III})/\text{Cr}(\text{II})$ exchange processes and ligand-exchange dynamics.⁵³ The replacement of inert Cr-Cl bonds with labile $\text{Cr-OSO}_2\text{CF}_3$ bonds^{79–81} was performed under soft conditions by using $\text{Ag}(\text{O}_3\text{SCF}_3)$ instead of an excess of triflic acid.²⁴ The addition of H_2biim finally provided $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3$ in moderate yield (37%, Fig. 7). Subsequent deprotonation with aqueous NaOH under stoichiometric conditions gave $[\text{Cr}(\text{phen})_2(\text{Hbiim})](\text{CF}_3\text{SO}_3)_2$, whereas the use of an excess of base yielded the doubly deprotonated complex $[\text{Cr}(\text{phen})_2(\text{biim})](\text{CF}_3\text{SO}_3)$. X-ray quality monocrystals could be grown by slow diffusion of diethyl ether into solutions of the complexes either in acetonitrile to give $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3(\text{H}_2\text{O})_{0.25}$ (Fig. 7 and Tables S18–S20†) or in methanol to provide $[\text{Cr}(\text{phen})_2(\text{biim})](\text{CF}_3\text{SO}_3)(\text{CH}_3\text{OH})_{1.5}$ (Fig. 7 and Tables S24–S26†). X-ray quality prisms of $[\text{Cr}(\text{phen})_2(\text{Hbiim})](\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_{0.5}$ (Fig. 7 and Tables S21–S23†) were isolated from a cooled (4 °C) aqueous solution.

The molecular structures of the three $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$ ($x = 2-0$) display pseudo-octahedral $[\text{CrN}_6]$ chromo-

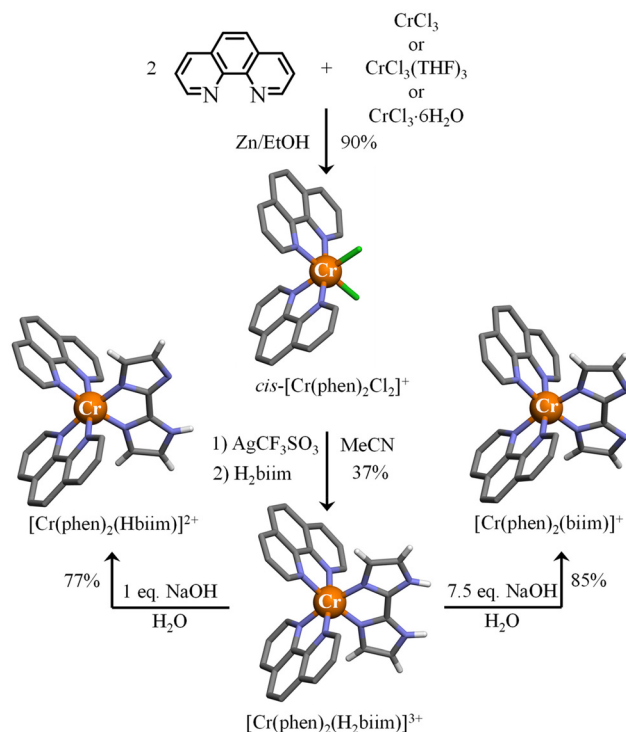


Fig. 7 Synthesis of the heteroleptic $\text{cis-}[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ (CCDC-1865022),⁵³ $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$, $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$ and $[\text{Cr}(\text{phen})_2(\text{biim})]^+$ complexes. The molecular structures of the metallic complexes are those found in the associated crystal structures. Color code: C = grey, N = blue, H = white, and Cr = orange. The counter-ions and hydrogen atoms (for 1,10-phenanthroline ligands) are omitted for clarity.

phores with bond lengths and trigonal distortions typical of chromium complexes bound by three didentate 5-membered chelate polyaromatic ligands (Appendix 3†), similar to the discussion in the previous section for the homoleptic analogues $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$, $[\text{Cr}(\text{Hbiim})_3]$ and $[\text{Cr}(\text{Hbiim})_2(\text{biim})]^-$ (see Appendix 2†). For the heteroleptic complexes, one notices that the Cr-N bond lengths are shorter for the bound biimidazole ligands compared to those of the bound phen ligands ($d_{\text{Cr-N}(\text{biim})} < d_{\text{Cr-N}(\text{phen})}$, Table 3). The contraction of the $d_{\text{Cr-N}(\text{biim})}$ bond lengths upon stepwise deprotonation can be assigned to the increased basicity of the bound biimidazole ligand. The compensating longer $d_{\text{Cr-N}(\text{phen})}$ bond lengths result from the reduced charge borne by the central chromium metal. In terms of intermolecular hydrogen bonds, the bound protonated H_2biim ligand in $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3(\text{H}_2\text{O})_{0.25}$ acts as a NH donor for acceptor oxygen atoms of triflate counter-anions and interstitial water molecules. For the mono-deprotonated bound Hbiim^- ligand in $[\text{Cr}(\text{phen})_2(\text{Hbiim})](\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_{0.5}$, intermolecular hydrogen bonds between two adjacent complexes through $\text{N-H}\cdots\text{N}$ bonds are observed (Fig. A3-3†), as previously described for $[\text{Cr}(\text{Hbiim})_3]$ (Fig. A2-4†). Finally, the totally deprotonated bound biim^{2-} ligand in $[\text{Cr}(\text{phen})_2(\text{biim})](\text{CF}_3\text{SO}_3)(\text{CH}_3\text{OH})_{1.5}$ is not involved in hydrogen bonding.



Table 3 Comparison of the average Cr–N bond lengths ($\bar{d}_{\text{Cr-N}}$)^a of complexes $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3(\text{H}_2\text{O})_{0.25}$, $[\text{Cr}(\text{phen})_2(\text{Hbiim})](\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_{0.5}$ and $[\text{Cr}(\text{phen})_2(\text{biim})](\text{CF}_3\text{SO}_3)(\text{CH}_3\text{OH})_{1.5}$ in their crystal structures

Complex	$\bar{d}_{\text{Cr-N}}/\text{\AA}$	$\bar{d}_{\text{Cr-N(phen)}}/\text{\AA}$	$\bar{d}_{\text{Cr-N(biim)}}/\text{\AA}$
$[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3$	2.04(2)	2.054(3)	2.024(7)
$[\text{Cr}(\text{phen})_2(\text{Hbiim})](\text{CF}_3\text{SO}_3)_2$	2.05(2)	2.062(6)	2.018(0)
$[\text{Cr}(\text{phen})_2(\text{biim})]\text{CF}_3\text{SO}_3$	2.05(4)	2.07(1)	1.997(5)

^a The standard deviations refer to deviations from the computed averages.

In the IR spectra of the heteroleptic complexes, the O–H stretching vibrations of co-crystallized water or methanol molecules involved in hydrogen bonding ($3500 \leq \nu_{\text{OH}} \leq 2500 \text{ cm}^{-1}$) hinder a straightforward interpretation of N–H stretching bands associated with the bound H_xbiim ligands ($x = 2-0$; Fig. S57†). On the other hand, and as previously mentioned for the related homoleptic complexes, the ESI-MS spectra recorded in acetonitrile do not vary significantly with the degree of protonation of the bound 2,2'-biimidazole ligands for the different $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$ cations ($x = 2-0$, Fig. S58†). High-resolution ESI-MS analyses confirm the formation of $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$ as the major gas-phase cation, regardless of the degree of protonation of the bound 2,2'-biimidazole ligand in the selected complex (Table S41 and Fig. S58–62†).

Acid–base properties of the heteroleptic $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ complex

The successive deprotonation of bound 2,2'-biimidazole in $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ has been quantitatively studied by pH metric titrations in water at fixed ionic strength (0.1 M KNO_3 , Fig. 8a). The two successive pH jumps ($5 \leq \text{pH} \leq 8$ and $9 \leq \text{pH} \leq 11$) are accompanied by concomitant abrupt changes in colors from yellow ($[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$) to dark orange ($[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$) and finally to dark brown ($[\text{Cr}(\text{phen})_2(\text{biim})]^+$, Fig. 8a). The associated occupancy factors $\theta_{[\text{Cr}(\text{phen})_2\text{biim}]^{\text{H}^+}}$ experimentally obtained with eqn (5) (red circles in Fig. 8b) display a two-step binding isotherm typical of the anti-cooperative successive fixation of two protons according to equilibria (6)–(7) and modeled with eqn (8). The best fits for the two successive deprotonation steps of $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ (black trace in Fig. 8b) correspond to $\text{p}K_{\text{a}1} = 4.67(3)$ and $\text{p}K_{\text{a}2} = 8.59(11)$, which are approximately eight orders of magnitude more acidic than those measured for free 2,2'-biimidazole ($\text{p}K_{\text{a}1} = 12.31$ and $\text{p}K_{\text{a}2} = 16.33$),²⁵

$$\theta_{[\text{Cr}(\text{phen})_2\text{biim}]^{\text{H}^+}} = \frac{[\text{H}^+]_{\text{bound}}}{2[\text{Cr}(\text{phen})_2\text{biim}]_{\text{tot}}} = \frac{2[\text{Cr}(\text{phen})_2\text{biim}]_{\text{tot}} - (V_{\text{NaOH}} \cdot c_{\text{NaOH}}/V_{\text{tot}}) - [\text{H}^+]}{2[\text{Cr}(\text{phen})_2\text{biim}]_{\text{tot}}} \quad (5)$$

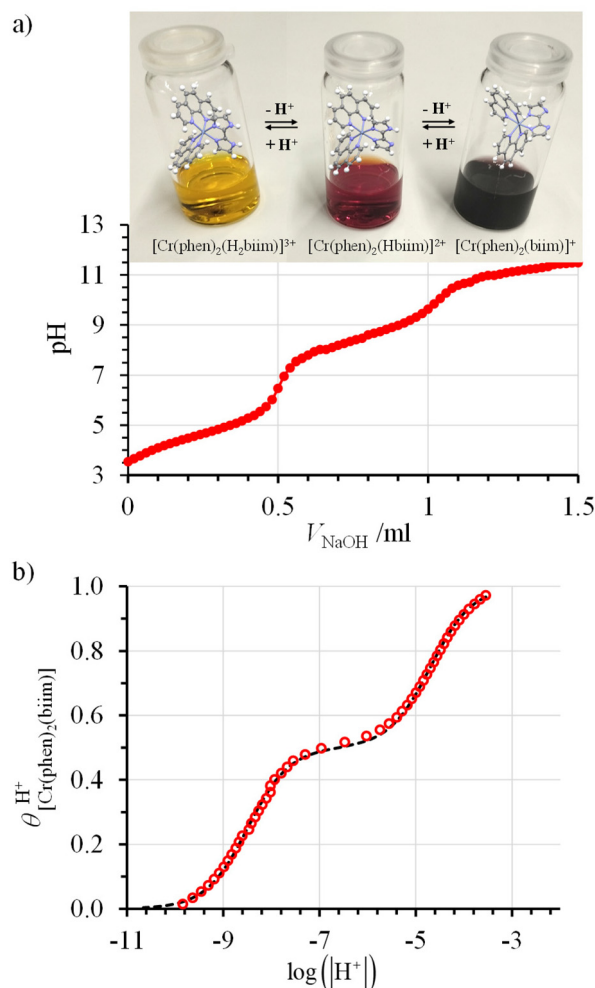
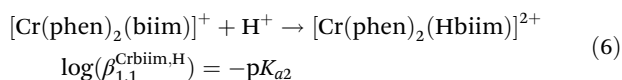
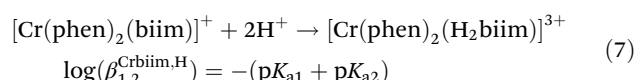


Fig. 8 (a) Titration of 51 mg (52 μmol) of $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3$ (10 mL aqueous KNO_3 0.1 M, $c = 5.2 \text{ mmol L}^{-1}$) with NaOH 0.1 N highlighting the color changes and (b) associated binding isotherm depicted as plots of experimental (red circles, eqn (5)) and fitted (dashed black trace, eqn (8)) occupancy factors as a function of $\log([\text{H}^+])$.



$$\theta_{[\text{Cr}(\text{phen})_2\text{biim}]^{\text{H}^+}} = \frac{\beta_{1,1}^{\text{Crbiim,H}}[\text{H}^+] + 2\beta_{1,2}^{\text{Crbiim,H}}[\text{H}^+]^2}{2(1 + \beta_{1,1}^{\text{Crbiim,H}}[\text{H}^+] + \beta_{1,2}^{\text{Crbiim,H}}[\text{H}^+]^2)} \quad (8)$$

Compared with $[\text{Co}^{\text{III}}(\text{en})_2(\text{H}_2\text{biim})]^{3+}$ ($\text{p}K_{\text{a}1} = 5.5$ and $\text{p}K_{\text{a}2} = 9.9$; ionic radius = $0.545 \text{ \AA}$),⁴¹ the one order of magnitude lower $\text{p}K_{\text{a}}$ measured for $[\text{Cr}^{\text{III}}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ (ionic radius = $0.615 \text{ \AA}$) suggests that the $\{\text{Cr}^{\text{III}}(\text{phen})_2\}^{3+}$ scaffold (with respect to $\{\text{Co}^{\text{III}}(\text{en})_2\}^{3+}$) better stabilizes the negative charges brought by the bound deprotonated 2,2'-biimidazole ligand. Consequently, upon successive deprotonation, one can reasonably predict the appearance of low energy $(\text{phen})\pi^* \leftarrow (\text{H}_x\text{biim})\pi$ ($x = 2-0$) intramolecular ligand-to-ligand charge transfer (LLCT) bands in the absorption spectra of $[\text{Cr}^{\text{III}}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$ upon deprotonation. These tran-

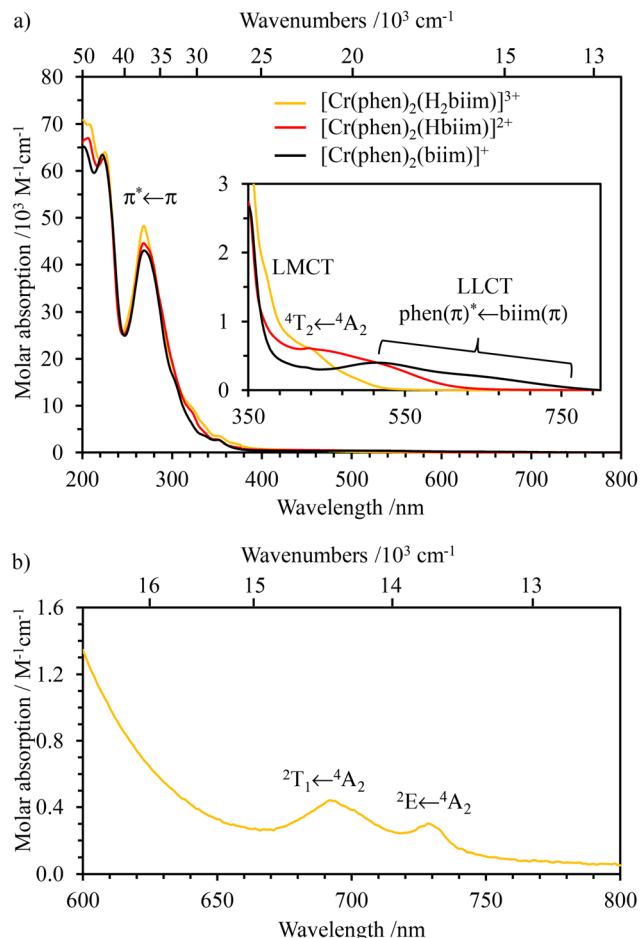


Fig. 9 Absorption spectra of (a) [Cr(phen)₂(H₂biim)]³⁺ (orange trace), [Cr(phen)₂(Hbiim)]²⁺ (red trace) and [Cr(phen)₂(biim)]⁺ (black trace) in CH₃CN (*c* ≈ 10^{−5} mol L^{−1}) and (b) [Cr(phen)₂(H₂biim)]³⁺ in CH₃CN (*c* ≈ 10^{−2} mol L^{−1}). LMCT = ligand to metal charge transfer and LLCT = ligand to ligand charge transfer.

sitions are confirmed by TD-DFT calculations (Fig. A4-2 to A4-10 and Tables A4-6 to A4-8 in Appendix 4†) and indeed observed in solution (Fig. 9).

Finally, taking advantage of the pH-dependence of the absorption spectra, the determination of the p*K*_a values in water at ionic strength close to zero (*I* ≈ 0) could be carried out with the help of spectrophotometry to give p*K*_{a1} = 3.9(1) and p*K*_{a2} = 7.8(1) (Fig. S63†), which are close to those determined at *I* = 0.1 M (KNO₃).

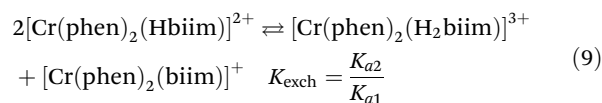
Photophysical properties of the heteroleptic [Cr(phen)₂(H_xbiim)]^{(1+x)+} (*x* = 2–0) complexes

The three heteroleptic complexes exhibit similar and intense absorption bands in the UV range (below 350 nm, Fig. 9a), which can be assigned to intraligand π–π* transitions (ILCT) completed by variable amounts of interligand (LLCT), ligand to metal (LMCT) and metal-to-ligand (MLCT) charge transfer bands (see Appendix 4† for TD-DFT calculations). The spectra differ in the visible domain (350–750 nm, highlighted in

Fig. 9a) mainly due to a shift of the interligand (phen)π* ← (H_xbiim)π (*x* = 0–2, LLCT) transitions toward lower energies upon successive deprotonations (Fig. S64 and Fig. A4-4, A4-7 and A4-9†). This shift is responsible for the color change accompanying the stepwise deprotonation of [Cr(phen)₂(H₂biim)]³⁺ (Fig. 8a). According to theoretical TD-DFT calculations (Table 1, entries 1–3) and CASSCF(7,12)/FIC-NEVPT2 (Table A4-2†) and in line with the trend observed in the homoleptic complexes, the ligand-field strength Δ, reminiscent of Cr(⁴T₂ ← ⁴A₂) transitions in octahedral geometry, also decreases with stepwise deprotonation: [Cr(phen)₂(H₂biim)]³⁺ (412.9 nm, Δ ≈ 24 219 cm^{−1}) > [Cr(phen)₂(Hbiim)]²⁺ (434 nm, Δ ≈ 23 042 cm^{−1}) > [Cr(phen)₂(biim)]⁺ (457.8 nm, Δ ≈ 21 844 cm^{−1}). This reduction in the ligand-field strength is accompanied by (i) a decrease of the computed total spin density at the chromium center (Fig. A4-1†) which reflects the reduced total positive charge borne by this atom and (ii) a negligible change in the estimated Racah parameters *B* and *C* (Table A4-1†). One can thus predict that the stronger interactions with the deprotonated 2,2-biimidazole ligand (*d*_{Cr–N(biim)} is becoming shorter) in [Cr(phen)₂(H_xbiim)]^{(1+x)+} (*x* = 2–0) are more than compensated by the removal of the bound 1,10-phenanthroline ligands (*d*_{Cr–N(phen)} is becoming longer) as exemplified in the molecular structures in the crystalline state (push–pull effect, Table 3).

The NIR absorption spectrum of [Cr(phen)₂(H₂biim)]³⁺ (Fig. 9b) exhibits two well-resolved absorption bands that are assigned to the spin-flip transitions Cr(²E ← ⁴A₂) and Cr(²T₁ ← ⁴A₂) assuming O_h symmetry and with ε = 0.27 and 0.19 M^{−1} cm^{−1}, respectively. For the deprotonated derivatives [Cr(phen)₂(Hbiim)]²⁺ and [Cr(phen)₂(biim)]⁺, the larger residual interligand charge transfer bands mask these weak forbidden spin-flip transitions (Fig. S65†). Consequently, Racah parameters *B* = 766 cm^{−1} and *C* = 2697 cm^{−1} (eqn (2) and (3), Table 1, entry 4) together with the radiative rate constant of *k*_{rad} = 65(3) s^{−1} (eqn (4), and Table 2, column 1), typical of [CrN₆] chromophores, could be estimated only for [Cr(phen)₂(H₂biim)]³⁺.

At room temperature in CH₃CN, only [Cr(phen)₂(H₂biim)]³⁺ is emissive and shows the typical dual Cr(²T₁ → ⁴A₂) and Cr(²E → ⁴A₂) emission observed for many Cr(III) complexes (Fig. 10a). In addition to [Cr(phen)₂(H₂biim)]³⁺, the NIR emission of the complex [Cr(phen)₂(Hbiim)]²⁺ can be detected at low temperature in frozen solvent mixtures (CH₃CN/C₂H₅CN 6 : 4 at 77 K, Fig. 10b), whereas [Cr(phen)₂(biim)]⁺ remains non-emissive. Compared with the emission band of [Cr(phen)₂(H₂biim)]³⁺ (λ_{max} = 732 nm; ν̄ = 13 661 cm^{−1}), the first deprotonated analog [Cr(phen)₂(Hbiim)]²⁺ shows a red-shifted Cr(²E → ⁴A₂) transition at λ_{max} = 750 nm; ν̄ = 13 333 cm^{−1} (Fig. 10b). Additionally, the spectrum of [Cr(phen)₂(Hbiim)]²⁺ contains a band foot at 733 nm originating from a small amount of [Cr(phen)₂(H₂biim)]³⁺, which is inevitably present in solution due to the proton-transfer equilibrium (9):



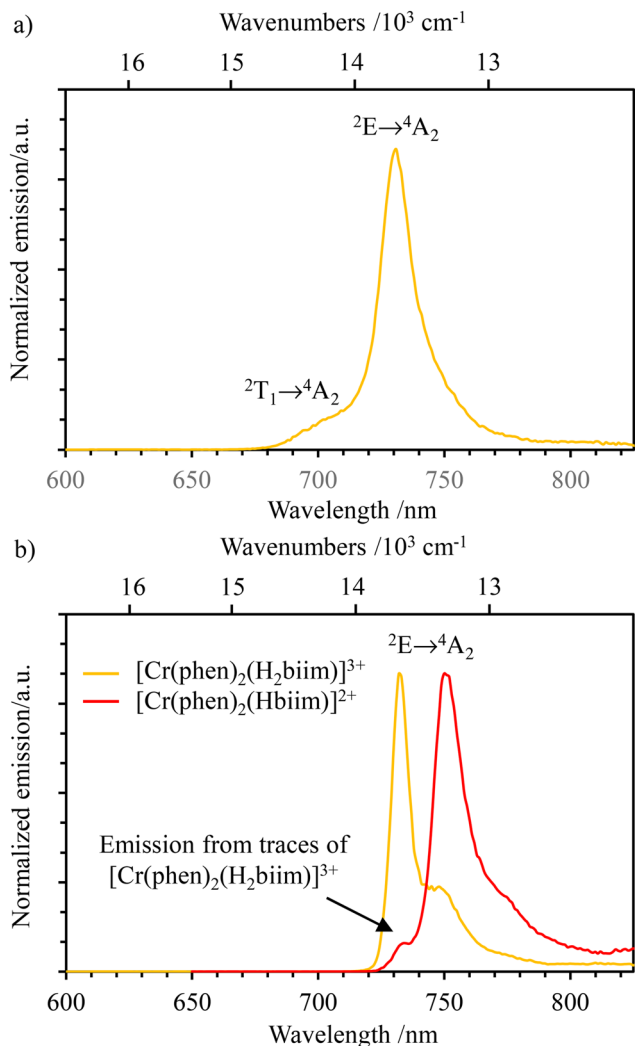


Fig. 10 Emission spectra ($\lambda_{\text{exc}} = 350$ nm) of (a) [Cr(phen)₂(H₂biim)]³⁺ at 293 K in CH₃CN and (b) [Cr(phen)₂(H₂biim)]³⁺ (orange trace) and [Cr(phen)₂(Hbiim)]²⁺ (red trace) at 77 K in frozen CH₃CN/C₂H₅CN (6 : 4).

Introducing K_{a1} and K_{a2} gives $K_{\text{exch}} = 1.2(2) \times 10^{-4}$, from which the ratio of the equilibrium concentration $\frac{[\text{Cr(phen)}_2(\text{Hbiim})]}{[\text{Cr(phen)}_2(\text{H}_2\text{biim})]} = \sqrt{K_{\text{exch}}} = 1.1(1) \times 10^{-2}$ implies contamination of [Cr(phen)₂(Hbiim)]²⁺ by *circa* 1% with the more emissive (protonated) [Cr(phen)₂(H₂biim)]³⁺ complex (red trace in Fig. 10b).

Excited state lifetimes for the NIR emission arising from the Cr(²E) excited state upon excitation at 355 nm were recorded in solution at room temperature and at 77 K for [Cr(phen)₂(H₂biim)]³⁺, and only at 77 K for [Cr(phen)₂(Hbiim)]²⁺ (Fig. S67–S70†). In frozen solutions at 77 K, [Cr(phen)₂(H₂biim)]³⁺ displays a mono-exponential decay of 2.94 ms, which is typical of Cr(III)-polyimine complexes (Table 2). The emission decay curve of [Cr(phen)₂(Hbiim)]²⁺ could not be fit with a mono-exponential function. Since the complex exists as a 98 : 1 : 1 mixture of [Cr(phen)₂(Hbiim)]²⁺, [Cr(phen)₂(H₂biim)]³⁺ and [Cr(phen)₂(biim)]⁺ (eqn (9)), one

expects multi-exponential decays weighted by the mole fractions and the quantum yields of each contributor. A rough bi-exponential fit (Fig. S70†) is compatible with the experimental decay curves showing a long component (1.77(9) ms), which is reminiscent of [Cr(phen)₂(H₂biim)]³⁺, and a short contribution (723(30) μ s) which is tentatively assigned to [Cr(phen)₂(Hbiim)]²⁺, for which the smaller energy gap between the emissive doublet state level Cr(²E) and the silent LLCT band probably boosts the efficiency of non-radiative decay (Fig. 11 and Appendix 4†). At room temperature, only the protonated complex [Cr(phen)₂(H₂biim)]³⁺ is emissive and it exhibits a mono-exponential emission decay of 38 μ s in deaerated CH₃CN. This excited state lifetime is orders of magnitude longer than those of the three isolated homoleptic parent complexes [Cr(H_xbiim)₃]ⁿ⁺ (Table 2) due to the replacement of two 2,2'-biimidazole ligands with two 1,10-phenanthroline units, which are devoid of high-energy N–H stretching vibrations. The lifetime of [Cr(phen)₂(H₂biim)]³⁺ is in the same range as that of [Cr(bpy)₃]³⁺; however, it is one order of magnitude shorter than that of [Cr(phen)₃]³⁺ (Table 2). The emission lifetime is reduced to 14 μ s in aerated solution because of some additional quenching *via* energy transfer to the ³O₂ molecules present in solution.

Finally, the global luminescence quantum yield of the complex [Cr(phen)₂(H₂biim)]³⁺ upon ligand-based excitation at $\lambda_{\text{exc}} = 450$ nm was determined experimentally using the relative method (Fig. S71†). We found $\phi_{\text{complex}}^{\text{global}} = 2.8(3) \times 10^{-3}$ in deaer-

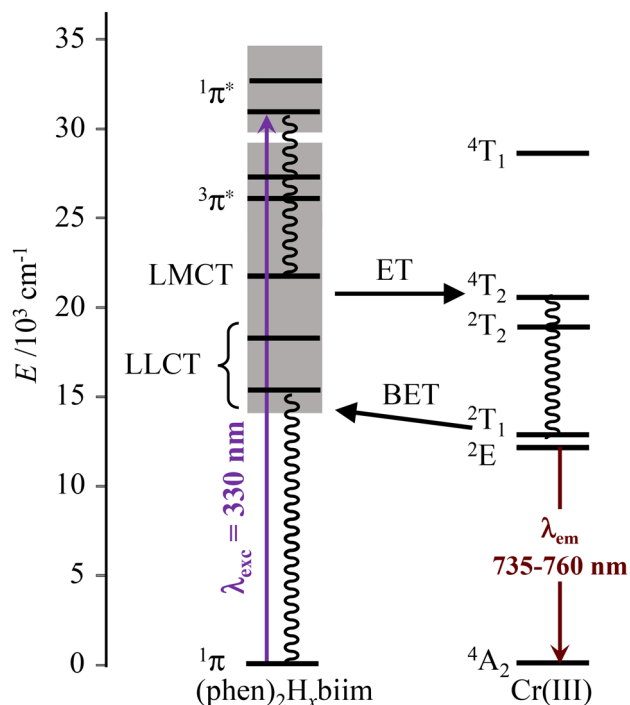


Fig. 11 Jablonski diagram of heteroleptic [Cr^{III}(phen)₂(H_xbiim)]^{(1+x)+} complexes showing the antenna effect upon UV excitation at 330 nm, the existence of low-energy ligand-to-ligand charge transfer excited levels and their potential unfavorable effect on the global quantum yields *via* back energy transfer (BET) processes.

ated acetonitrile and $\phi_{\text{complex}}^{\text{global}} = 9.5(9) \times 10^{-4}$ in the presence of dioxygen at room temperature. One further notes that the intrinsic Cr(III)-centered quantum yields calculated with the help of the emission lifetimes $\tau_{\text{tot}}(^2\text{E})$ and $k_{\text{rad}}(^2\text{E})$ collected at room temperature (Table 2 and eqn (10)) amount to $\phi_{\text{complex}}^{\text{intrinsic}} = 2.5 \times 10^{-3}$ in deaerated acetonitrile and $\phi_{\text{complex}}^{\text{intrinsic}} = 9.1 \times 10^{-4}$ in aerated acetonitrile.

$$\phi_{\text{complex}}^{\text{intrinsic}} = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{non-rad}}} = \frac{\tau_{\text{tot}}}{\tau_{\text{rad}}} \quad (10)$$

Since (i) $\phi_{\text{complex}}^{\text{global}} = \eta_{\text{sens}} \cdot \phi_{\text{complex}}^{\text{intrinsic}}$ and (ii) $\phi_{\text{complex}}^{\text{global}} \approx \phi_{\text{complex}}^{\text{intrinsic}}$, one concludes that the ligand-to-metal sensitization process is close to being quantitative ($\eta_{\text{sens}} \approx 100\%$). These values are in the same range as those reported for $[\text{Cr}(\text{bpy})_3]^{3+}$ ($\phi_{\text{complex}}^{\text{global, noair}} = 1.7 \times 10^{-3}$ in deaerated acetonitrile and $\phi_{\text{complex}}^{\text{global, air}} = 8.9 \times 10^{-4}$ in aerated water),^{70,71,79,80} but four times smaller than that of $[\text{Cr}(\text{phen})_3]^{3+}$ ($\phi_{\text{complex}}^{\text{global, noair}} = 1.2 \times 10^{-2}$ in deaerated water + 1 M HCl),^{53,81} which makes $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ a moderate emitter for a Cr(III) complex.⁷²

Conclusions

In line with the only minor interest attracted by the homoleptic $[\text{Cr}(\text{H}_2\text{biim})_3]^{7+}$ during the past few decades,^{35–38} we confirm here that their low solubility in any common solvent upon stepwise deprotonation, together with their poorly attracting photo-physical properties (a short phosphorescence lifetime and negligible intrinsic quantum yield), makes them poorly adapted to be involved in the complex-as-ligand strategy for programming the assemblies of polymetallic optically-active Cr-based complexes. The solution to the problem arises from the successful synthesis of the soluble heteroleptic $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$ ($x = 2-0$) complexes *via* a modified Kane-Maguire strategy. The bound H_2biim ligand can be stepwise deprotonated in solution at pH compatible for further complexation processes with d-block or f-block cations. The deprotonation processes are accompanied by characteristic color changes resulting from the appearance of low-energy intramolecular interligand $(\text{phen})\pi^* \leftarrow (\text{H}_x\text{biim})\pi$ ($x = 2-0$, LLCT) ligand-to-ligand charge transfer transitions confirmed by theoretical TD-DFT calculations. The latter reversible process makes the putative heterometallic dyads $[\text{Cr}(\text{phen})_2(\text{biim})-\text{M}^{z+}]^{(z+1)+}$ (M^{z+} is an open-shell d- or f-block cation) reminiscent of protonated $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ in terms of photophysical properties, which paves the way for their use as sensitizers in luminescent polymetallic assemblies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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