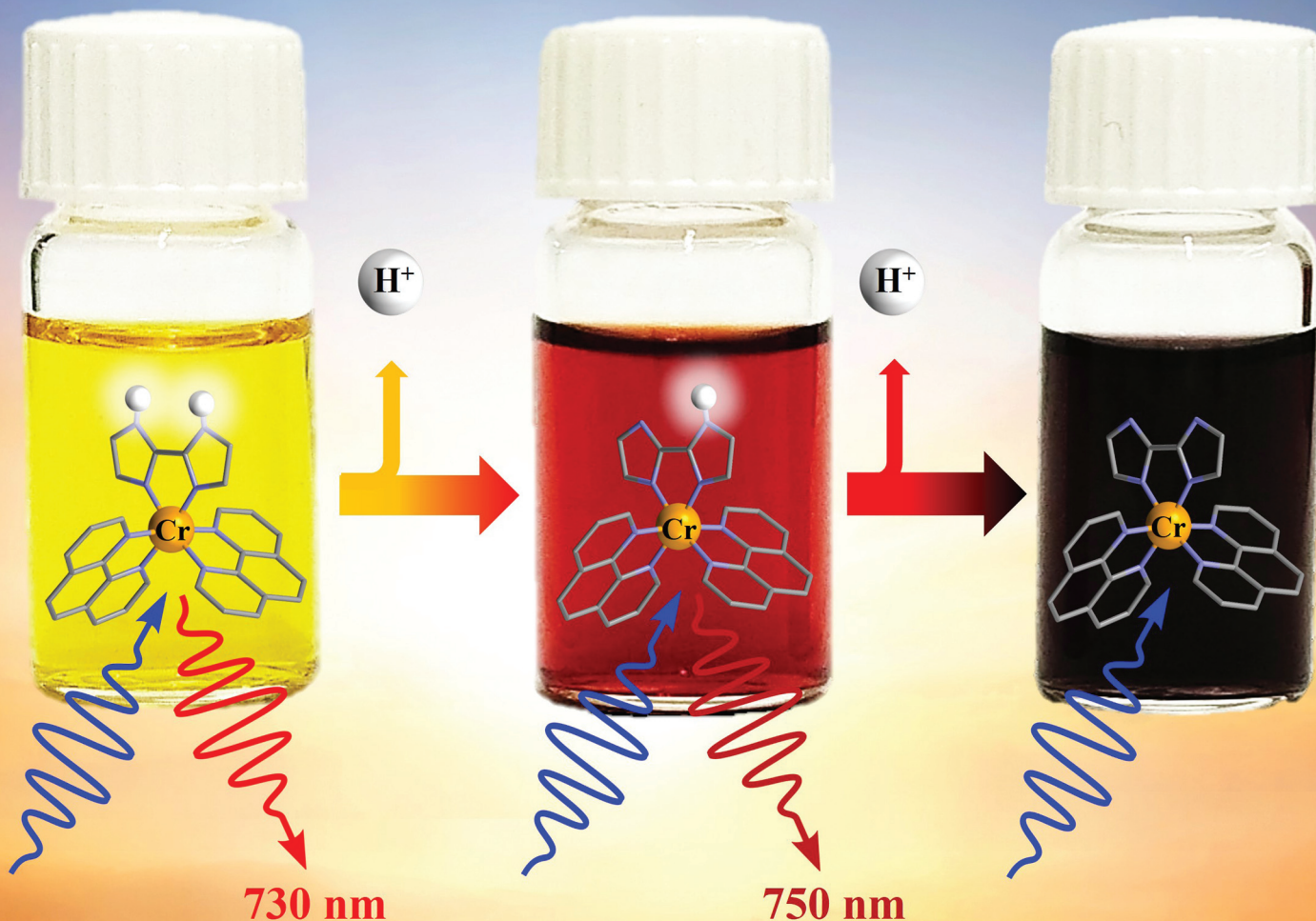


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**PAPER**

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complexes

## PAPER

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## Taming 2,2'-biimidazole ligands in trivalent chromium complexes†

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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 (H<sub>2</sub>biim) 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(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> 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 [CrN<sub>6</sub>] 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<sup>III</sup>-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)<sub>2</sub>(H<sub>x</sub>biim)]<sup>(1+x)+</sup> (x = 2–0) complexes overcomes the latter limitations and allows (i) the synthesis and characterization of these [CrN<sub>6</sub>] 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 [CrX<sub>6</sub>] units ideal partners for programming, tuning and rationalizing magnetic coupling with neighbouring paramagnetic d-block<sup>1–5</sup> and f-block<sup>6–10</sup> cations. In this context, many of the chromium-containing heterometallic assemblies exploit the

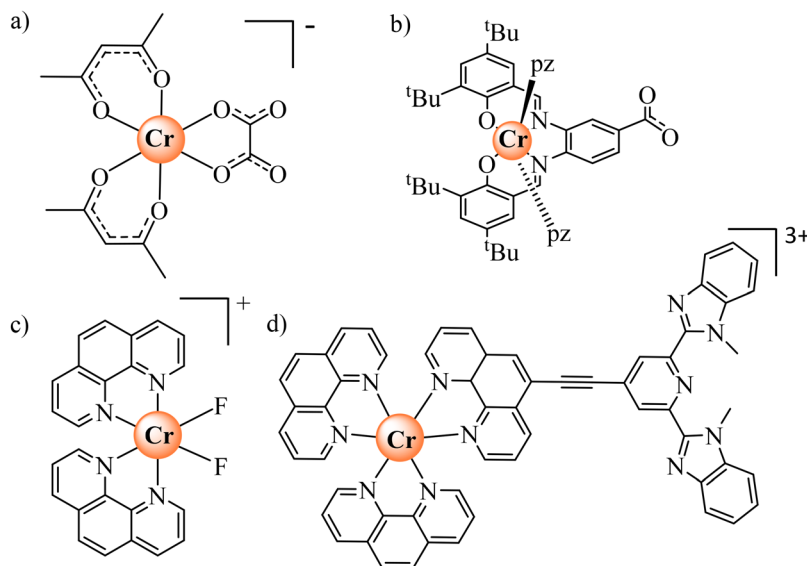
kinetically inert [Cr(CN)<sub>6</sub>]<sup>3–</sup> synthon, which behaves as a 'complex-as-ligand' connecting cationic metals *via* cyanide bridges in solid state materials.<sup>1–10</sup> The realization that, beyond magnetic properties, both lanthanide-based light downshifting<sup>11,12</sup> and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

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

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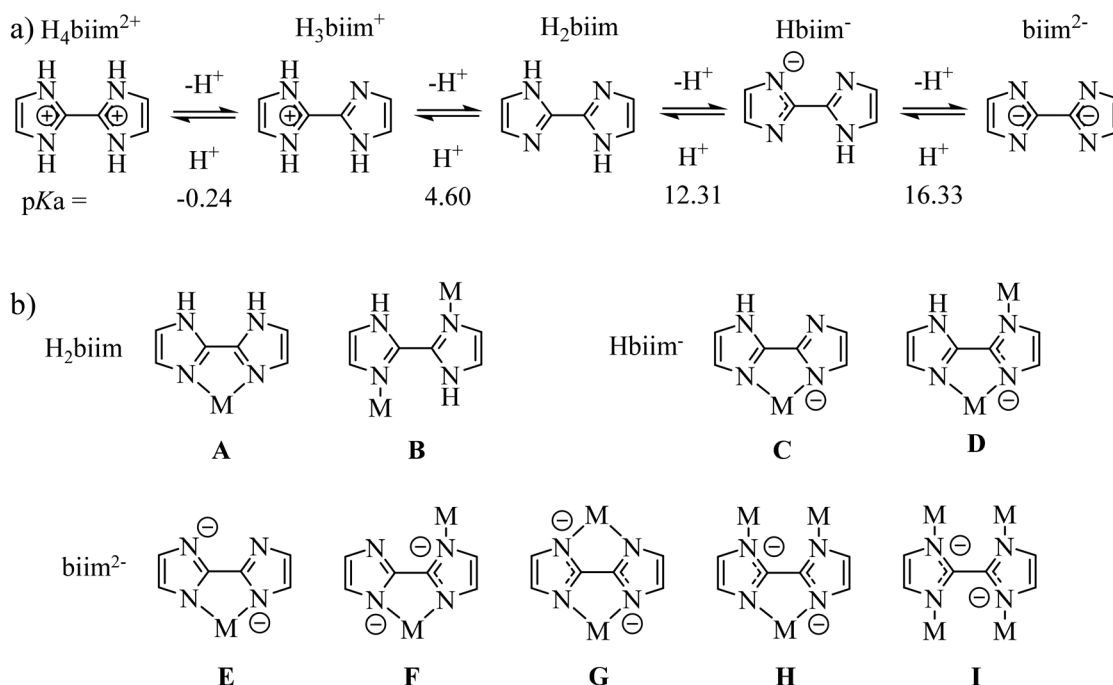


**Scheme 1** Kinetically-inert heteroleptic six-coordinate Cr<sup>III</sup> complexes used as complex-as-ligand when preparing multimetallic assemblies.<sup>12,18–21</sup>

tic six-coordinate complexes could be prepared, in which an oxalate (Scheme 1a),<sup>12</sup> a phenyl-carboxylate (Scheme 1b),<sup>19</sup> a difluoride (Scheme 1c)<sup>20</sup> or an extended ethyne-bis(benzimidazole)pyridine (Scheme 1d)<sup>21</sup> 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 [CrN<sub>6</sub>]

chromophores are ideal for maximizing phosphorescence quantum yields, emission lifetimes and sensitization in ‘molecular rubies’,<sup>22–24</sup> there is clearly a need for the design of novel [CrN<sub>6</sub>] analogues working as complex-as-ligand, but using more accessible and reliable bridging units.

With this in mind, the 2,2′-biimidazole ligand (H<sub>2</sub>biim, Scheme 2a)<sup>25</sup> 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 (H<sub>4</sub>biim<sup>2+</sup>) with pK<sub>a</sub> values measured in DMF : H<sub>2</sub>O = 7 : 3 (I = 0.1 M).<sup>25</sup> (b) Different coordination modes encountered in the literature for H<sub>2</sub>biim (A<sup>26,27</sup> and B<sup>28</sup>), Hbiim<sup>–</sup> (C and D)<sup>30</sup> and biim<sup>2–</sup> (E–I).<sup>31–34</sup>





sensing anions (mode A in Scheme 2b)<sup>26,27</sup> or connect other cations in a linear way (mode B in Scheme 2b).<sup>28</sup> More often,<sup>29</sup> multimetallic assemblies are obtained after stepwise deprotonation of the bound 2,2'-biimidazole ligand to give bridging Hbiim<sup>−</sup> (modes C and D in Scheme 2b)<sup>30</sup> and biim<sup>2−</sup> scaffolds (modes E–I in Scheme 2b).<sup>31–34</sup> Surprisingly, the studies dealing with the complexation of inert Cr<sup>III</sup> 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.<sup>35–38</sup> To the best of our knowledge, only the molecular structures of [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>,<sup>36</sup> [Cr(H<sub>2</sub>biim)<sub>2</sub>(Hbiim)]<sup>2+</sup> (ref. 37) and [Cr(Hbiim)<sub>3</sub>]<sup>36</sup> 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(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> in 94% yield (Fig. 1).<sup>35</sup>

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<sup>III</sup>,<sup>36–38</sup> 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 [L<sub>2</sub>Cr(H<sub>2</sub>biim)]<sup>3+</sup> has been made, while related systems with inert 4d and 5d metal ions have been designed regularly to access the two crucial pK<sub>a</sub> values for their use as complex-as-ligand (Table S1 in the ESI†).<sup>25,39–47</sup> In order to provide new perspectives for exploiting 2,2'-biimidazole as a bridging ligand between photo-physically-active Cr<sup>III</sup> and promising open-shell lanthanides, we

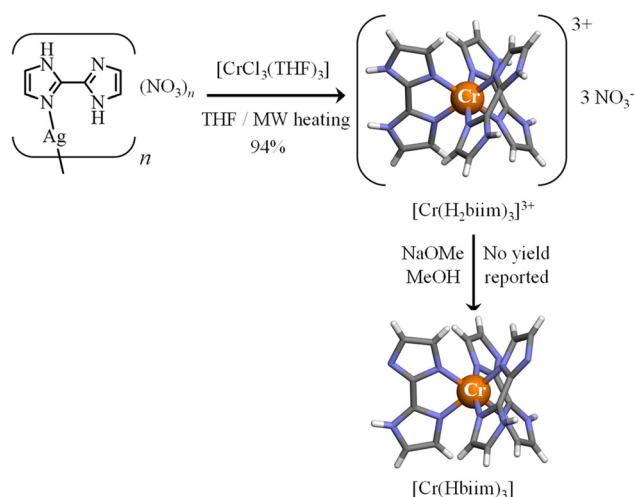
report here on the molecular structures and photophysical properties of the accessible and isolable homoleptic complexes [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(Hbiim)<sub>3</sub>] and [Cr(Hbiim)<sub>2</sub>(biim)]<sup>−</sup> in solution and in the solid state. The second part proposes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

## Results and discussion

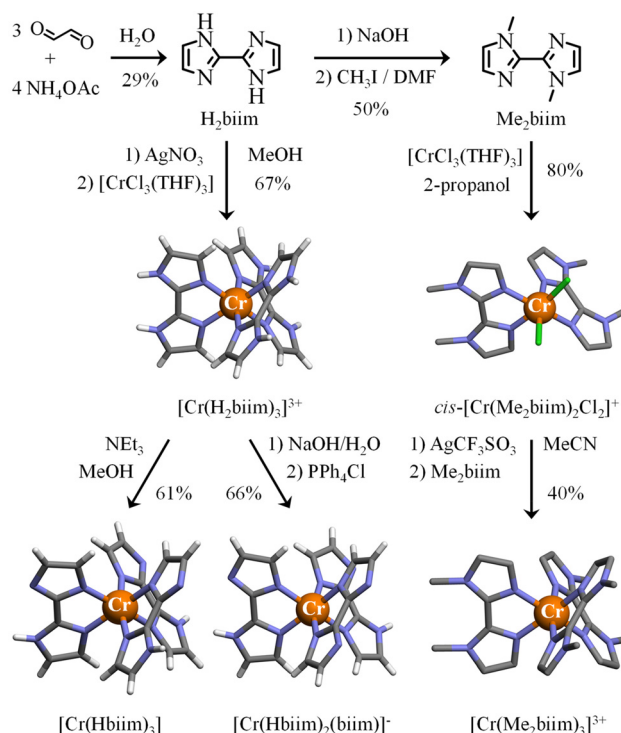
### Preparation and structures of the homoleptic [Cr(Me<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(Hbiim)<sub>3</sub>] and [Cr(Hbiim)<sub>2</sub>(biim)]<sup>−</sup> complexes

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

The original literature synthesis of [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> involved the reaction of CrCl<sub>3</sub>·3THF with [Ag(H<sub>2</sub>biim)]NO<sub>3</sub> in MeOH<sup>36</sup> or in THF<sup>35</sup> (Fig. 1) because the formation of highly insoluble AgCl drove the reaction to completion. To simplify the procedure, the intermediate [Ag(H<sub>2</sub>biim)]NO<sub>3</sub> was not isolated in this work, but was formed *in situ* by mixing AgNO<sub>3</sub>



**Fig. 1** Synthesis of [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> (ref. 35) and [Cr(Hbiim)<sub>3</sub>].<sup>36</sup> The molecular structures of the complexes are those found in the crystal structures of [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> (CCDC-603707) and [Cr(Hbiim)<sub>3</sub>](C<sub>6</sub>H<sub>6</sub>·2H<sub>2</sub>O) (CCDC-603730).<sup>36</sup> Color code: C = grey, N = blue, H = white, and Cr = orange.



**Fig. 2** Synthesis of ligands 2,2'-biimidazole (H<sub>2</sub>biim) and 1,1'-dimethyl-2,2'-bi-1*H*-imidazole (Me<sub>2</sub>biim) and their homoleptic [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(Hbiim)<sub>3</sub>], [Cr(Hbiim)<sub>2</sub>(biim)]<sup>−</sup> and [Cr(Me<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> 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 Me<sub>2</sub>biim ligands) are omitted for clarity.

and H<sub>2</sub>biim in MeOH. Then CrCl<sub>3</sub>·3THF was added into the resulting solution of [Ag(H<sub>2</sub>biim)]NO<sub>3</sub>. The purification method was identical to that used in ref. 35 and [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> was isolated in good yield (Fig. 2). Recrystallization by vapor diffusion of Et<sub>2</sub>O 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(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> at 290 K (Fig. 2, Tables S2–S3 and Fig. S1†).<sup>36</sup> The synthesis of [Cr(Hbiim)<sub>3</sub>] was first described by Gruia *et al.*,<sup>36</sup> where they used a stoichiometric amount of NaOMe to deprotonate [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> in MeOH. However, the complete insolubility of the formed neutral [Cr(Hbiim)<sub>3</sub>] complex did not allow any reproducible recrystallization techniques. To overcome this problem, a methanolic solution of [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> was treated in this work with vapor diffusion of an excess of volatile triethylamine, the limited pK<sub>a</sub> of which (10.74)<sup>50</sup> prevented any double deprotonation of the bound Hbiim ligand and finally gave crystals of [Cr(Hbiim)<sub>3</sub>] with good yield (61%) and in a reproducible way (Fig. 2, Tables S4–S6 and Fig. S2†). Further deprotonation of [Cr(Hbiim)<sub>3</sub>] could not be obtained by Gruia *et al.*,<sup>36</sup> but some partial reports of analogs of [Cr(biim)<sub>3</sub>]<sup>3–</sup>, *i.e.* Ba<sub>1.5</sub>[Co(biim)<sub>3</sub>]<sup>41</sup> and K<sub>3</sub>[Ru(biim)<sub>3</sub>]<sup>51</sup> that were obtained using harsh basic conditions (aqueous NaOH 2 M/BaCl<sub>2</sub> and <sup>t</sup>BuOK 1.2 M in MeOH, respectively) have been noted. Consequently, [Cr(Hbiim)<sub>3</sub>] 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 PPh<sub>4</sub>Cl immediately resulted in the formation of an orange precipitate. Recrystallization from MeOH by vapor diffusion of <sup>t</sup>BuOMe provided block-shaped crystals of [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub>(CH<sub>3</sub>OH) 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<sub>x</sub>biim)<sub>3</sub>]<sup>n+</sup> units display standard pseudo-octahedral arrangements of the six bound nitrogen donor atoms, with a compression along the pseudo-C<sub>3</sub> 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 ligands<sup>23</sup> as reported for related [Cr(bipy)<sub>3</sub>]<sup>3+</sup> (bipy = 2,2'-bipyridine, 79.1°)<sup>52</sup> and [Cr(phen)<sub>3</sub>]<sup>3+</sup> (phen = 1,10-phenanthroline, 81.0°) complexes.<sup>53</sup> The Cr–N distances in [Cr(H<sub>x</sub>biim)<sub>3</sub>]<sup>n+</sup> do not vary drastically (2.028–2.037 Å, compared with averages of 2.042 Å for [Cr(bipy)<sub>3</sub>]<sup>3+</sup> and 2.051 Å for [Cr(phen)<sub>3</sub>]<sup>3+</sup>) 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)<sub>3</sub>]<sup>3+</sup> and [Cr(phen)<sub>3</sub>]<sup>3+</sup> on one hand, and the family of [Cr(H<sub>x</sub>biim)<sub>3</sub>]<sup>n+</sup> 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<sup>–</sup> hydrogen-bond acceptors when they are deprotonated. For the fully protonated [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> complex, the weak N–H...O hydrogen bonds observed between

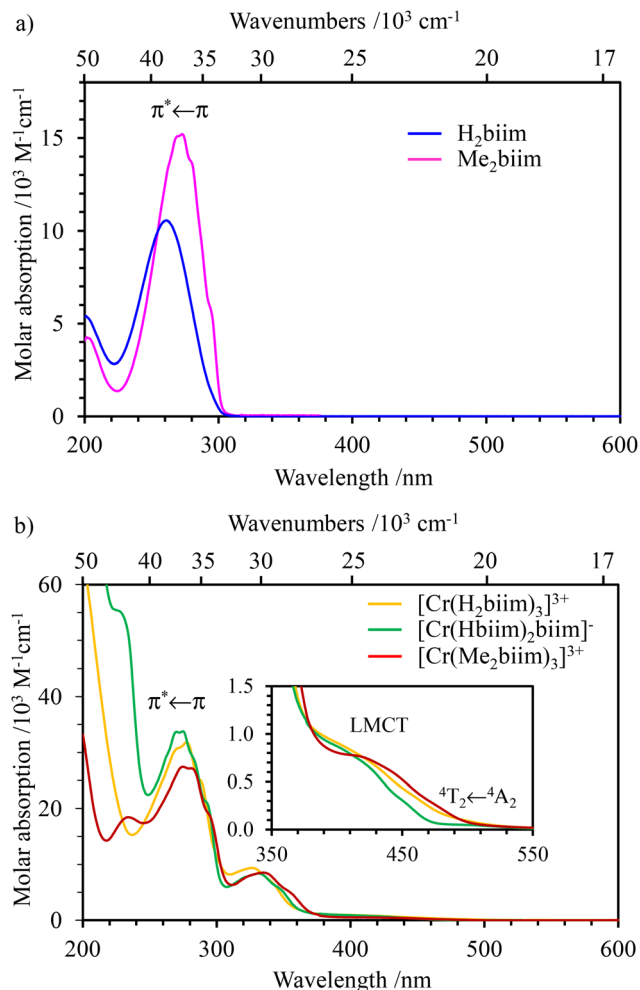
the bound ligand and the nitrate counter-anion (Fig. A2-2†) are responsible for the *circa* 400 cm<sup>–1</sup> decreases of the N–H stretching frequency in the vibrational spectrum with respect to the free ligand ( $\nu(\text{NH}) \approx 3000 \text{ cm}^{-1}$  in Fig. S14 and S18-top, Table S29†). The formation of strong intermolecular N–H...N hydrogen bonds observed in the deprotonated complexes [Cr(Hbiim)<sub>3</sub>] (Fig. A2-4†) and [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub> (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(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> *via* the Kane-Maguire synthetic strategy (Fig. 2) maintains the pseudo-octahedral structure of the [CrN<sub>6</sub>] core (Tables S16–S17 and Fig. S7†),<sup>54</sup> but it limits intermolecular hydrogen bonds in the crystal structure (Fig. A2-10 in Appendix 2†).

The spectroscopic properties of the ligands H<sub>2</sub>biim and Me<sub>2</sub>biim and the chromium complexes [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>, [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub> and [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> could be recorded in methanol or in acetonitrile. Unfortunately, the neutral complex [Cr(Hbiim)<sub>3</sub>] 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<sub>x</sub>biim)<sub>3</sub>]<sup>n+</sup>) together with (i) partial ligand dissociation to give 1 : 2 complexes ([Cr(H<sub>x</sub>biim)<sub>2</sub>]<sup>n+</sup> + H<sub>2</sub>biim) 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)<sub>2</sub>(biim)]<sup>–</sup> anion (negative mode) for [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub> (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.

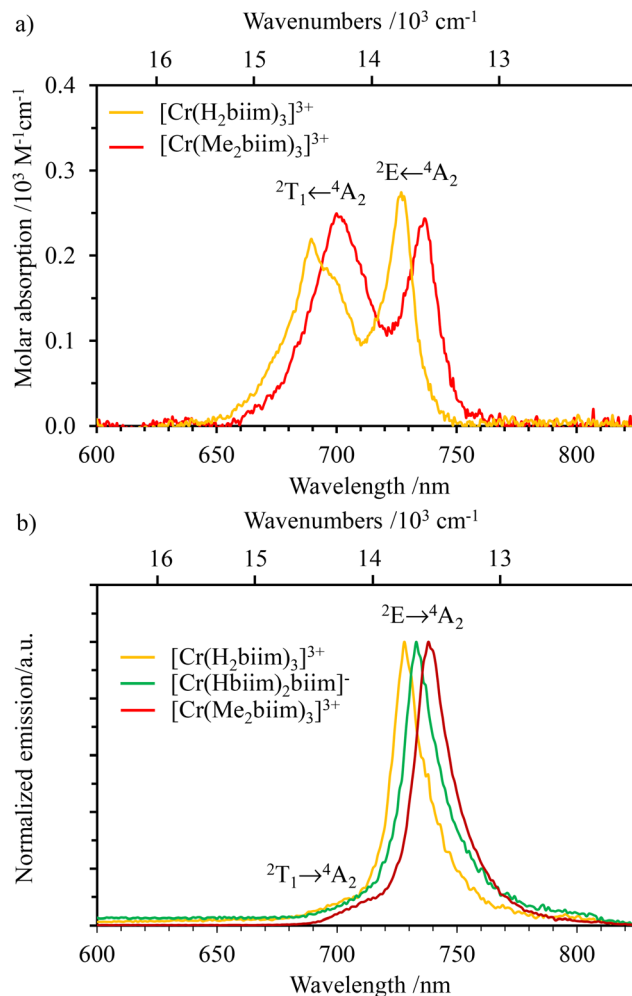
### Photophysical properties of the homoleptic [Cr(Me<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(Hbiim)<sub>3</sub>] and [Cr(Hbiim)<sub>2</sub>(biim)]<sup>–</sup> complexes

The absorption (Fig. 3 and 4a) and emission (Fig. 4b and S39†) spectra of the ligands H<sub>2</sub>biim and Me<sub>2</sub>biim and the complexes [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>, [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub> and [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> could be recorded in MeOH. Unfortunately, the neutral complex [Cr(Hbiim)<sub>3</sub>] 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 Cr<sup>3+</sup> 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 [CrN<sub>6</sub>] chromophores (Fig. 3).<sup>29,55–57</sup> The spin-allowed, but parity forbidden ligand-field Cr(<sup>4</sup>T<sub>2</sub> ← <sup>4</sup>A<sub>2</sub>) 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.<sup>58–63</sup> Careful spectral deconvolutions are required (Fig. S41–S43 and Tables





**Fig. 3** UV-visible absorption spectra of (a) non-coordinated ligands H<sub>2</sub>biim (purple) and Me<sub>2</sub>biim (dark blue) and (b) complexes [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> (NO<sub>3</sub>)<sub>3</sub> (orange), [Cr(Hbiim)<sub>2</sub>(biim)]<sup>−</sup> PPh<sub>4</sub> (green) and [Cr(Me<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> (CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (red) in MeOH at 293 K.



**Fig. 4** NIR (a) absorption spectra of [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> (water) and [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (acetonitrile) and (b) emission ( $\lambda_{\text{exc}} = 330$  nm) spectra of complexes [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> (orange), [Cr(Hbiim)<sub>2</sub>(biim)]<sup>−</sup> PPh<sub>4</sub> (green) and [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (red) in MeOH at 293 K.

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

Interestingly, for pseudo-octahedral d<sup>3</sup> complexes,  $E(^4T_2)$  provides a straightforward estimation of the ligand-field splitting (eqn (1)),<sup>64,65</sup> which covers a narrow  $19\,956 \leq \Delta \leq 21\,026$  cm<sup>−1</sup> range for [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(Hbiim)<sub>2</sub>(biim)]<sup>−</sup> and [Cr(Me<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> 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,<sup>66</sup> 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 (H<sub>2</sub>biim), 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  $\theta$  angular distort-

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<sup>−1</sup> >  $\Delta[\text{Cr}(\text{Me}_2\text{biim})_3]^{3+} \approx 20\,500$  cm<sup>−1</sup> >  $\Delta[\text{Cr}(\text{tpy})_2]^{3+} = 18\,750$  cm<sup>−1</sup> (Table 1).

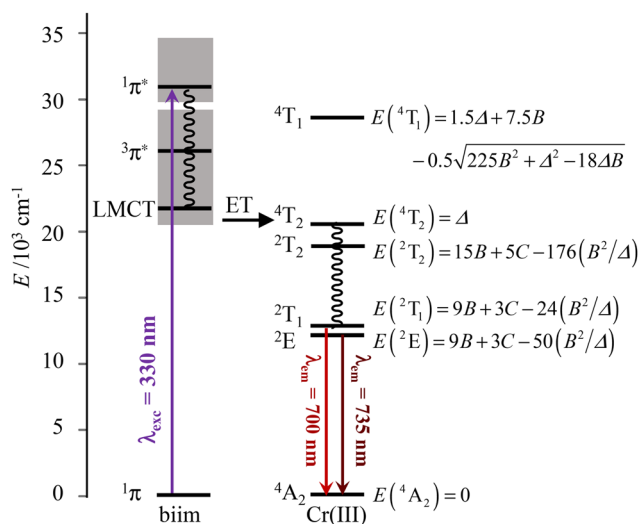
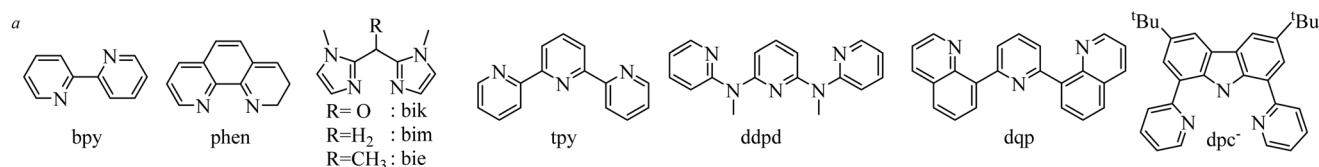
The interelectronic repulsion is estimated using the Racah parameters *B* (eqn (2)) and *C* (eqn (3)), which requires the energy of the lowest doublet levels  $E(^2E)$  and  $E(^2T_1)$  to be accessible (Fig. 5).<sup>64,65</sup>

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

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

Assuming an *O<sub>h</sub>* symmetry, the ground state absorption bands Cr(<sup>2</sup>E ← <sup>4</sup>A<sub>2</sub>) and Cr(<sup>2</sup>T<sub>1</sub> ← <sup>4</sup>A<sub>2</sub>) have very weak intensities ( $0.05 < \epsilon < 1$  M<sup>−1</sup> cm<sup>−1</sup>) due to the breaking of both parity

| Complex                                                  | $E(^4T_2)/\text{cm}^{-1}$ | $E(^2T_1)/\text{cm}^{-1}$ | $E(^2E)/\text{cm}^{-1}$ | $\Delta/\text{cm}^{-1}$ | $B/\text{cm}^{-1}$ | $C/\text{cm}^{-1}$ | $E(^4T_2) - E(^2E)/\text{cm}^{-1}$ | $\Delta/B$ | $C/B$ | 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  $^2\text{E}$  and  $^2\text{T}_1$  using the Strickler–Berg eqn (4)<sup>67,68</sup>, which is derived from Einstein’s relationship for spontaneous emission (Table 2, column 2 and Table S40†).<sup>69</sup>

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

Here  $c$  is the speed of light in vacuum ( $\text{cm s}^{-1}$ ),  $n$  is the refractive index of the solvent,  $N_A$  is the Avogadro number ( $\text{mol}^{-1}$ ),  $g_{\text{GS}}$  is the degeneracy of the ground state ( $g(^4\text{A}_2) = 4$ ),  $g_{\text{ES}}$  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 ( $\text{cm}^{-1}$ ) and  $\int \epsilon(\tilde{\nu})d\tilde{\nu}$  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),<sup>58,69–73</sup> but fall within the expected range for pseudo-octahedral  $[\text{CrN}_6]$  chromophores (Table S40†).<sup>70–77</sup> 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(II) lifetimes ( $\tau$ ) and radiative ( $k_{\text{rad}}$ ) and non-radiative ( $k_{\text{non-rad}}$ ) relaxation rate constants and intrinsic quantum yields ( $\phi_{\text{complex}}^{\text{intrinsic}} = k_{\text{rad}}/(k_{\text{rad}} + k_{\text{non-rad}})$ ) of chromium complexes

| Complex                                                  | $k_{\text{rad}}/\text{s}^{-1}$ | $\tau^{293\text{K, Ar}}/\mu\text{s}$ | $k_{\text{non-rad}}^{293\text{K, Ar}}/10^3\text{ s}^{-1}$ | $\phi_{\text{complex}}^{\text{intrinsic}}$ | $\tau^{293\text{K, air}}/\mu\text{s}$ | $k_{\text{non-rad}}^{293\text{K, air}}/10^3\text{ s}^{-1}$ | $\phi_{\text{complex}}^{\text{intrinsic}}$ | $\tau^{77\text{K, air}}/\mu\text{s}$ | $k_{\text{non-rad}}^{77\text{K}}/\text{s}^{-1}$ | $\phi_{\text{complex}}^{\text{intrinsic}}$ | Ref.                 |
|----------------------------------------------------------|--------------------------------|--------------------------------------|-----------------------------------------------------------|--------------------------------------------|---------------------------------------|------------------------------------------------------------|--------------------------------------------|--------------------------------------|-------------------------------------------------|--------------------------------------------|----------------------|
| $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$              | 75(4)                          | 0.47(2) <sup>d</sup>                 | 2120(106)                                                 | $3(1) \times 10^{-5}$                      | 0.44(2) <sup>d</sup>                  | 2260(113)                                                  | $3(1) \times 10^{-5}$                      | 2950(150) <sup>e</sup>               | 263(13)                                         | $2.0(6) \times 10^{-1}$                    | This work            |
| $[\text{Cr}(\text{Hbiim})_2(\text{biim})]^{3+}$          | —                              | 0.178(9) <sup>d</sup>                | —                                                         | —                                          | 0.141(7) <sup>d</sup>                 | —                                                          | —                                          | 2780(140) <sup>e</sup>               | —                                               | —                                          | This work            |
| $[\text{Cr}(\text{Me}_2\text{biim})_3]^{3+}$             | 73(4)                          | 4.28(4) <sup>d</sup>                 | 234(12)                                                   | $3(1) \times 10^{-4}$                      | 3.31(9) <sup>d</sup>                  | 302(1)                                                     | $2.4(8) \times 10^{-4}$                    | 3005(150) <sup>e</sup>               | 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) <sup>d</sup>                   | 26(7)                                                     | $2.5(8) \times 10^{-3}$                    | 14(1) <sup>d</sup>                    | 71(7)                                                      | $9(3) \times 10^{-4}$                      | 2940(140) <sup>e</sup>               | 18                                              | $1.9(6) \times 10^{-1}$                    | This work            |
| $[\text{Cr}(\text{bpy})_3]^{3+}$                         | 182                            | 74 <sup>h</sup>                      | 13.3                                                      | $1.4(4) \times 10^{-2}$                    | 52 <sup>h</sup>                       | 19                                                         | $9(3) \times 10^{-3}$                      | 5000 <sup>f</sup>                    | $\approx 0$                                     | $9(3) \times 10^{-1}$                      | 54, 58 and 70-72     |
|                                                          |                                | 39 <sup>d</sup>                      | 25.5                                                      | $7(2) \times 10^{-3}$                      | 29 <sup>d</sup>                       | 34                                                         | $5(2) \times 10^{-3}$                      | 6500 <sup>f</sup>                    | $\approx 0$                                     | $\approx 1$                                |                      |
| $[\text{Cr}(\text{phen})_3]^{3+}$                        | 319                            | 356 <sup>h</sup>                     | 2.49                                                      | $1.1(4) \times 10^{-1}$                    | 74 <sup>h</sup>                       | 13                                                         | $2.4(7) \times 10^{-2}$                    | 2100 <sup>g</sup>                    | 157                                             | $6.7(2) \times 10^{-1}$                    | 53, 54, 58 and 70-73 |
|                                                          |                                | 34 <sup>d</sup>                      | 29.1                                                      | $1.1(3) \times 10^{-2}$                    | 22 <sup>d</sup>                       | 45                                                         | $7(2) \times 10^{-3}$                      | 5300 <sup>f</sup>                    | $\approx 0$                                     | $\approx 1$                                |                      |
|                                                          |                                | 224 <sup>f</sup>                     | 4.15                                                      | $7(2) \times 10^{-2}$                      | 37 <sup>f</sup>                       | 27                                                         | $1.2(3) \times 10^{-2}$                    | —                                    | —                                               | —                                          |                      |
|                                                          |                                | 270 <sup>k</sup>                     | 3.38                                                      | $9(3) \times 10^{-2}$                      | 0.14 <sup>f</sup>                     | —                                                          | —                                          | 540 <sup>i</sup>                     | —                                               | —                                          | 61, 74 and 75        |
| $[\text{Cr}(\text{tpy})_2]^{3+}$                         | —                              | —                                    | —                                                         | —                                          | —                                     | —                                                          | —                                          | 670 <sup>g</sup>                     | —                                               | —                                          |                      |
| $[\text{Cr}(\text{dqp})_2]^{3+}$                         | 30                             | 1270 <sup>h</sup>                    | 0.76                                                      | $4(1) \times 10^{-2}$                      | 83 <sup>h</sup>                       | 12                                                         | $2.5(8) \times 10^{-3}$                    | 3070 <sup>i</sup>                    | 296                                             | $9(3) \times 10^{-2}$                      | 24                   |
|                                                          |                                | 2140 <sup>f</sup>                    | 0.44                                                      | $6(2) \times 10^{-2}$                      | 31 <sup>f</sup>                       | 32                                                         | $9(3) \times 10^{-4}$                      | —                                    | 296                                             | $9(3) \times 10^{-2}$                      |                      |
| $[\text{Cr}(\text{CN})_6]^{3-}$                          | 97                             | —                                    | —                                                         | —                                          | 0.12 <sup>i</sup>                     | 8330                                                       | $1.2(4) \times 10^{-5}$                    | 3950 <sup>i</sup>                    | 156                                             | $4(1) \times 10^{-1}$                      | 72                   |
| $[\text{Cr}(\text{bik})_3]^{3+}$                         | 31                             | 209 <sup>f</sup>                     | 4.75                                                      | $7(2) \times 10^{-3}$                      | 128 <sup>f</sup>                      | 7.8                                                        | $4(1) \times 10^{-3}$                      | 8220 <sup>g</sup>                    | 91                                              | $2.6(8) \times 10^{-1}$                    | 57                   |
| $[\text{Cr}(\text{biim})_3]^{3+}$                        | 37                             | 131 <sup>f</sup>                     | 7.60                                                      | $5(2) \times 10^{-3}$                      | 73 <sup>f</sup>                       | 14                                                         | $2.7(8) \times 10^{-3}$                    | 6750 <sup>g</sup>                    | 111                                             | $2.5(8) \times 10^{-1}$                    | 57                   |
| $[\text{Cr}(\text{bie})_3]^{3+}$                         | 60                             | 7 <sup>f</sup>                       | 143                                                       | $4(1) \times 10^{-4}$                      | 8 <sup>f</sup>                        | 125                                                        | $5(2) \times 10^{-4}$                      | 5250 <sup>g</sup>                    | 130                                             | $3(1) \times 10^{-1}$                      | 57                   |

<sup>a</sup> Recorded in degassed solution at room temperature. <sup>b</sup> Recorded in air-equilibrated solution at room temperature. <sup>c</sup> Recorded in a frozen solvent mixture at 77 K. <sup>d</sup> In MeOH. <sup>e</sup> In MeOH/H<sub>2</sub>O. <sup>f</sup> In CH<sub>3</sub>CN. <sup>g</sup> In CH<sub>3</sub>CN/C<sub>2</sub>H<sub>5</sub>CN. <sup>h</sup> In H<sub>2</sub>O. <sup>i</sup> In H<sub>2</sub>O/DMSO. <sup>j</sup> In aq. HClO<sub>4</sub>/MeOH. <sup>k</sup> In aq. HCl.

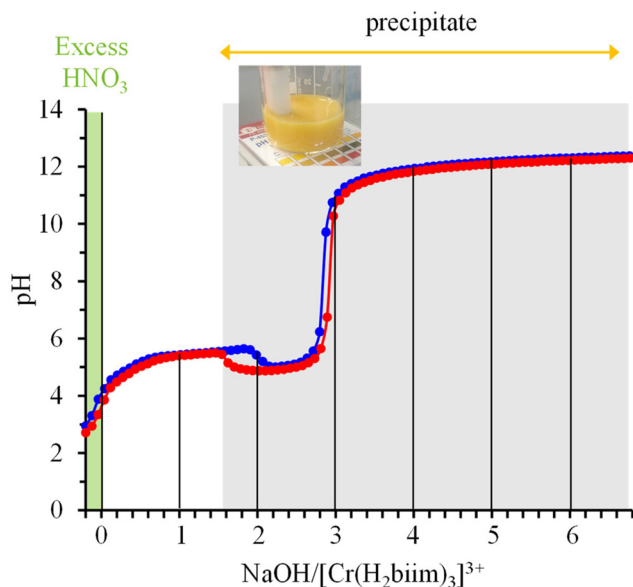
shifted NIR spin-flip Cr(<sup>2</sup>E → <sup>4</sup>A<sub>2</sub>) phosphorescence at 730–740 nm together with weak shoulders corresponding to Cr(<sup>2</sup>T<sub>1</sub> → <sup>4</sup>A<sub>2</sub>) within the 700–710 nm domain (Fig. 4b and 5). The latter dual emission disappears at 77 K (Fig. S39†) as a result of the depopulation of the high-energy Cr(<sup>2</sup>T<sub>1</sub>) level, and a single band Cr(<sup>2</sup>E → <sup>4</sup>A<sub>2</sub>) contributes to phosphorescence. Very similar results are observed in the solid state upon 330 nm excitation for the four complexes [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>, [Cr(Hbiim)<sub>3</sub>], [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub> and [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (Fig. S40b†), which ultimately demonstrate (i) the expected negligible Stokes shifts affecting the spin-flip Cr(<sup>2</sup>T<sub>1</sub>, <sup>2</sup>E ↔ <sup>4</sup>A<sub>2</sub>) 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/H<sub>2</sub>O solutions, the characteristic lifetime of the emissive Cr(<sup>2</sup>E) levels for [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> ( $\tau^{77\text{K}} = 3.0(1)$  ms), [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub> ( $\tau^{77\text{K}} = 2.7(1)$  ms) and [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> ( $\tau^{77\text{K}} = 3.0(1)$  ms) tends toward the radiative lifetime  $\tau_{\text{rad}} = 13.4(7)$  ms, in agreement with minor non-radiative vibrational quenching constants at this temperature for rigid triple-helical units, as similarly reported for [Cr(bpy)<sub>3</sub>]<sup>3+</sup> and [Cr(phen)<sub>3</sub>]<sup>3+</sup> (Table 2 column 8). At room temperature, the Cr(<sup>2</sup>E) lifetimes drastically drop below the microsecond range for [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> and [Cr(Hbiim)<sub>2</sub>(biim)]PPh<sub>4</sub>, which possess high-energy N–H oscillators, while the decrease of the lifetime for the methylated analogue [Cr(Me<sub>2</sub>biim)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> ( $\tau^{293\text{K, Ar}} = 4.28(4)$  μs) is less dramatic and mirrors those reported for [Cr(bpy)<sub>3</sub>]<sup>3+</sup> and [Cr(phen)<sub>3</sub>]<sup>3+</sup> (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(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> in MeOH corresponds to the largest vibrational quenching process along the series of [Cr(N<sup>n</sup>N<sup>n</sup>)<sub>3</sub>]<sup>3+</sup> chromophores collected in Table 2. Finally, the presence of <sup>3</sup>O<sub>2</sub> 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 [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup>, [Cr(Hbiim)<sub>3</sub>] and [Cr(Hbiim)<sub>2</sub>(biim)]<sup>3+</sup> complexes

In order to extract the acid–base thermodynamic constants connecting [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> with its successive deprotonated forms [Cr(H<sub>2</sub>biim)<sub>2</sub>(Hbiim)]<sup>2+</sup> ( $K_{\text{a1}}$ ), [Cr(H<sub>2</sub>biim)(Hbiim)<sub>2</sub>]<sup>+</sup> ( $K_{\text{a2}}$ ), [Cr(Hbiim)<sub>3</sub>] ( $K_{\text{a3}}$ ) and [Cr(Hbiim)<sub>2</sub>(biim)]<sup>+</sup> ( $K_{\text{a4}}$ ), we performed two successive pH-metric titrations of aqueous solutions of [Cr(H<sub>2</sub>biim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> using NaOH as the titrant. An initial addition of 0.2 equivalents of HNO<sub>3</sub> ensured that the complex exists initially in its fully protonated form [Cr(H<sub>2</sub>biim)<sub>3</sub>]<sup>3+</sup> (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 [Cr(Hbiim)<sub>3</sub>] (Fig. 6). It is therefore not possible to extract the searched pK<sub>a</sub> values and one can only estimate qualitatively pK<sub>a1</sub>, pK<sub>a2</sub> < 7. Moreover, the preservation of [Cr(Hbiim)<sub>3</sub>] as a precipitate in the presence of a large excess





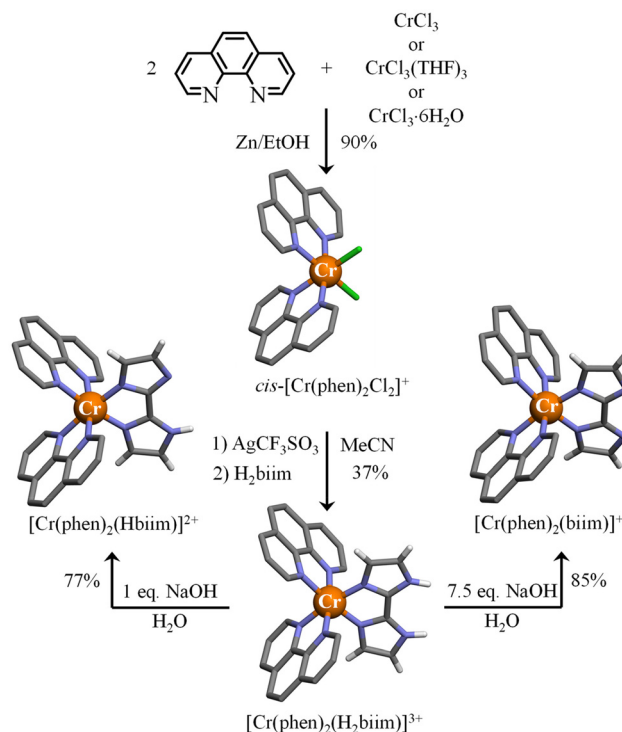
**Fig. 6** Reproducible acid–base titrations (blue trace for titration 1 and red trace for titration 2) of a solution of  $[\text{Cr}(\text{H}_2\text{biim})_3](\text{NO}_3)_3 + 0.2 \text{ eq. HNO}_3$  with NaOH (water, 293 K) highlighting the formation of an insoluble yellow precipitate.

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

### 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).<sup>54</sup> Taking advantage of the *trans* influence,<sup>78</sup> the complexation of 2.0 eq. of 1,10-phenanthroline (phen) to  $\text{CrCl}_3$  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.<sup>53</sup> The replacement of inert Cr–Cl bonds with labile Cr–OSO<sub>2</sub>CF<sub>3</sub> bonds<sup>79–81</sup> was performed under soft conditions by using  $\text{Ag}(\text{O}_3\text{SCF}_3)$  instead of an excess of triflic acid.<sup>24</sup> The addition of  $\text{H}_2\text{biim}$  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  $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$  cations ( $x = 2-0$ ) 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),<sup>53</sup>  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ ,  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  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  $\text{H}_2\text{biim}$  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  $\text{Hbiim}^-$  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 N–H...N bonds are observed (Fig. A3-3†), as previously described for  $[\text{Cr}(\text{Hbiim})_3]$  (Fig. A2-4†). Finally, the totally deprotonated bound  $\text{biim}^{2-}$  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 ( $\bar{d}_{\text{Cr-N}}$ )<sup>a</sup> 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)                                 |

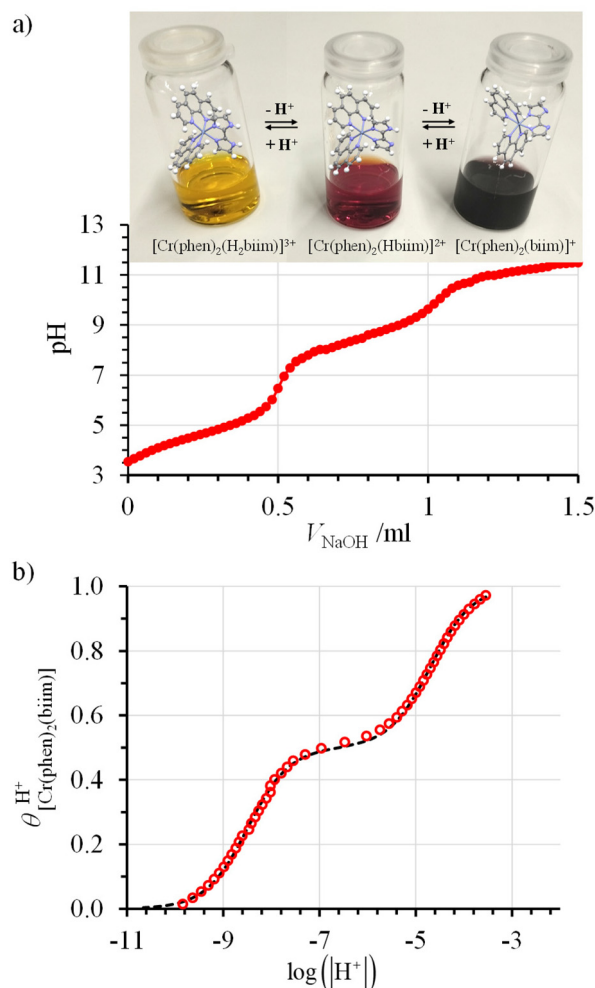
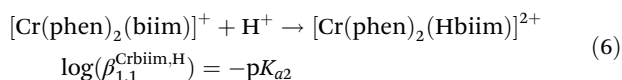
<sup>a</sup>The standard deviations refer to deviations from the computed averages.

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  $\text{H}_x\text{biim}$  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†).

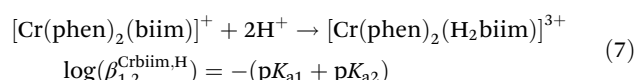
### Acid–base properties of the heteroleptic $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ complex

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  $\text{KNO}_3$ , 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  $\text{p}K_{\text{a}2} = 16.33$ ),<sup>25</sup>

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

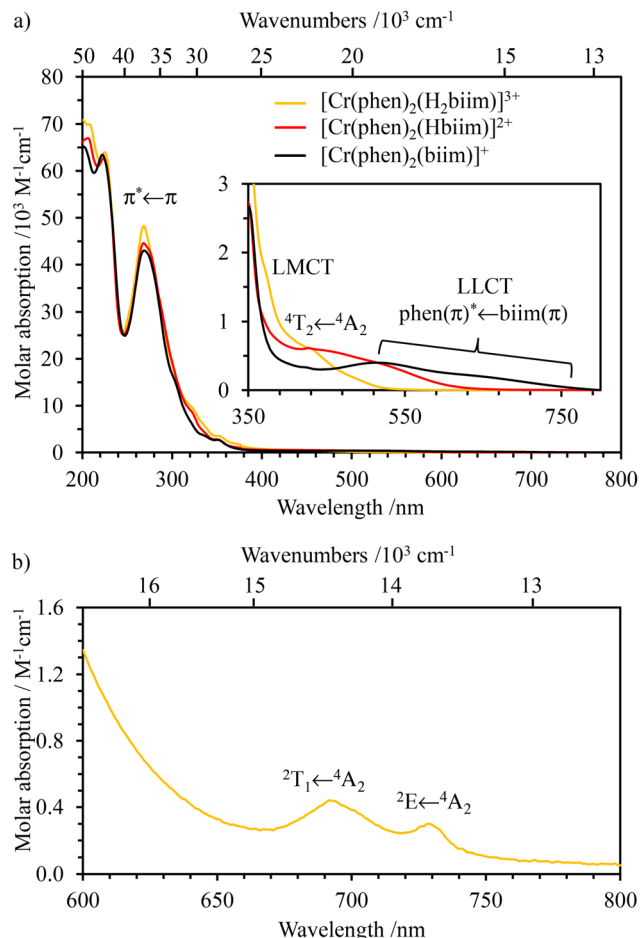


**Fig. 8** (a) Titration of 51 mg (52  $\mu\text{mol}$ ) of  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})](\text{CF}_3\text{SO}_3)_3$  (10 mL aqueous  $\text{KNO}_3$  0.1 M,  $c = 5.2 \text{ mmol L}^{-1}$ ) with NaOH 0.1 N highlighting the color changes and (b) associated binding isotherm depicted 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 =  $0.545 \text{ \AA}$ ),<sup>41</sup> 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)  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  (orange trace),  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  (red trace) and  $[\text{Cr}(\text{phen})_2(\text{biim})]^+$  (black trace) in  $\text{CH}_3\text{CN}$  ( $c \approx 10^{-5} \text{ mol L}^{-1}$ ) and (b)  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  in  $\text{CH}_3\text{CN}$  ( $c \approx 10^{-2} \text{ mol L}^{-1}$ ). 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  $\text{pK}_a$  values in water at ionic strength close to zero ( $I \approx 0$ ) could be carried out with the help of spectrophotometry to give  $\text{pK}_{a1} = 3.9(1)$  and  $\text{pK}_{a2} = 7.8(1)$  (Fig. S63†), which are close to those determined at  $I = 0.1 \text{ M}$  ( $\text{KNO}_3$ ).

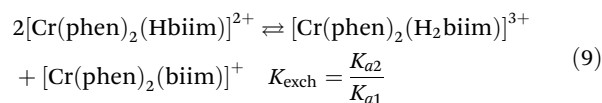
### Photophysical properties of the heteroleptic $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$ ( $x = 2-0$ ) complexes

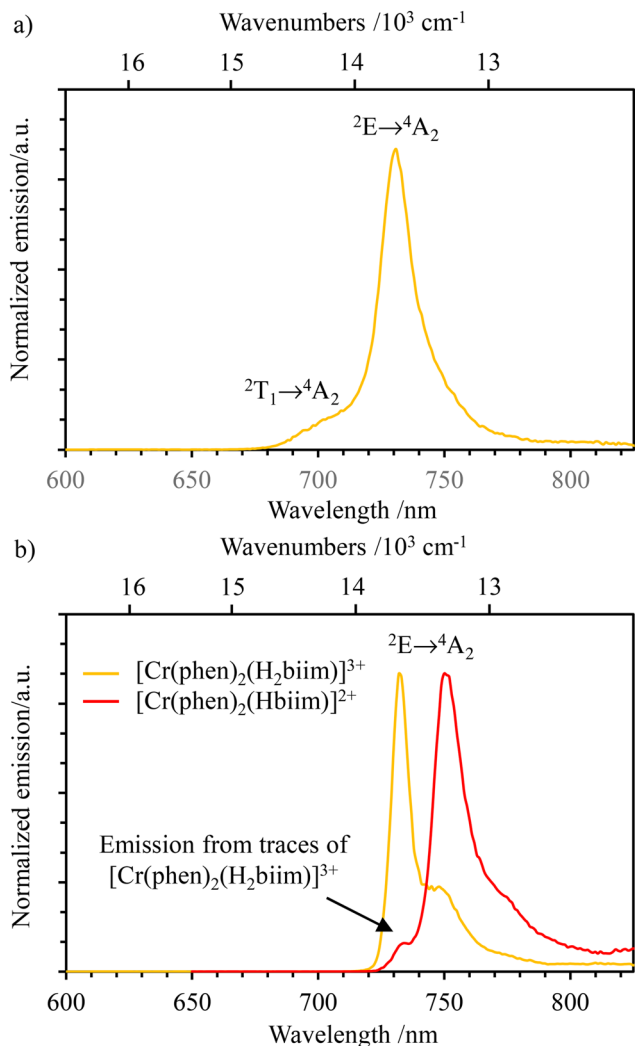
The three heteroleptic complexes exhibit similar and intense absorption bands in the UV range (below 350 nm, Fig. 9a), which can be assigned to intraligand  $\pi-\pi^*$  transitions (ILCT) completed by variable amounts of interligand (LLCT), ligand to metal (LMCT) and metal-to-ligand (MLCT) charge transfer 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  $(\text{phen})\pi^* \leftarrow (\text{H}_x\text{biim})\pi$  ( $x = 0-2$ , 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  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  (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  $\Delta$ , reminiscent of  $\text{Cr}({}^4\text{T}_2 \leftarrow {}^4\text{A}_2)$  transitions in octahedral geometry, also decreases with stepwise deprotonation:  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  ( $412.9 \text{ nm}$ ,  $\Delta \approx 24\,219 \text{ cm}^{-1}$ ) >  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  ( $434 \text{ nm}$ ,  $\Delta \approx 23\,042 \text{ cm}^{-1}$ ) >  $[\text{Cr}(\text{phen})_2(\text{biim})]^+$  ( $457.8 \text{ nm}$ ,  $\Delta \approx 21\,844 \text{ cm}^{-1}$ ). 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 ( $\bar{d}_{\text{Cr-N}(\text{biim})}$  is becoming shorter) in  $[\text{Cr}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$  ( $x = 2-0$ ) are more than compensated by the removal of the bound 1,10-phenanthroline ligands ( $\bar{d}_{\text{Cr-N}(\text{phen})}$  is becoming longer) as exemplified in the molecular structures in the crystalline state (push-pull effect, Table 3).

The NIR absorption spectrum of  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  (Fig. 9b) exhibits two well-resolved absorption bands that are assigned to the spin-flip transitions  $\text{Cr}({}^2\text{E} \leftarrow {}^4\text{A}_2)$  and  $\text{Cr}({}^2\text{T}_1 \leftarrow {}^4\text{A}_2)$  assuming  $O_h$  symmetry and with  $\epsilon = 0.27$  and  $0.19 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. For the deprotonated derivatives  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  and  $[\text{Cr}(\text{phen})_2(\text{biim})]^+$ , the larger residual interligand charge transfer bands mask these weak forbidden spin-flip transitions (Fig. S65†). Consequently, Racah parameters  $B = 766 \text{ cm}^{-1}$  and  $C = 2697 \text{ cm}^{-1}$  (eqn (2) and (3), Table 1, entry 4) together with the radiative rate constant of  $k_{\text{rad}} = 65(3) \text{ s}^{-1}$  (eqn (4), and Table 2, column 1), typical of  $[\text{CrN}_6]$  chromophores, could be estimated only for  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ .

At room temperature in  $\text{CH}_3\text{CN}$ , only  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  is emissive and shows the typical dual  $\text{Cr}({}^2\text{T}_1 \rightarrow {}^4\text{A}_2)$  and  $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$  emission observed for many  $\text{Cr}(\text{III})$  complexes (Fig. 10a). In addition to  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ , the NIR emission of the complex  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  can be detected at low temperature in frozen solvent mixtures ( $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{CN}$  6 : 4 at 77 K, Fig. 10b), whereas  $[\text{Cr}(\text{phen})_2(\text{biim})]^+$  remains non-emissive. Compared with the emission band of  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  ( $\lambda_{\text{max}} = 732 \text{ nm}$ ;  $\tilde{\nu} = 13\,661 \text{ cm}^{-1}$ ), the first deprotonated analog  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  shows a red-shifted  $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$  transition at  $\lambda_{\text{max}} = 750 \text{ nm}$ ;  $\tilde{\nu} = 13\,333 \text{ cm}^{-1}$  (Fig. 10b). Additionally, the spectrum of  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  contains a band foot at 733 nm originating from a small amount of  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ , which is inevitably present in solution due to the proton-transfer equilibrium (9):





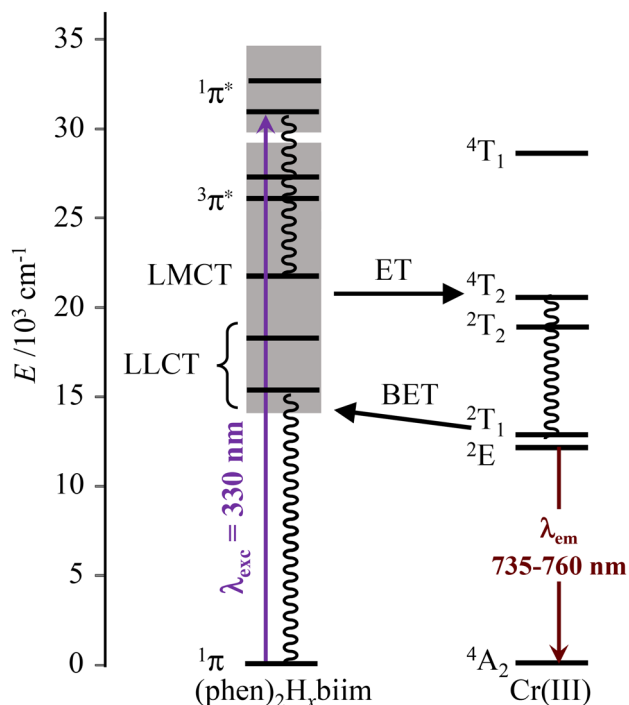
**Fig. 10** Emission spectra ( $\lambda_{\text{exc}} = 350 \text{ nm}$ ) of (a)  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  at 293 K in  $\text{CH}_3\text{CN}$  and (b)  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  (orange trace) and  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  (red trace) at 77 K in frozen  $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{CN}$  (6 : 4).

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

Excited state lifetimes for the NIR emission arising from the  $\text{Cr}(\text{E})$  excited state upon excitation at 355 nm were recorded in solution at room temperature and at 77 K for  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ , and only at 77 K for  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  (Fig. S67–S70†). In frozen solutions at 77 K,  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  displays a mono-exponential decay of 2.94 ms, which is typical of  $\text{Cr}(\text{III})$ -polyimine complexes (Table 2). The emission decay curve of  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$  could not be fit with a mono-exponential function. Since the complex exists as a 98 : 1 : 1 mixture of  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$ ,  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  and  $[\text{Cr}(\text{phen})_2(\text{biim})]^+$  (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  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$ , and a short contribution (723(30)  $\mu\text{s}$ ) which is tentatively assigned to  $[\text{Cr}(\text{phen})_2(\text{Hbiim})]^{2+}$ , for which the smaller energy gap between the emissive doublet state level  $\text{Cr}(\text{E})$  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  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  is emissive and it exhibits a mono-exponential emission decay of 38  $\mu\text{s}$  in deaerated  $\text{CH}_3\text{CN}$ . This excited state lifetime is orders of magnitude longer than those of the three isolated homoleptic parent complexes  $[\text{Cr}(\text{H}_x\text{biim})_3]^{n+}$  (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  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  is in the same range as that of  $[\text{Cr}(\text{bpy})_3]^{3+}$ ; however, it is one order of magnitude shorter than that of  $[\text{Cr}(\text{phen})_3]^{3+}$  (Table 2). The emission lifetime is reduced to 14  $\mu\text{s}$  in aerated solution because of some additional quenching *via* energy transfer to the  $^3\text{O}_2$  molecules present in solution.

Finally, the global luminescence quantum yield of the complex  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  upon ligand-based excitation at  $\lambda_{\text{exc}} = 450 \text{ nm}$  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  $[\text{Cr}^{\text{III}}(\text{phen})_2(\text{H}_x\text{biim})]^{(1+x)+}$  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)  $\phi_{\text{complex}}^{\text{global}} \simeq \phi_{\text{complex}}^{\text{intrinsic}}$ , 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),<sup>70,71,79,80</sup> 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),<sup>53,81</sup> which makes  $[\text{Cr}(\text{phen})_2(\text{H}_2\text{biim})]^{3+}$  a moderate emitter for a Cr(III) complex.<sup>72</sup>

## 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,<sup>35–38</sup> 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  $\text{H}_2\text{biim}$  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  $[\text{Cr}(\text{phen})_2(\text{biim})-\text{M}^{z+}]^{(z+1)+}$  ( $\text{M}^{z+}$  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.

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