

## PAPER

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## Identifying charge-transfer and trip–multiplet states in Co(I), Co(II), and Co(III) phthalocyanines using (magneto)optical spectroscopy and (TD)DFT calculations†‡

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Herein we compare the electronic structures of the Co(I), Co(II), and Co(III) phthalocyanines, which were elucidated using UV-vis-NIR and magnetic circular dichroism (MCD) spectroscopy as well as density functional theory (DFT) and time-dependent DFT (TDDFT) calculations. The NIR triplet–multiplet bands in  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{I}}\text{L}_2$  (L = nil, Py, or  $n\text{BuNH}_2$ ; R = H or  $\text{tert-Bu}$ ) complexes were studied by MCD spectroscopy for the first time and compared to those reported earlier by us in  $\text{Pc}^{\text{R}4}(2-)\text{Cu}$  (R =  $\text{tert-Bu}$  or  $\text{SO}_3\text{Na}$ ) compounds (*J. Porphyrins Phthalocyanines* 2025, **29**, 110–122). In all cases, a Faraday MCD pseudo A-term was observed for this transition. DFT and TDDFT calculations successfully explained a systematic blue-shift in the metal-to-ligand charge-transfer (MLCT) and B1-band transitions going from  $[\text{Pc}^{\text{R}4}(2-)\text{Co}]^-$  to  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{I}}\text{L}_2$  to  $[\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{III}}\text{X}_2]^-$  (X =  $\text{CN}^-$  or  $\text{Br}^-$ ) complexes. Additionally, absorption bands observed in the 370–530 nm spectral envelope in  $[\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{III}}\text{X}_2]^-$  complexes were assigned with a high level of confidence for the first time. This work provides the first combined systematic experimental and theoretical study that highlights similarities and differences in (magneto)optical spectroscopy of cobalt phthalocyanines spanning three oxidation states at the central metal ion.

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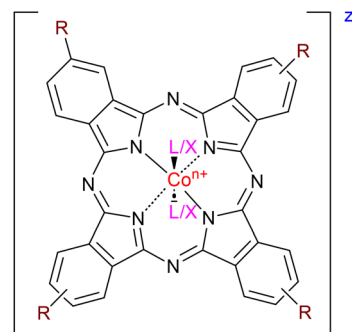
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## Introduction

Transition-metal phthalocyanines are well-known blue or green pigments<sup>1–3</sup> that have many applications including catalysis,<sup>4–15</sup> photocatalysis,<sup>16–20</sup> electrocatalysis,<sup>21–28</sup> light-harvesting,<sup>29–34</sup> molecular electro- or chemochromic sensing,<sup>35–40</sup> photodynamic and catalytic cancer therapy,<sup>41–47</sup> semiconductors,<sup>48–51</sup> and fluorescence (bio)imaging.<sup>52–54</sup> In particular, cobalt phthalocyanine is known for its ability to oxidize thiols to disulfides (the so-called “Merox” process or jet fuel sweetening process).<sup>55–62</sup> During the catalytic cycle, the cobalt ion cycles between Co(III) and Co(I). The ability to characterize both metal-centered oxidation and reduction processes in cobalt phthalocyanine is well-documented, and a number of



Complex	n	z	R	L	X
$[\text{Pc}(2-)\text{Co}]^-$	1	1	H	none	none
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$	2	0	tBu	none	none
$\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$	2	0	H	Py	none
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$	2	0	tBu	Py	none
$\text{Pc}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$	2	0	H	$n\text{BuNH}_2$	none
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$	2	0	tBu	$n\text{BuNH}_2$	none
$[\text{Pc}(2-)\text{Co}^{\text{III}}(\text{CN})_2]^-$	3	1	H	none	$\text{CN}^-$
$[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$	3	1	tBu	none	$\text{Br}^-$

Fig. 1 General structure of the phthalocyanines and systems discussed in this report.

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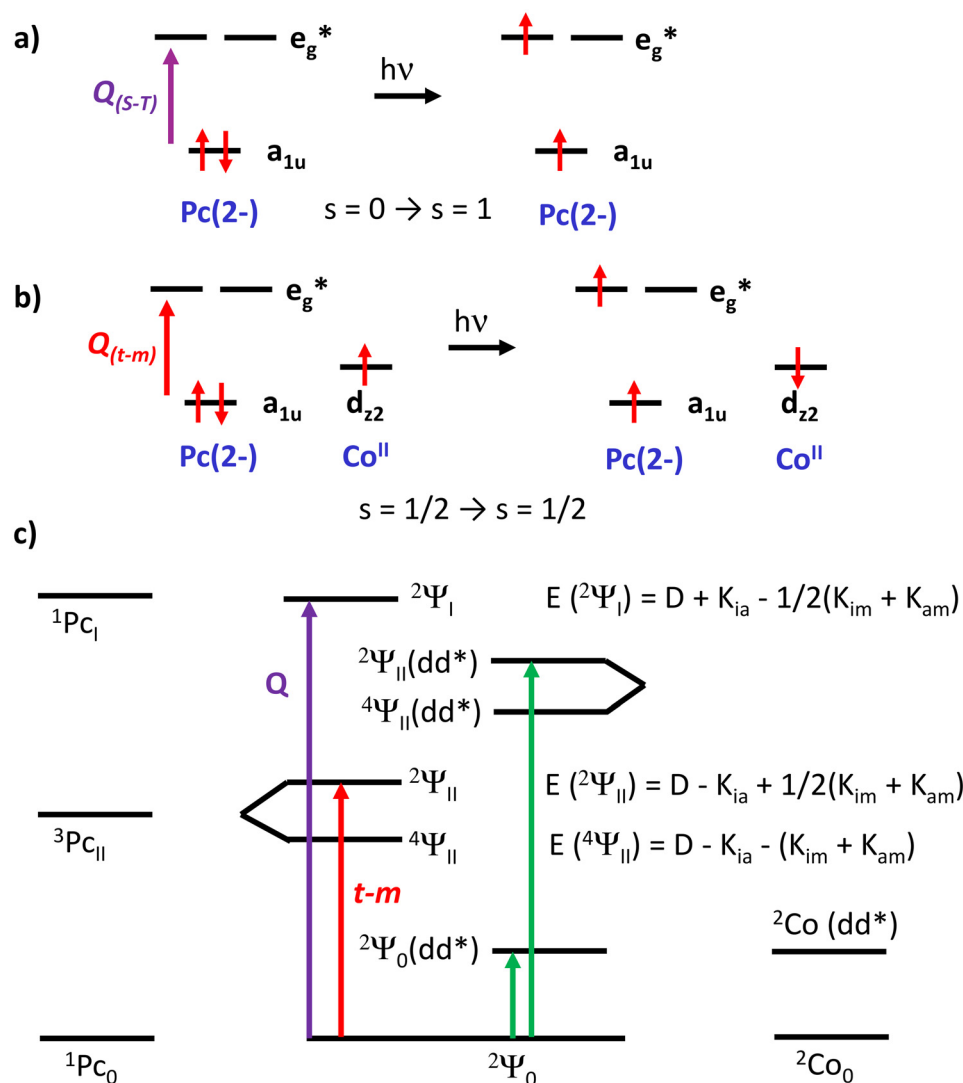
† Dedicated to the memory of Professor Barry Lever (A. B. P. Lever).

‡ Electronic supplementary information (ESI) available: Additional UV-Vis-NIR spectra and DFT and TDDFT information (PDF). See DOI: <https://doi.org/10.1039/d5dt00628g>

Co(III),<sup>63–73</sup> Co(II),<sup>74–80</sup> and Co(I)<sup>81–85</sup> phthalocyanine complexes coordinated to the Pc(2-) ligand have been isolated and characterized by a variety of experimental methods. Such behavior is uncommon due to the redox non-innocence of the phthalocyanine ligand. Thus, taking into consideration the incomplete d-orbital subset in cobalt phthalocyanines, investigating these systems in a systematic way using optical and magnetooptical spectroscopy in combination with modern density functional theory (DFT) and time-dependent DFT (TDDFT) methods provides a unique opportunity to study the influence of the oxidation state at the central metal ion on the charge-transfer processes as well as phthalocyanine-centered  $\pi$ - $\pi^*$  transitions in a systematic way (Fig. 1).

In particular, the  $d^6$ - $d^8$  electronic configurations in Co(III)-Co(I) phthalocyanine systems allow us to study the trends in

energies of the  $d_\pi$  (Co)  $\rightarrow$   $1b_{1u}^*$ ,  $1b_{2u}^*$  (Pc) metal-to-ligand charge-transfer (MLCT) transitions. In addition, Co(II) (but not Co(III) or Co(I)) phthalocyanine complexes have a weak set of bands observed in the NIR region of their UV-Vis-NIR spectra. These bands were initially assigned as d-d transitions.<sup>86–89</sup> However, Lever and co-workers assigned these bands as triplet-multiplet (t-m) transitions.<sup>90</sup> Zerner and Cory introduced the theory of t-m transitions for paramagnetic porphyrins and their analogs in the early 1990s.<sup>91</sup> Indeed, although singlet-triplet transitions in diamagnetic transition-metal phthalocyanines are spin-forbidden, Ishii and co-workers observed such a transition in  $\text{Pc}^{\text{tBu}}(2-)\text{Ir}^{\text{III}}\text{Cl}(\text{Py})$  at 959 nm.<sup>92</sup> Similar to the Q-band, this transition is degenerate (Fig. 2a) and results in a weak but observable Faraday A-term by magnetic circular dichroism (MCD) spectroscopy.

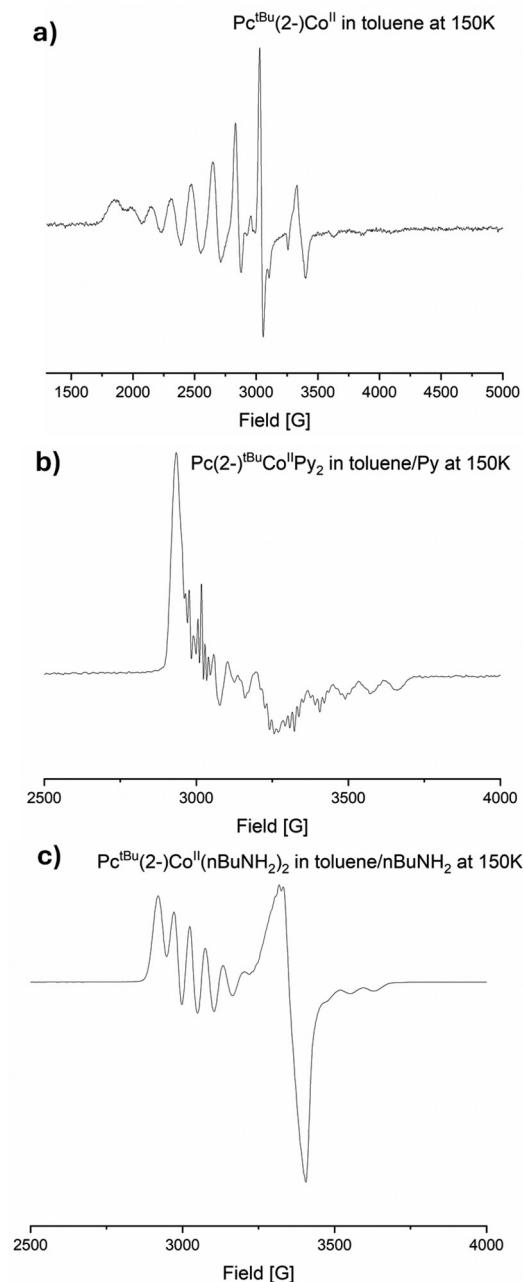


**Fig. 2** Simplified illustration of the singlet-triplet (a) and triplet-multiplet (b) transitions. Simplified representation of the excited states in the low-energy region of the cobalt(II) ( $s = \frac{1}{2}$ ) phthalocyanine systems (c). The energies of the selected transitions are given on a side panel ( $K_{ia}$  is an exchange integral between occupied and virtual orbitals in the phthalocyanine ligand;  $K_{im}$  is an exchange integral between occupied orbitals in the phthalocyanine ligand and cobalt(II) center;  $K_{am}$  is an exchange integral between unoccupied orbitals in the phthalocyanine ligand and cobalt(II) center;  $D$  is an offset energy).<sup>91</sup>

In the case of paramagnetic transition-metal phthalocyanines, a metal–ligand exchange can provide a path for spin-allowed t–m transitions that include a triplet state at the phthalocyanine ligand (Fig. 2b; see original paper by Cory and Zerner<sup>91</sup> for detailed discussion). In triplet–multiplet transitions, the organic chromophore (*i.e.*, phthalocyanine) goes from the singlet state to a triplet state, while the multiplicity of the transition-metal phthalocyanine remains the same (*i.e.* doublet in the case of cobalt(II) phthalocyanines, Fig. 2b).<sup>91</sup> Again, such an excited state will be doubly degenerate for all paramagnetic transition-metal phthalocyanines with effective  $D_{4h}$  or  $C_{4v}$  symmetry and thus should be associated with a Faraday A-term in their MCD spectra, unless a complex possesses a doubly degenerate ground state (*i.e.*  $[\text{Pc}(2-)\text{Fe}^{\text{III}}(\text{CN})_2]^-$  has a  $^2\text{E}_g$  ground state), which will have both Q- and t–m transitions better described using Faraday  $C_A$ -terms.<sup>93</sup> Indeed, we recently observed Faraday A-terms for the t–m transitions in two copper(II) phthalocyanines.<sup>94</sup> Moreover, since both singlet–singlet Pc-centered ligand excitations lead to the traditional phthalocyanine Q-band (Fig. 2c) and phthalocyanine-centered singlet–triplet excitations (Fig. 2b) exhibit nearly pure  $1a_{1u} \rightarrow 1e_g^*$  single-electron character, one might expect that the Q- and t–m bands will exhibit similar vibronic progression components. Again, we reported this phenomenon for copper(II) phthalocyanines.<sup>94</sup> Thus, investigation of the NIR absorption and MCD spectra in paramagnetic ( $s = \frac{1}{2}$ ) Co(II) phthalocyanines should resolve the ambiguous NIR band assignments for d–d and t–m transitions. Because of the increased tendency towards aggregation and lower solubility of unsubstituted phthalocyanines, we used a highly soluble, less aggregating *tert*-butyl substituted phthalocyanine core as it is well-known<sup>95–97</sup> that the introduction of the *tert*-butyl groups into the phthalocyanine chromophore does not significantly change its optical properties (Fig. 1). Finally, as we demonstrated for copper(II) and vanadyl(IV) phthalocyanines,<sup>94</sup> TDDFT calculations are able to accurately predict the energies of t–m transitions, allowing us to solidify proposed band assignments in the NIR region for  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}}\text{L}_2$  ( $\text{R} = \text{H}$  or *tert*-Bu;  $\text{L} = \text{nil}$ , Py, or  $n\text{BuNH}_2$ ).

## Results and discussion

The cobalt(I–III) phthalocyanine derivatives discussed in this paper are shown in Fig. 1. Synthetic procedures for all cobalt phthalocyanines outlined in this report are well-developed except for  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$ . Indeed, diamagnetic  $[\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{I}}]^-$  complexes can be prepared by the reduction of  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}}$  with  $\text{NaBH}_4$  in DMF.<sup>98,99</sup> Axially coordinated  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}}\text{L}_2$  ( $\text{L} = \text{Py}$  or  $n\text{BuNH}_2$ ) can be synthesized by the reaction of  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}}$  and excess ligand.<sup>74–80</sup> Coordination of two axial ligands in these compounds was confirmed by both UV-Vis spectroscopy and EPR spectroscopy (Fig. 3 and Table 1). Indeed, EPR spectra of the  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$ ,  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$ , and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  complexes correlate well with EPR



**Fig. 3** 150 K EPR spectra of the  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  complex in toluene (a),  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$  complex in 95/5% (v/v) toluene/pyridine (b), and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  complex in 95/5% (v/v) toluene/ $n\text{BuNH}_2$  (c).

spectra previously published by Larin and co-workers<sup>101,102</sup> for *tert*-butyl- and by Cariati and co-workers<sup>86,87</sup> for unsubstituted phthalocyanine ligands. Additionally, coordination of two pyridine ligands as well as a low-spin  $(d_{xy})^2(d_{xz}, d_{yz})^4(d_{z^2})^1$  electronic configuration in  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$  complex can be proven by observation of five-line superhyperfine splitting in their EPR spectra (Fig. 3).<sup>101,102</sup> Simple addition of cyanide anion to a solution of  $\text{Pc}(2-)\text{Co}^{\text{II}}$  in DMF leads to axial coordination and destabilization of the  $d_{z^2}$  orbital, making it easier for oxygen to oxidize the central metal ion to diamagnetic Co(III) upon the

**Table 1** EPR parameters for selected cobalt(II) phthalocyanines

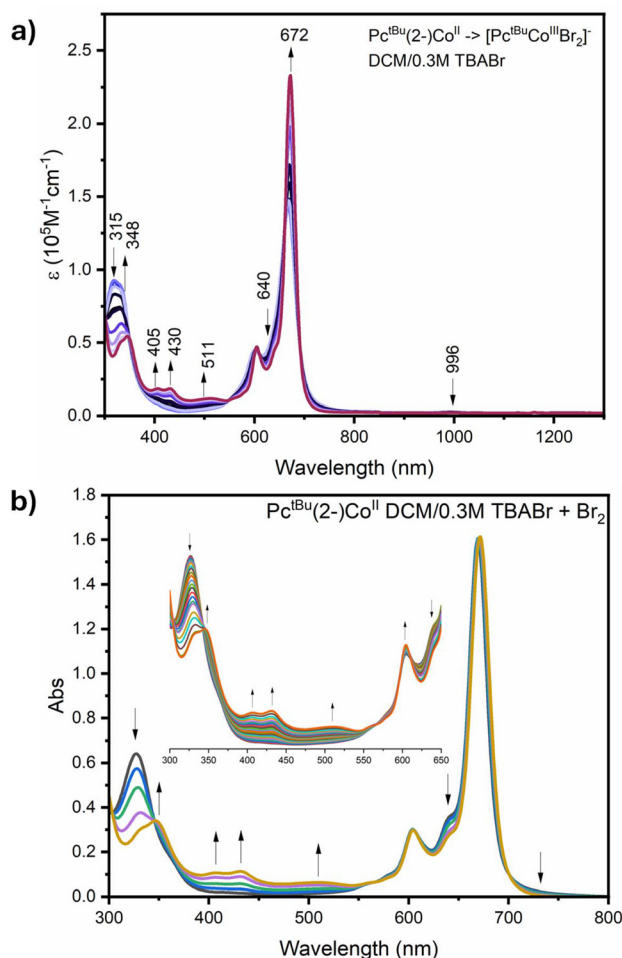
Compound	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}^{\text{Co}}, \text{cm}^{-1}$	$a_{\perp}^{\text{Co}}, \text{cm}^{-1}$	$a_{\parallel}^{\text{N}}, \text{cm}^{-1}$	$a_{\perp}^{\text{N}}, \text{cm}^{-1}$	Ref.
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$	1.945	2.677	149.9	195.5			101 <sup>a</sup>
	1.95	2.78	150	190			tw <sup>d</sup>
$\text{Pc}(2-)\text{Co}^{\text{II}}/\text{calc.}$	2.004	2.314	195	31			tw
$\beta\text{-Pc}(2-)\text{Co}^{\text{II}}$	1.89	2.94	150	280			104 <sup>b</sup>
$\alpha\text{-Pc}(2-)\text{Co}^{\text{II}}$	1.99	2.60	110	64			104 <sup>b</sup>
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$	2.013	2.250	75.2		15	11	101 <sup>a</sup>
	2.01	2.21	85		14	10	tw <sup>e</sup>
$\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2/\text{calc.}$	1.994	2.155	113	61			tw
$\text{Pc}(2-)\text{Co}^{\text{II}}(4\text{-MePy})_2$	2.015	2.25	77	12	14		86 <sup>c</sup>
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$	2.01	2.18		53			tw <sup>f</sup>
$\text{Pc}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2/\text{calc.}$	1.991	2.136, 2.135	76	102			tw
$\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(i\text{BuNH}_2)_2$	2.011	2.186	70.4	57.5	14.5		101 <sup>a</sup>

<sup>a</sup> 77 K, PhMe. <sup>b</sup> Diluted with  $\text{PcZn}$ . <sup>c</sup> 4-MePy/DCM (70/30, v/v) 77 K. <sup>d</sup> 150 K PhMe, tw = this work. <sup>e</sup> 150 K Py/PhMe (5/95, v/v). <sup>f</sup> 150 K  $n\text{BuNH}_2$ /PhMe (5/95, v/v).

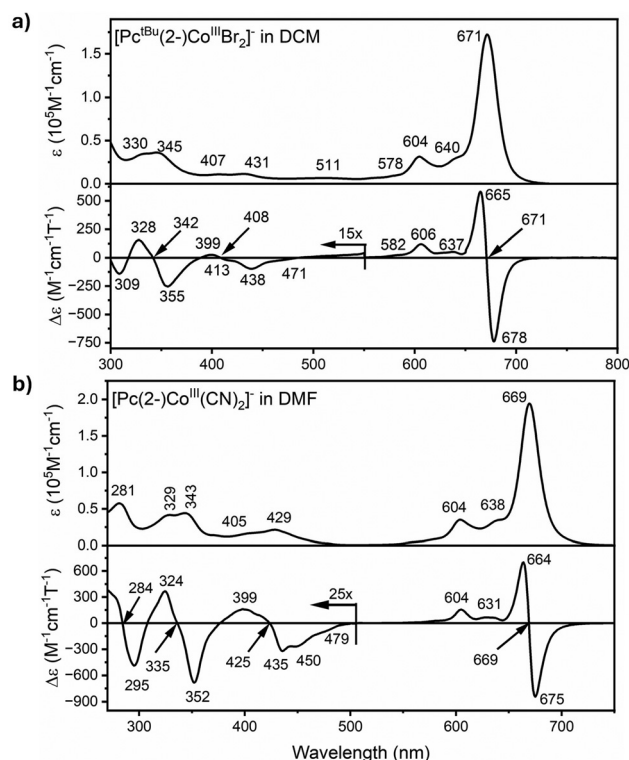
formation of  $[\text{Pc}(2-)\text{Co}^{\text{III}}(\text{CN})_2]^-$ .<sup>72,73,103</sup> Synthesis of the  $[\text{Pc}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$  complex was reported by Homborg and co-authors.<sup>71</sup> It involves the preparation of  $[\text{Pc}(1-)\text{Co}^{\text{III}}(\text{TFA})]^+$  cation (TFA = trifluoroacetate) and its interaction with HBr. We found that  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$  can be prepared in two different ways. First,

a simple electrochemical oxidation of  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  in the DCM/0.3 M TBABr system leads to the formation of  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$  (Fig. 4a). Thus, one can use bulk electrolysis to synthesize this compound. Electrochemical oxidation allowed us to develop a more convenient way of preparing  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$ . Indeed, oxidation of  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  in DCM/0.3 M TBABr with a solution of bromine in DCM results in the clean formation of  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$  suitable for spectroscopic studies (Fig. 4b).

Formation of square planar  $\text{Pc}(2-)\text{Co}^{\text{II}}$ <sup>105</sup> and  $[\text{Pc}(2-)\text{Co}^{\text{I}}]^-$ <sup>100,106</sup> as well as tetragonally distorted  $[\text{Pc}(2-)\text{Co}^{\text{III}}(\text{CN})_2]^-$ ,<sup>65,107–109</sup>  $[\text{Pc}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$ ,<sup>71</sup> and  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$ <sup>110,111</sup> was confirmed by



**Fig. 4** Formation of  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$  under spectroelectrochemical oxidation conditions in DCM/0.3 M TBABr (a) and under chemical oxidation conditions using bromine as an oxidant in the same solvent system (b).



**Fig. 5** UV-Vis and MCD spectra of  $[\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{III}}\text{Br}_2]^-$  in DCM (a) and  $[\text{Pc}(2-)\text{Co}^{\text{III}}(\text{CN})_2]^-$  in DMF.

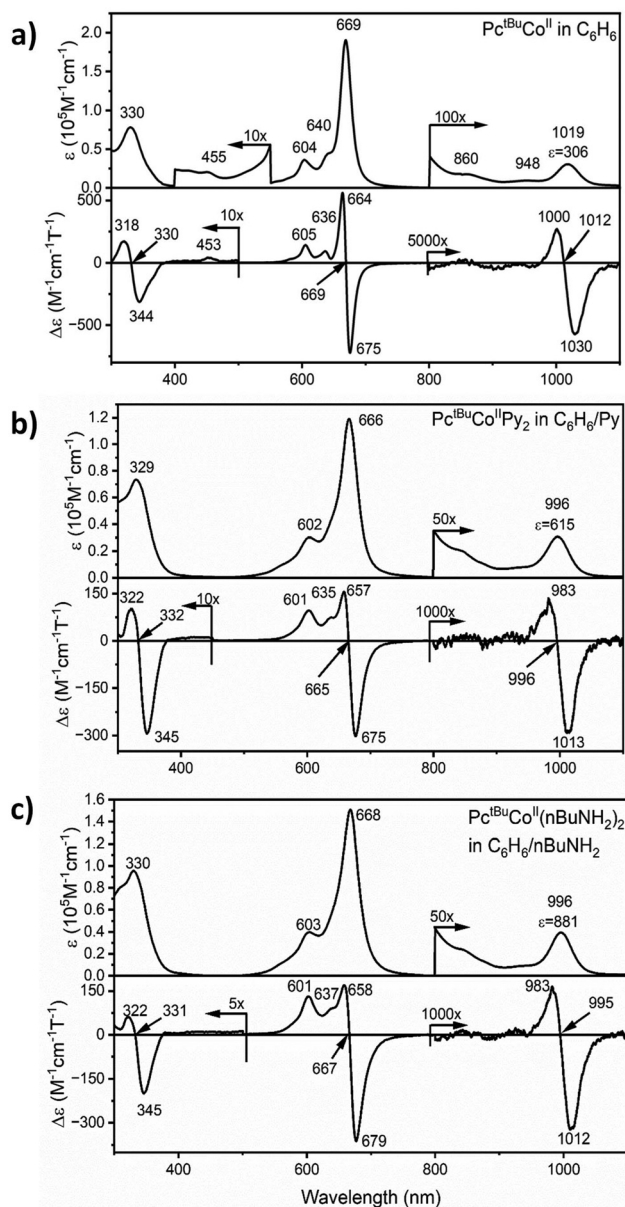


X-ray crystallography in previous reports. The UV-Vis-NIR and MCD spectra of  $[\text{Pc}(2\text{-})\text{Co}^{\text{I}}]^-$ ,  $[\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{I}}]^-$ ,  $\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{II}}$ ,  $\text{Pc}(2\text{-})\text{Co}^{\text{II}}\text{Py}_2$ ,  $\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{II}}\text{Py}_2$ ,  $\text{Pc}(2\text{-})\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$ ,  $\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$ ,  $[\text{Pc}(2\text{-})\text{Co}^{\text{III}}(\text{CN})_2]^-$ , and  $[\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{III}}\text{Br}_2]^-$  are grouped by the oxidation state of the central metal ion and shown in Fig. 5–7 and ESI Fig. S1–4.†

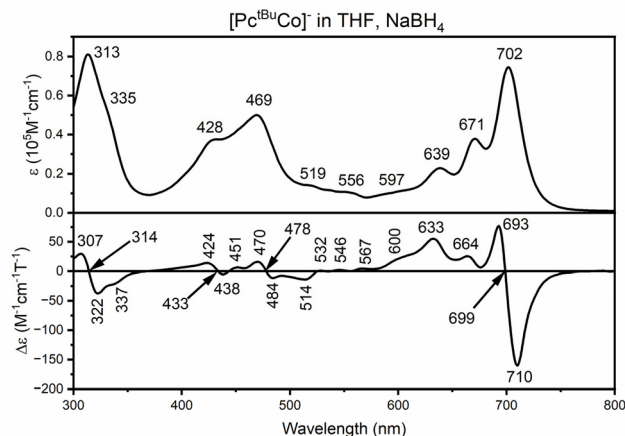
For cobalt(III) derivatives, in addition to the Q-bands and their vibronic satellites observed in the 550–700 nm region and split B-bands observed in the 300–350 nm region, additional transitions were detected between 400 and 550 nm (Fig. 5). Specifically, bands at 429 and 405 nm were detected for the  $[\text{Pc}(2\text{-})\text{Co}^{\text{III}}(\text{CN})_2]^-$  complex. The transition at 429 nm is

associated with a MCD Faraday A-term centered at 425 nm. However, in addition to this A-term, two visible shoulders with a negative amplitude were observed at 450 and 479 nm followed by an MCD signal with a positive amplitude at 399 nm (Fig. 5). Two additional visible Faraday A-terms observed at 335 and 284 nm are associated with the absorption bands observed at 343 and 281 nm. In the case of the UV-Vis spectrum of the  $[\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{III}}\text{Br}_2]^-$  complex (which is indistinguishable from the UV-Vis spectrum of  $[\text{Pc}(2\text{-})\text{Co}^{\text{III}}\text{Br}_2]^-$  published by Homborg and co-workers),<sup>71</sup> additional bands at 511, 431, and 407 nm were observed. The low-energy band at 511 nm is not associated with a clear MCD signal, while the absorption band at 431 nm is associated with a Faraday B-term of negative amplitude centered at 438 nm along with a shoulder at 471 nm. The absorption band at 407 nm is associated with a MCD A-term centered at 408 nm. These signals are better separated than the bands observed for the  $[\text{Pc}(2\text{-})\text{Co}^{\text{III}}(\text{CN})_2]^-$  complex in the same spectral envelope. As expected, the MCD spectra of both cobalt(III) complexes are dominated by a very strong Faraday A-term associated with the  $Q_{0-0}$  transition. No signals were detected for both cobalt(III) systems with energies lower than that of the  $Q_{0-0}$  transition.

$\text{Pc}(2\text{-})\text{Co}^{\text{II}}\text{Py}_2$  and  $\text{Pc}(2\text{-})\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  were studied first for cobalt(II) derivatives. In both cases, spectra were dominated by absorption in the Q- and B-band regions (ESI Fig. S3 and S4†). The Q-band is associated with a strong MCD A-term centered close to the absorption maxima. The MCD spectra in the B-band region are indicative of several transitions present in this spectral envelope. Additionally, a series of low-energy, low-intensity bands between 800 and 1000 nm was observed in both cases. These were previously assigned as d–d<sup>86–89</sup> or t–m<sup>90</sup> transitions, and their nature will be discussed in detail in the next section. The lowest energy band in the NIR region is associated with an MCD A-term (ESI Fig. S3 and S4†). However, because of the limited solubility and pronounced aggregation at higher concentrations of the  $\text{Pc}(2\text{-})\text{Co}^{\text{II}}\text{Py}_2$  and  $\text{Pc}(2\text{-})\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  complexes with unsubstituted phthalate



**Fig. 6** UV-Vis and MCD spectra of  $\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{II}}$  in benzene (a),  $\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{II}}\text{Py}_2$  in benzene/pyridine (95/5%, b), and  $\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  in benzene/ $n\text{BuNH}_2$  (95/5%, c).



**Fig. 7** UV-Vis and MCD spectra of  $[\text{Pc}^{\text{tBu}}(2\text{-})\text{Co}^{\text{I}}]^-$  in THF.

cyanine cores, we were not able to obtain a well-resolved spectroscopic signature in the MCD spectra for the bands observed between 940 and 810 nm. Moreover, the parent  $\text{Pc}(2-)\text{Co}^{\text{II}}$  has limited solubility in non-coordinating solvents that are transparent between 270 and 1000 nm. Thus, we moved to *tert*-butyl substituted phthalocyanine derivatives to overcome these problems. UV-Vis-NIR and MCD spectra of  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$ ,  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$ , and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  complexes are shown in Fig. 6. These closely follow the spectra of the unsubstituted  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$  and  $\text{Pc}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  derivatives. The vibronic satellites in the UV-Vis-NIR and MCD spectra of  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  in the Q-band region are much better resolved, with the  $\text{Q}_{0-0}$  transition being significantly narrower compared to the  $\text{Q}_{0-0}$  tran-

sitions in  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$  and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  complexes. The broader  $\text{Q}_{0-0}$  bands in  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$  and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$  complexes can be explained with the equilibria between hexa-, penta- and tetra-coordinated complexes in solution (*i.e.*,  $\text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}}\text{L}_2 \rightleftharpoons \text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}}\text{L} + \text{L} \rightleftharpoons \text{Pc}^{\text{R}4}(2-)\text{Co}^{\text{II}} + \text{L}$ ).<sup>74–80</sup> Next, because we were able to increase the concentrations of *tert*-butyl derivatives, we obtained improved resolution of the transitions observed in the NIR region both in the absorption and MCD spectra. Similar to the  $\text{Pc}(2-)\text{Fe}^{\text{II}}\text{L}_2$  complexes reported previously,<sup>112</sup> the nature of the solvent and the coordination of axial ligands have a very minor influence on the energy of the  $\text{Q}_{0-0}$  band. The same is true for the lowest-energy band observed in the NIR region. The lowest energy

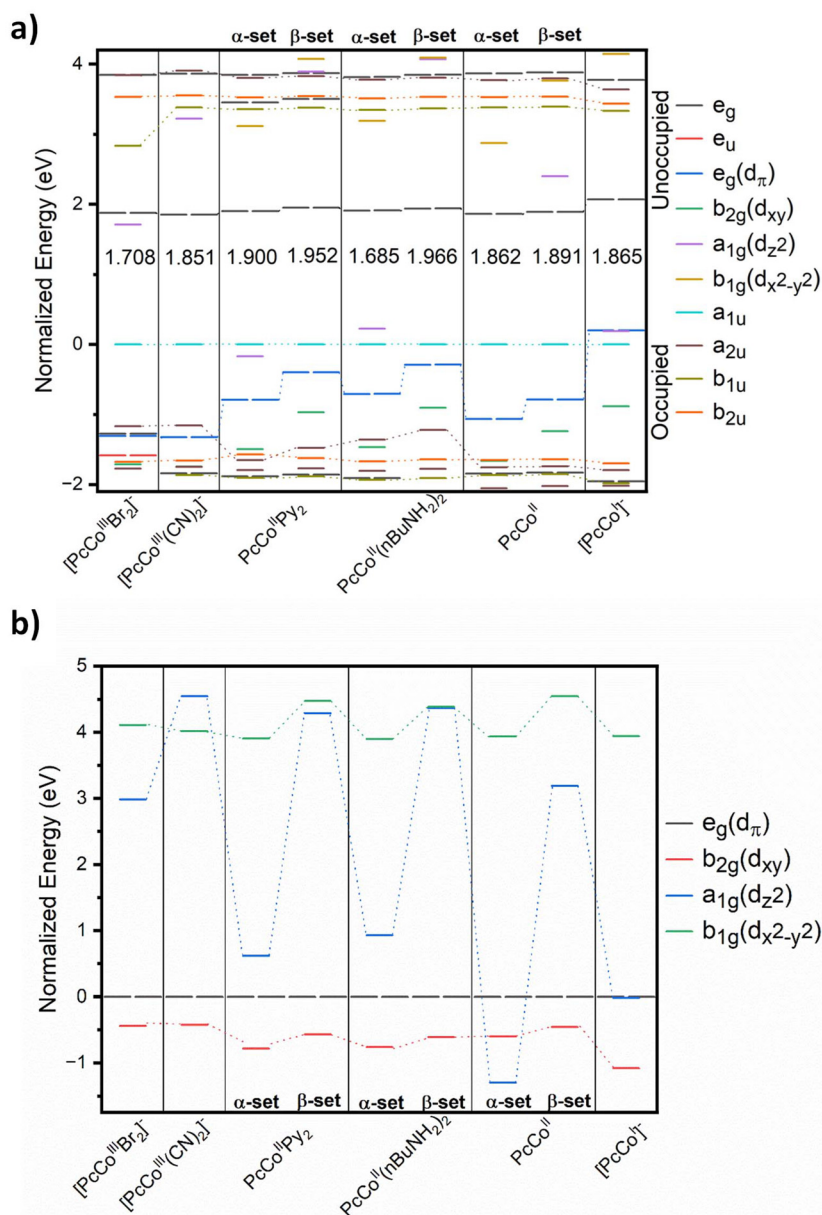
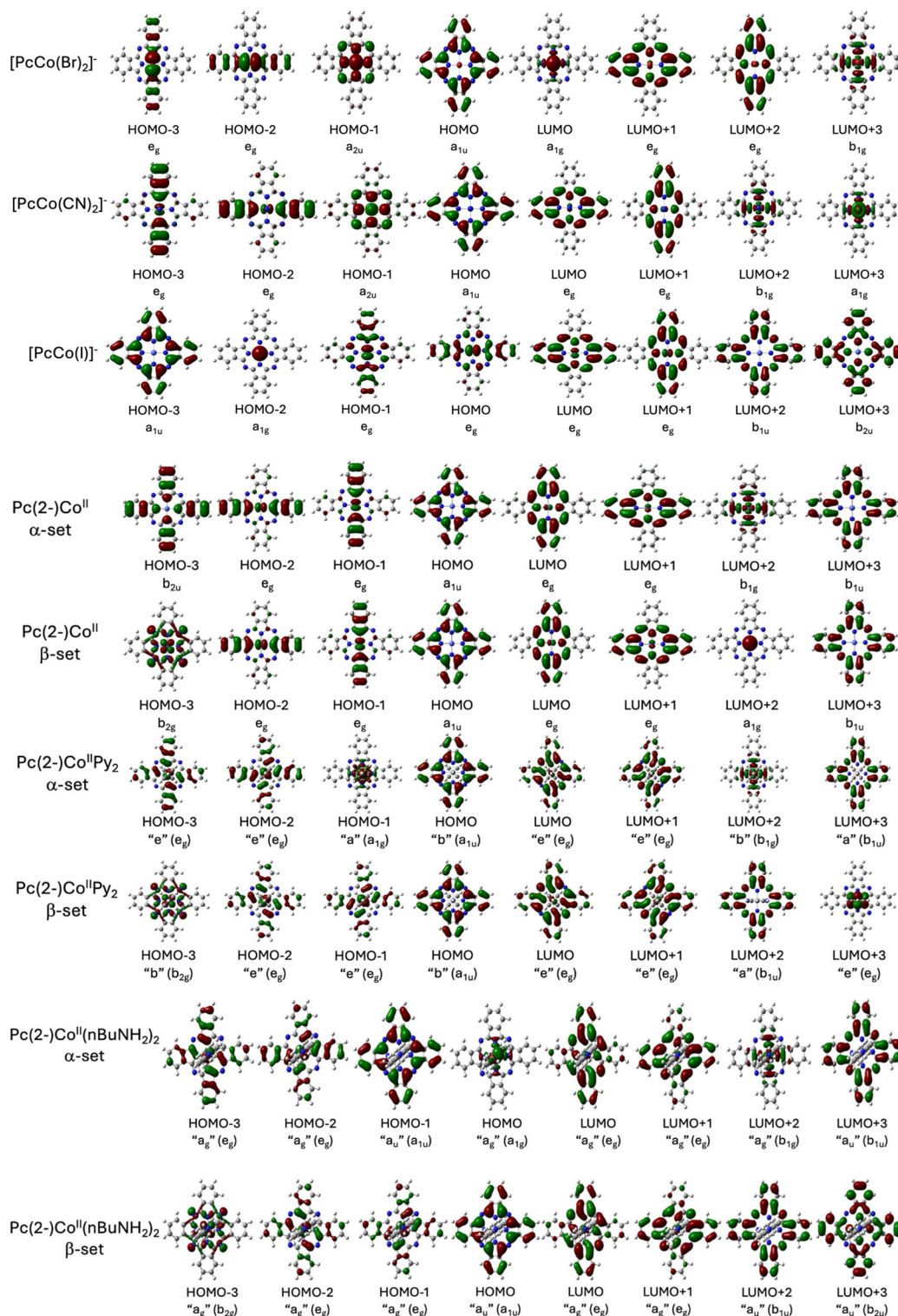


Fig. 8 DFT-predicted energy diagrams for the frontier orbital manifolds of cobalt phthalocyanine derivatives (relative to the phthalocyanine-centered "1a<sub>1u</sub>" MO, a) and zoomed-in d-orbital manifolds (relative to the cobalt-centered  $e_g$  MOs, b).



**Fig. 9** DFT-predicted frontier orbitals in cobalt phthalocyanines; the isosurface value of the orbitals is 0.02. For Pc(2-)Co<sup>II</sup>Py<sub>2</sub> and Pc(2-)Co<sup>II</sup>(nBuNH<sub>2</sub>)<sub>2</sub> complexes, the effective *D*<sub>4h</sub> symmetries are given in parentheses.

NIR band is associated with a MCD A-term, confirming the degenerate nature of this excited state.

Finally, the UV-Vis and MCD spectra of the [Pc<sup>R4</sup>(2-)Co<sup>I</sup>]<sup>-</sup> anion have very rich spectroscopic signatures between 400 and

600 nm (Fig. 7 and ESI Fig. S1 and S2†). There are at least three MCD A-terms visible in this spectral envelope located at ~430, ~475, and ~530 nm (Fig. 7). The two most intense bands are associated with the absorption bands at 428 nm and



**Table 2** DFT-predicted molecular orbital compositions for diamagnetic cobalt(III) and cobalt(I) complexes<sup>a</sup>

[Pc(2-)Co <sup>III</sup> (Br) <sub>2</sub> ] <sup>-</sup>					
MO	E, eV	Symm	Pc	Co	Br
191	-0.043	a <sub>1g</sub>	5.19	93.26	1.56
190, 189	-1.151	e <sub>g</sub>	99.15	0.68	0.17
188	-1.155	a <sub>2u</sub>	96.81	1.35	1.84
187	-1.462	b <sub>2u</sub>	99.99	0.00	0.01
186	-1.619	b <sub>1u</sub>	100	0.00	0.00
185	-2.159	b <sub>1g</sub>	55.54	44.46	0.00
184, 183	-3.118	e <sub>g</sub>	97.52	1.76	0.72
<b>182</b>	<b>-3.287</b>	<b>a<sub>1g</sub></b>	<b>16.82</b>	<b>42.74</b>	<b>40.43</b>
<b>181</b>	<b>-4.995</b>	<b>a<sub>1u</sub></b>	<b>100</b>	<b>0.00</b>	<b>0.00</b>
180	-6.160	a <sub>2u</sub>	57.11	1.30	41.58
179, 178	-6.267	e <sub>g</sub>	20.48	2.39	77.14
177, 176	-6.302	e <sub>g</sub>	45.69	41.99	12.32
175, 174	-6.579	e <sub>u</sub>	15.72	1.88	82.4
173	-6.670	b <sub>2u</sub>	99.99	0.00	0.01
172	-6.707	b <sub>2g</sub>	75.56	24.44	0.00
171	-6.769	a <sub>2u</sub>	99.39	0.16	0.45
170, 169	-6.868	e <sub>g</sub>	99.76	0.07	0.17
168	-6.889	b <sub>1u</sub>	100	0.00	0.00
[Pc(2-)Co <sup>III</sup> (CN) <sub>2</sub> ] <sup>-</sup>					
MO	E, eV	Symm	Pc	Co	CN
168	-1.151	a <sub>2u</sub>	97.36	0.444	2.20
166, 167	-1.193	e <sub>g</sub>	98.91	0.860	0.24
165	-1.500	b <sub>2u</sub>	100	0.00	0.00
164	-1.673	b <sub>1u</sub>	100	0.00	0.00
163	-1.832	a <sub>1g</sub>	24.18	41.11	34.71
162	-2.365	b <sub>1g</sub>	54.91	45.09	0.00
<b>160, 161</b>	<b>-3.205</b>	<b>e<sub>g</sub></b>	<b>97.54</b>	<b>2.08</b>	<b>0.38</b>
<b>159</b>	<b>-5.056</b>	<b>a<sub>1u</sub></b>	<b>100</b>	<b>0.00</b>	<b>0.00</b>
158	-6.213	a <sub>2u</sub>	70.15	1.06	28.79
157, 156	-6.378	e <sub>g</sub>	66.65	32.3	1.04
155	-6.713	b <sub>2u</sub>	100	0.00	0.00
154	-6.80	b <sub>2g</sub>	78.94	21.06	0.00
153	-6.805	a <sub>2u</sub>	99.29	0.14	0.57
152, 151	-6.898	e <sub>g</sub>	99.11	0.51	0.38
150	-6.920	b <sub>1u</sub>	100	0.00	0.00
[Pc(2-)Co <sup>I</sup> ] <sup>-</sup>					
MO	E, eV	Symm	Pc	Co	
154	-0.548	b <sub>1g</sub>	57.62	42.38	
153, 152	-0.919	e <sub>g</sub>	98.62	1.38	
151	-1.050	a <sub>2u</sub>	97.64	2.36	
150	-1.253	b <sub>2u</sub>	100	0.00	
149	-1.355	b <sub>1u</sub>	100	0.00	
<b>148, 147</b>	<b>-2.624</b>	<b>e<sub>g</sub></b>	<b>87.08</b>	<b>12.92</b>	
<b>146, 145</b>	<b>-4.490</b>	<b>e<sub>g</sub></b>	<b>35.06</b>	<b>64.94</b>	
144	-4.504	a <sub>1g</sub>	2.96	97.04	
143	-4.691	a <sub>1u</sub>	100	0.00	
142	-5.572	b <sub>2g</sub>	36.23	63.77	
141	-6.388	b <sub>2u</sub>	100	0.00	
140	-6.484	a <sub>2u</sub>	99.73	0.27	
139, 138	-6.644	e <sub>g</sub>	99.88	0.12	
137	-6.675	b <sub>1u</sub>	100	0.00	
136	-6.709	a <sub>2u</sub>	98.1	1.9	

<sup>a</sup> All complexes have D<sub>4h</sub> symmetry; the frontier orbitals are formatted in bold/italic. The C<sup>2</sup> method was used to calculate contributions.

469 nm. However, both UV-Vis and MCD spectra are indicative of the presence of a larger number of transitions in this region. In particular, the Faraday A-term at ~530 nm and the

B-term at ~545 nm are associated with shoulders at 519 and 556 nm observed in the UV-Vis spectrum of [Pc<sup>R4</sup>(2-)Co<sup>I</sup>]<sup>-</sup>. Stillman and Thomson suggested that the B-band in [Pc(2-)Co<sup>I</sup>]<sup>-</sup> should be observed in the 400–500 nm region,<sup>98</sup> while Lever indicated that MLCT transitions should be present in this spectral envelope.<sup>113</sup> The Q<sub>0-0</sub> band is red-shifted compared to those in cobalt(III) and cobalt(II) derivatives. There is also a strong MCD B-term at ~630 nm with positive amplitude present in the spectrum of the [Pc(2-)Co<sup>I</sup>]<sup>-</sup> anion (ESI Fig. S1†). This MCD B-term is close to but not perfectly aligned with the absorption band at 637 nm observed in the UV-Vis spectrum of [Pc(2-)Co<sup>I</sup>]<sup>-</sup>. Interestingly, the positive amplitude component of the A-term associated with the Q<sub>0-0</sub> band in the [Pc(2-)Co<sup>I</sup>]<sup>-</sup> anion has significantly lower intensity compared to the negative amplitude component of the same transition. This could be reflective of the aggregation of [Pc(2-)Co<sup>I</sup>]<sup>-</sup> in DMF. Indeed, it is well-known that phthalocyanine H-aggregates,<sup>114–117</sup> cofacial μ-oxo dimers,<sup>118–122</sup> and double-decker systems<sup>123–128</sup> have blue-shifted Q<sub>0-0</sub>-bands and exhibit MCD A-terms. If both the monomer and H-aggregate of the [Pc(2-)Co<sup>I</sup>]<sup>-</sup> anion are present in solution, then the positive amplitude component of the A-term in the monomer will be reduced because of the negative component of the A-term of the H-aggregate (ESI Fig. S5†). When *tert*-butyl substituted [Pc<sup>tBu</sup>(2-)Co<sup>I</sup>]<sup>-</sup> was studied by MCD spectroscopy in DMF (ESI Fig. 2†) and THF (Fig. 7), the Q<sub>0-0</sub> band was observed as a more symmetric A-term and the amplitude of the band associated with the H-aggregate was significantly reduced (we should note that the A-term of the H-aggregate should overlap with the Q<sub>0-2</sub> band and thus, the positive amplitude signal in ~630 nm region should not completely disappear). As expected for the low spin, diamagnetic d<sup>8</sup> system, no weak NIR absorption bands were observed in the UV-Vis-NIR and MCD spectra of [Pc(2-)Co<sup>I</sup>]<sup>-</sup>.

#### Analysis of the excited states in cobalt phthalocyanine complexes using DFT and TDDFT calculations

The MCD spectra of [Pc(2-)Co<sup>III</sup>(CN)<sub>2</sub>]<sup>-</sup>, Pc(2-)Co<sup>II</sup>Py<sub>2</sub>, and [Pc(2-)Co<sup>I</sup>]<sup>-</sup> complexes in the UV-Vis region between ~270 and 800 nm were first reported by Thomson and Stillman in their pioneering work in 1974.<sup>98</sup> These are consistent with our data. Understandably, the only spectral interpretation the authors were able to provide at that time was based on general ligand-field theory considerations and comparison with the spectra of closed-shell zinc(II) and iron(II) derivatives. Based on these considerations, Thomson and Stillman suggested that the MCD A-term observed between ~400–470 nm for [Pc(2-)Co<sup>I</sup>]<sup>-</sup> belongs to the B1 band.<sup>98</sup> Beyond these initial studies, several MCD spectra of substituted Pc<sup>Rn</sup>(2-)Co<sup>II</sup>Py<sub>2</sub> complexes were published through the years.<sup>75–80</sup> In the middle of the 1980s, Lever and co-authors attempted to analyze the energies of the charge-transfer states in phthalocyanine cobalt complexes based on their electrochemical reduction and oxidation potentials.<sup>113</sup> This analysis led to the conclusion that at least some charge-transfer transitions should be present between 400 and 500 nm for [Pc(2-)Co<sup>I</sup>]<sup>-</sup>.



Table 3 DFT-predicted molecular orbital compositions for paramagnetic cobalt(II) complexes<sup>a</sup>

Pc(2-)Co <sup>II</sup> ( <i>n</i> BuNH <sub>2</sub> ) <sub>2</sub> <sup>b</sup>											
α-Set						β-Set					
MO	<i>E</i> , eV	Symm	Pc	Co	<i>n</i> BuNH <sub>2</sub>	MO	<i>E</i> , eV	Symm	Pc	Co	<i>n</i> BuNH <sub>2</sub>
198	0.171	a <sub>u</sub>	99.93	0.04	0.03	197	−0.136	a <sub>g</sub>	5.78	87.82	6.400
197	−0.204	a <sub>g</sub>	5.51	87.48	7.01	196	−0.867	a <sub>g</sub>	54.54	44.73	0.73
196	−1.113	a <sub>g</sub>	99.07	0.83	0.11	195	−0.888	a <sub>g</sub>	11.87	63.68	24.45
195	−1.115	a <sub>g</sub>	98.51	1.18	0.31	194	−1.111	a <sub>g</sub>	98.91	0.99	0.10
194	−1.150	a <sub>u</sub>	91.04	6.05	2.91	193	−1.113	a <sub>g</sub>	98.4	1.29	0.31
193	−1.415	a <sub>u</sub>	99.68	0.04	0.28	192	−1.153	a <sub>u</sub>	91.07	6.01	2.93
192	−1.581	a <sub>u</sub>	99.8	0.07	0.12	191	−1.424	a <sub>u</sub>	99.67	0.04	0.28
191	−1.736	a <sub>g</sub>	56.22	43.51	0.26	190	−1.588	a <sub>u</sub>	99.8	0.08	0.12
190	−3.018	a <sub>g</sub>	95.48	4.09	0.43	189	−2.991	a <sub>g</sub>	93.14	6.38	0.48
189	−3.020	a <sub>g</sub>	95.39	4.09	0.53	188	−2.992	a <sub>g</sub>	93.1	6.36	0.53
188	−4.705	a <sub>g</sub>	15.08	45.14	39.78	187	−4.958	a <sub>u</sub>	99.94	0.01	0.05
187	−4.928	a <sub>u</sub>	99.94	0.01	0.05	186	−5.246	a <sub>g</sub>	29.19	69.94	0.87
186	−5.631	a <sub>g</sub>	35.2	64.08	0.72	185	−5.252	a <sub>g</sub>	29.33	69.73	0.94
185	−5.636	a <sub>g</sub>	35.36	63.83	0.81	184	−5.860	a <sub>g</sub>	33.16	66.82	0.02
184	−6.288	a <sub>u</sub>	55.57	2.27	42.16	183	−6.178	a <sub>u</sub>	48.81	2.63	48.56
183	−6.394	a <sub>g</sub>	55.92	44.05	0.03	182	−6.598	a <sub>u</sub>	99.55	0.02	0.43
182	−6.598	a <sub>u</sub>	99.56	0.02	0.42	181	−6.734	a <sub>u</sub>	96.74	1.41	1.85
181	−6.733	a <sub>u</sub>	96.74	1.41	1.86	180	−6.838	a <sub>g</sub>	99.41	0.31	0.28
180	−6.835	a <sub>g</sub>	99.73	0.18	0.09	179	−6.839	a <sub>g</sub>	99.59	0.29	0.12
179	−6.835	a <sub>g</sub>	99.68	0.20	0.11	178	6.865	a <sub>u</sub>	99.89	0.02	0.09
178	−6.860	a <sub>u</sub>	99.89	0.02	0.09	177	−6.950	a <sub>g</sub>	78.11	17.12	4.78

Pc(2-)Co <sup>II</sup> Py <sub>2</sub> <sup>c</sup>											
α-Set						β-Set					
MO	<i>E</i> , eV	Symm	Pc	Co	Py	MO	<i>E</i> , eV	Symm	Pc	Co	Py
202	0.141	b	99.99	0.00	0.01	201	−0.062	a	4.37	92.37	3.27
201	−0.090	a	4.50	91.64	3.86	200	−0.936	b	44.84	28.45	26.71
200	−0.979	a	3.59	0.00	96.41	199	−0.982	a	3.59	0.00	96.41
199	−1.026	b	12.57	1.16	86.28	198	−1.079	b	18.52	14.1	67.38
197, 198	−1.138	e	96.76	0.84	2.40	197	−1.118	a	11.71	58.47	29.82
196	−1.178	b	91.95	1.51	6.54	195, 196	−1.137	e	96.7	0.96	2.34
195	−1.455	a	98.22	0.00	1.78	194	−1.181	b	91.9	1.45	6.65
193, 194	−1.524	e	4.86	0.63	94.51	193	−1.463	a	98.2	0.00	1.8
192	−1.622	a	98.69	0.60	0.71	191, 192	−1.500	e	4.75	0.71	94.54
191	−1.866	b	55.46	43.69	0.86	190	−1.628	a	98.68	0.59	0.73
189, 190	−3.081	e	94.84	3.79	1.37	188, 189	−3.056	e	92.9	5.71	1.39
188	−4.981	b	99.98	0.01	0.01	187	−5.007	b	99.98	0.00	0.01
187	−5.154	a	13.07	46.04	40.89	185, 186	−5.407	e	30.82	67.77	1.41
185, 186	−5.770	e	38.36	60.36	1.27	184	−5.973	b	33.29	66.13	0.59
184	−6.475	b	59.56	33.87	6.57	183	−6.482	b	70.65	0.45	28.91
183	−6.551	b	73.39	8.78	17.83	182	−6.630	a	97.82	0.00	2.18
182	−6.631	a	97.83	0.00	2.17	181	−6.776	b	96.43	0.33	3.24
181	−6.776	b	95.88	0.67	3.45	179, 180	−6.866	e	99.37	0.35	0.29
179, 180	−6.863	e	99.54	0.23	0.23	178	−6.890	a	99.27	0.11	0.62
178	−6.887	a	99.29	0.16	0.55	176, 177	6.992	e	76.10	18.67	5.22

Pc(2-)Co <sup>II</sup>									
α-Set					β-Set				
MO	<i>E</i> , eV	Symm	Pc	Co	MO	<i>E</i> , eV	Symm	Pc	Co
156	0.066	a <sub>1u</sub>	100	0.00	155	−0.029	a <sub>1g</sub>	8.33	91.67
155	−0.122	a <sub>1g</sub>	9.16	90.84	153, 154	−1.239	e <sub>g</sub>	99.28	0.72
153, 154	−1.240	e <sub>g</sub>	99.37	0.63	152	−1.324	a <sub>2u</sub>	98.23	1.77
152	−1.335	a <sub>2u</sub>	97.61	2.39	151	−1.358	b <sub>1g</sub>	55.45	44.55
151	−1.576	b <sub>2u</sub>	100	0.00	150	−1.584	b <sub>2u</sub>	100	0.00
150	−1.722	b <sub>1u</sub>	100	0.00	149	−1.726	b <sub>1u</sub>	100	0.00
149	−2.232	b <sub>1g</sub>	56.95	43.05	148	−2.719	a <sub>1g</sub>	4.10	95.9
147, 148	−3.243	e <sub>g</sub>	97.03	2.97	146, 147	−3.229	e <sub>g</sub>	95.99	4.01
146	−5.105	a <sub>1u</sub>	100	0.00	145	−5.120	a <sub>1u</sub>	100	0.00

Table 3 (Contd.)

Pc(2-)Co <sup>II</sup>									
$\alpha$ -Set					$\beta$ -Set				
MO	<i>E</i> , eV	Symm	Pc	Co	MO	<i>E</i> , eV	Symm	Pc	Co
144, 145	−6.169	<i>e<sub>g</sub></i>	52.75	47.25	143, 144	−5.905	<i>e<sub>g</sub></i>	40.6	59.4
143	−6.758	<i>b<sub>2u</sub></i>	100	0.00	142	−6.357	<i>b<sub>2g</sub></i>	44.7	55.3
142	−6.769	<i>b<sub>2g</sub></i>	72.55	27.45	141	−6.761	<i>b<sub>2u</sub></i>	100	0.00
141	−6.859	<i>a<sub>2u</sub></i>	99.99	0.01	140	−6.860	<i>a<sub>2u</sub></i>	99.99	0.01
139, 140	−6.949	<i>e<sub>g</sub></i>	99.92	0.08	138, 139	−6.951	<i>e<sub>g</sub></i>	99.9	0.10
138	−6.969	<i>b<sub>1u</sub></i>	100	0.00	137	−6.972	<i>b<sub>1u</sub></i>	100	0.00
137	−7.161	<i>a<sub>2u</sub></i>	98.04	1.96	136	−7.142	<i>a<sub>2u</sub></i>	98.45	1.55

<sup>a</sup> Frontier orbitals are formatted in bold/italic. The C<sup>2</sup> method was used to calculate contributions. <sup>b</sup> Effective symmetry of the Pc(2-)Co<sup>II</sup>(*n*BuNH<sub>2</sub>)<sub>2</sub> complex is *D*<sub>4h</sub>. However, the highest possible point group in DFT calculations is *C*<sub>i</sub>. Thus, orbital symmetries in this table are provided for *C*<sub>i</sub> point group. <sup>c</sup> Effective symmetry of the Pc(2-)Co<sup>II</sup>Py<sub>2</sub> complex is *D*<sub>4h</sub>. However, the highest possible point group in DFT calculations is *D*<sub>2d</sub>. Thus, orbital symmetries in this table are provided for the *D*<sub>2d</sub> point group.

Table 4 Allowed charge-transfer transitions for low-spin (*S* = 0) cobalt(III) phthalocyanines<sup>a</sup>

Single-electron transition	Excited state	CT type	Polarization	Expected MCD term
<i>e<sub>g</sub></i> → <i>b<sub>1u</sub></i> <sup>*</sup> , <i>b<sub>2u</sub></i> <sup>*</sup> , <i>a<sub>2u</sub></i> <sup>*</sup> , <i>a<sub>1u</sub></i> <sup>*</sup>	<sup>1</sup> E <sub>u</sub>	MLCT or ILCT	<i>x,y</i>	A
<i>b<sub>2g</sub></i> → <i>b<sub>1u</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	MLCT	<i>z</i>	B
<i>b<sub>2u</sub></i> → <i>b<sub>1g</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	LMCT	<i>z</i>	B
<i>a<sub>2u</sub></i> → <i>a<sub>1g</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	LMCT	<i>z</i>	B
<i>e<sub>u</sub></i> → <i>b<sub>1g</sub></i> <sup>*</sup> , <i>a<sub>1g</sub></i> <sup>*</sup>	<sup>1</sup> E <sub>u</sub>	LMCT	<i>x,y</i>	A
<i>e<sub>u</sub></i> → <i>e<sub>g</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	ILCT	<i>z</i>	B

<sup>a</sup> The ground-state configuration of cobalt(III) is (*b<sub>2g</sub>*)<sup>2</sup>(*e<sub>g</sub>*)<sup>4</sup> and the ground state symmetry term is <sup>1</sup>A<sub>1g</sub>.

Table 5 Allowed charge-transfer transitions for low-spin (*S* = 1/2) cobalt(III) phthalocyanines<sup>a</sup>

Single-electron transition	Excited state	CT type	Polarization	Expected MCD term
<i>e<sub>g</sub></i> → <i>b<sub>1u</sub></i> <sup>*</sup> , <i>b<sub>2u</sub></i> <sup>*</sup> , <i>a<sub>2u</sub></i> <sup>*</sup> , <i>a<sub>1u</sub></i> <sup>*</sup>	<sup>2</sup> E <sub>u</sub>	MLCT	<i>x,y</i>	A
<i>b<sub>2g</sub></i> → <i>b<sub>1u</sub></i> <sup>*</sup>	<sup>2</sup> A <sub>2u</sub>	MLCT	<i>z</i>	B
<i>a<sub>1g</sub></i> → <i>a<sub>2u</sub></i> <sup>*</sup>	<sup>2</sup> A <sub>2u</sub>	MLCT	<i>z</i>	B
<i>e<sub>g</sub></i> → <i>e<sub>u</sub></i> <sup>*</sup>	<sup>2</sup> A <sub>2u</sub>	MLCT	<i>z</i>	B
<i>b<sub>2u</sub></i> → <i>b<sub>1g</sub></i> <sup>*</sup>	<sup>2</sup> A <sub>2u</sub>	LMCT	<i>z</i>	B
<i>a<sub>2u</sub></i> → <i>a<sub>1g</sub></i> <sup>*</sup>	<sup>2</sup> A <sub>2u</sub>	LMCT	<i>z</i>	B
<i>b<sub>1u</sub></i> , <i>b<sub>2u</sub></i> , <i>a<sub>2u</sub></i> , <i>a<sub>1u</sub></i> → <i>e<sub>g</sub></i> <sup>*</sup>	<sup>2</sup> E <sub>u</sub>	ILCT	<i>x,y</i>	A

<sup>a</sup> The ground-state configuration of cobalt(III) is (*b<sub>2g</sub>*)<sup>2</sup>(*e<sub>g</sub>*)<sup>4</sup>(*d<sub>z<sup>2</sup></sub>*)<sup>1</sup> and the ground state symmetry term is <sup>2</sup>A<sub>1g</sub>.

Since modern theoretical methods allow us to calculate the energies of both charge-transfer and  $\pi$ - $\pi^*$  transitions in transition-metal phthalocyanines and their derivatives with high (0.1–0.2 eV) accuracy,<sup>129</sup> it is logical to compare theoretical and experimental (magneto)optical properties of the cobalt phthalocyanine complexes spanning the +1 and +3 oxidation states at the central metal ion and resolve existing controversies. The DFT-predicted energy diagram and frontier MOs for

Table 6 Allowed charge-transfer transitions for low-spin (*S* = 0) cobalt(I) phthalocyanines<sup>a</sup>

Single-electron transition	Excited state	CT type	Polarization	Expected MCD term
<i>e<sub>g</sub></i> → <i>b<sub>1u</sub></i> <sup>*</sup> , <i>b<sub>2u</sub></i> <sup>*</sup> , <i>a<sub>2u</sub></i> <sup>*</sup> , <i>a<sub>1u</sub></i> <sup>*</sup>	<sup>1</sup> E <sub>u</sub>	MLCT	<i>x,y</i>	A
<i>b<sub>2g</sub></i> → <i>b<sub>1u</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	MLCT	<i>z</i>	B
<i>a<sub>1g</sub></i> → <i>a<sub>2u</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	MLCT	<i>z</i>	B
<i>b<sub>2u</sub></i> → <i>b<sub>1g</sub></i> <sup>*</sup>	<sup>1</sup> A <sub>2u</sub>	LMCT	<i>z</i>	B

<sup>a</sup> The ground-state configuration of cobalt(I) is (*b<sub>2g</sub>*)<sup>2</sup>(*e<sub>g</sub>*)<sup>4</sup>(*d<sub>z<sup>2</sup></sub>*)<sup>2</sup> and the ground state symmetry term is <sup>1</sup>A<sub>1g</sub>.

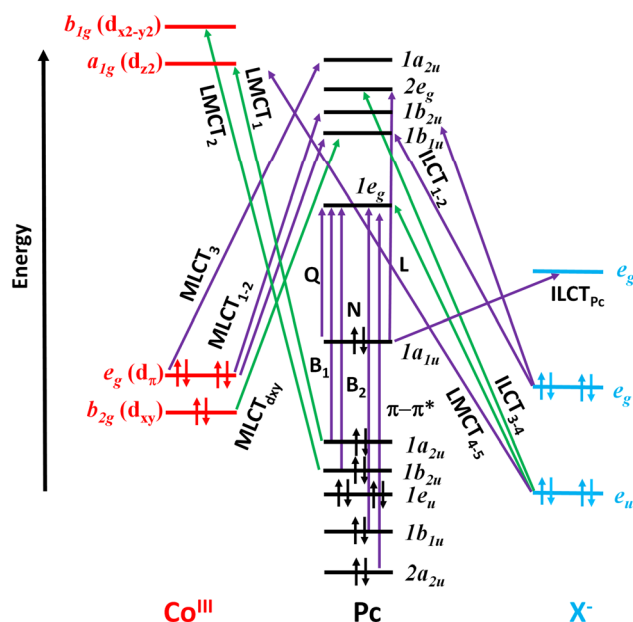


Fig. 10 Simplified diagram for symmetry-allowed transitions in cobalt(III) phthalocyanines with *D*<sub>4h</sub> symmetry. Violet arrows show transitions that should result in degenerate excited states and MCD A-terms.

all the target complexes are shown in Fig. 8 and 9 and ESI Fig. S6–S11.† The DFT-predicted orbital compositions are listed in Tables 2 and 3. As expected, the diamagnetic Co(III) derivatives have  $(d_{xy})^2(d_{xz,yz})^4$  electronic configurations ( $^1A_{1g}$  ground state in  $D_{4h}$  symmetry), the paramagnetic ( $s = \frac{1}{2}$ ) Co(II) complexes have  $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^1$  electronic configurations ( $^2A_{1g}$  ground state in  $D_{4h}$  effective symmetry), and the diamagnetic cobalt(I) anion has a  $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^2$  electronic configuration ( $^1A_{1g}$  ground state in  $D_{4h}$  symmetry). The DFT-predicted presence of the unpaired electron in the  $d_{z^2}$  orbital in cobalt(II) derivatives correlates well with the EPR spectra of these complexes. The corresponding DFT-predicted spin densities are shown in ESI Fig. S12.† The transitions allowed by group theory for these states are listed in Tables 4–6 and graphically shown in Fig. 10–12.

In the case of  $[Pc(2-)Co^{III}Br_2]^-$ , one might expect that the long Co–Br bond distance and weak axial ligand field result in a relatively stable unoccupied  $d_{z^2}$  orbital and bromide contribution to the occupied frontier orbitals. Indeed, DFT calculations predict that the LUMO in this complex has nearly equal contributions from the cobalt(III)  $d_{z^2}$  orbital and two bromine ligands (Table 2). Additionally, bromide contributes to the HOMO–2/–3 ( $e_g$  (Br)) pair of MOs and the HOMO–6/–7 ( $e_u$  (Br)) pair of MOs. Cobalt-centered  $d_\pi$  orbitals form the HOMO–4/–5 ( $e_g$  ( $d_\pi$ )) pair and are well-separated ( $\sim 1.3$  eV) from the phthalocyanine-centered HOMO ( $1a_{1u}$ ). This situation is very different from  $Pc(2-)Fe^{II}L_2$  derivatives with the same  $d^6$  electron configuration and spin state in which iron-centered orbitals are close in energy to the phthalocyanine-centered  $1a_{1u}$  orbital.<sup>112,130</sup> This difference can be explained by the change in oxidation state in cobalt(III) versus iron(II). Unsurprisingly, such stabilization leads to significantly higher TDDFT-predicted energies of MLCT1 ( $e_g(d_\pi) \rightarrow 1b_{1u}^*$ ) and MLCT2 ( $e_g(d_\pi) \rightarrow 1b_{2u}^*$ ) compared to the iron(II) analogs.<sup>112</sup> Indeed, these charge-transfer bands were predicted at 281 and 269 nm, respectively (Table S1†). Since MLCT1 and MLCT2 transitions are located in the B-band region, they heavily overlap with a number of the other bands, making their identification in the experimental spectra nearly impossible. Since the LUMO has predominantly Co/Br character and the HOMO and HOMO–1 are predominantly phthalocyanine-centered orbitals, it opens the possibility for  $Pc \rightarrow LUMO$  symmetry forbidden LMCT1 ( $1a_{1u} \rightarrow a_{1g}^*$  (Co  $d_{z^2}$ /Br)) and symmetry allowed LMCT2 ( $1a_{2u} \rightarrow a_{1g}^*$  (Co  $d_{z^2}$ /Br)) transitions. Indeed, the symmetry-allowed LMCT2 band was predicted by TDDFT calculations at 477 nm and can be associated with the MCD B-term observed at 440 nm (Fig. 13 and Table S1†). Additionally, TDDFT calculations predict two closely spaced doubly degenerate transitions at 445 and 434 nm that have fairly strong intensities. These are heavily dominated by  $1e_u$  (Br)  $\rightarrow a_{1g}^*$  (Co  $d_{z^2}$ /Br) and  $1a_{2u}$  (Pc)  $\rightarrow 1e_g^*$  (Pc) single-electron excitations, with the former contribution accounting slightly more for the first excited state and the latter contribution accounting slightly more for the second excited state (Table S1†). These could be responsible for the MCD A-term (B1 band) observed at 408 nm in the spectrum of  $[Pc^{tBu}(2-)Co^{III}Br_2]^-$  (Fig. 13). We are unsure

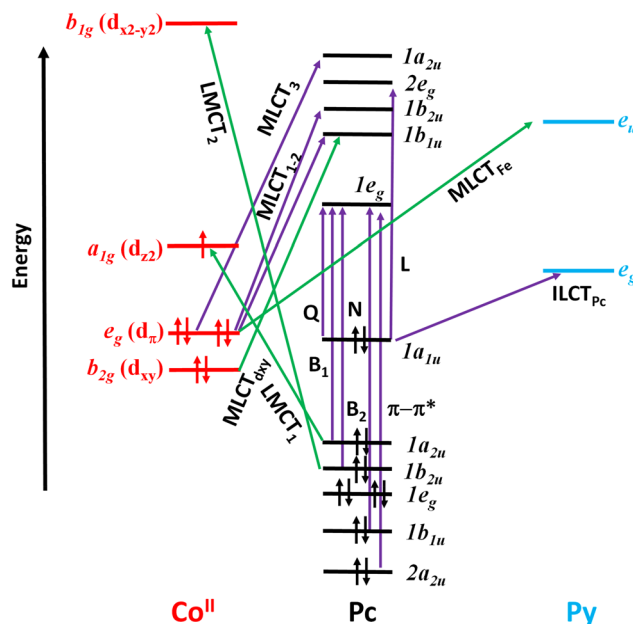


Fig. 11 Simplified diagram for symmetry-allowed transitions in cobalt(II) phthalocyanines with  $D_{4h}$  (effective) symmetry. Violet arrows show transitions that should result in degenerate excited states and MCD A-terms.

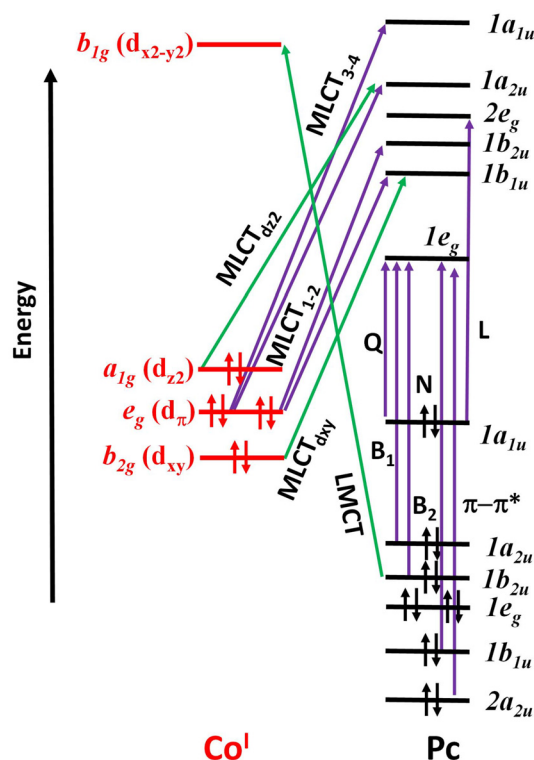
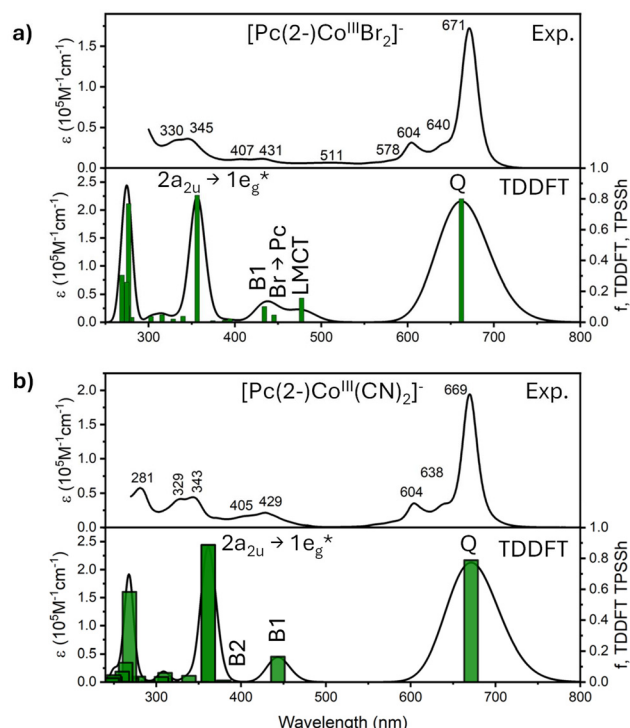


Fig. 12 Simplified diagram for symmetry-allowed transitions in cobalt(I) phthalocyanines with  $D_{4h}$  symmetry. Violet arrows show transitions that should result in degenerate excited states and MCD A-terms.



**Fig. 13** Experimental (top) versus TDDFT-predicted (bottom) UV-Vis spectra of  $[Pc(2-)Co^{III}(Br)_2]^-$  (a) and  $[Pc(2-)Co^{III}(CN)_2]^-$  (b).

of the nature of the 511 nm band observed in the absorption spectrum of this compound. This band has no intensity in the MCD spectrum in a 1.6 T magnetic field, while TDDFT calculations predict two symmetry-forbidden excited states in this region. The first one predicted at 509 nm originates from an almost pure  $1a_{1u} \rightarrow b_{1g}^*$  (Co  $d_{x^2-y^2}/Pc$ ) single-electron transition and has substantial LMCT character. The second state is doubly degenerate and originates from  $e_g$  (Br)  $\rightarrow a_{1g}^*$  (Co  $d_{z^2}/Br$ ) (93%) single-electron excitations (predicted at 486 nm). Homborg and co-authors have shown that the  $\sim 510$  nm band in  $[Pc(2-)Co^{III}(Br)_2]^-$  undergoes a systematic blueshift when axial bromide ligands are replaced with chloride and fluoride ligands.<sup>71</sup> Since the influence of the axial ligands on the energies of the  $1a_{1u}$  (Pc) and  $b_{1g}^*$  (Co  $d_{x^2-y^2}/Pc$ ) orbitals is expected to be small, while the energies of the  $e_g$  (Br) and  $a_{1g}^*$  (Co  $d_{z^2}/Br$ ) orbitals should strongly depend on the nature of the axial ligands, we can speculate that the 511 nm band is dominated by the  $e_g$  (Br)  $\rightarrow a_{1g}^*$  (Co  $d_{z^2}/Br$ ) single-electron excitation, which gains intensity *via* vibronic coupling. Next, two more symmetry-allowed non-degenerate charge-transfer bands were predicted around 390 nm. One band is dominated (92%) by the  $e_u$  (Br)  $\rightarrow 1e_g^*$  (Pc) single-electron excitation, and the other has 93% of  $2a_{2u}$  (Pc)  $\rightarrow a_{1g}^*$  (Co  $d_{z^2}/Br$ ) LMCT nature. Phthalocyanine-centered (here and below, we are following Stillman's nomenclature for the phthalocyanine-centered excited states)<sup>131</sup> Q- ( $1a_{1u} \rightarrow 1e_g^*$ ), B2- ( $1b_{2u} \rightarrow 1e_g^*$ ),  $2a_{2u} \rightarrow 1e_g^*$ , B3- ( $1b_{1u} \rightarrow 1e_g^*$ ) and L-bands ( $1a_{1u} \rightarrow 2e_g^*$ ) were predicted at 662, 374, 356, 349, and 340 nm and are closely

related to the bands observed in the UV-Vis and MCD spectra of  $[Pc^{tBu}(2-)Co^{III}(Br)_2]^-$  (Fig. 13). Finally, two more symmetry-allowed doubly degenerate charge-transfer transitions were predicted by TDDFT calculations between 300 and 330 nm (Table S1†). The first one (329 nm) belongs to almost pure  $1e_u$  (Pc)  $\rightarrow a_{1g}^*$  (Co  $d_{z^2}/Br$ ) single-electron excitation, while the second (316 nm) has  $e_u$  (Br)  $\rightarrow b_{1g}^*$  (Co  $d_{x^2-y^2}/Pc$ ) single-electron excitation character.

In the case of the  $[Pc(2-)Co^{III}(CN)_2]^-$  anion, one might expect that because of the shorter Co–CN bond distance and strong axial ligand field, the unoccupied  $d_{z^2}$  orbital will be destabilized relative to the phthalocyanine-centered  $1e_g^*$  orbitals. Indeed, DFT calculations predict that the LUMO and LUMO+1 in this complex are the classic Gouterman  $1e_g^*$  orbitals<sup>132–134</sup> followed by the  $d_{x^2-y^2}$  (45%)/Pc (55%) LUMO+2 and  $d_{z^2}$  (41%)/CN (35%)/Pc (24%) LUMO+3 (Table 2). These orbitals are predicted to have  $\sim 0.9$  and  $\sim 1.4$  eV higher energies than the Gouterman  $1e_g^*$  MOs. In addition, the cyanide ligands contribute to the HOMO–1 ( $1a_{2u}$  orbital), although their contribution to this orbital is smaller than that of the bromide ligands in  $[Pc(2-)Co^{III}(Br)_2]^-$ . The energy separation between phthalocyanine-centered  $1a_{1u}$  HOMO and  $1a_{2u}$  HOMO–2 is similar for both complexes. Finally, the axial ligands contribute to the HOMO–10/–11 ( $e_g$  (CN/ $d_\pi$ )) pair of MOs and the HOMO–15/–16 ( $e_u$  (CN/Pc)) pair of MOs. Cobalt-centered  $d_\pi$  orbitals form the HOMO–2/–3 ( $e_g$  ( $d_\pi$ )) pair, which is, again,  $\sim 1.3$  eV more stable than the phthalocyanine-centered HOMO. Such electronic structure precludes observation of the low-energy LMCT and MLCT transitions. Indeed, energies of the MLCT1 ( $e_g$  ( $d_\pi$ )  $\rightarrow 1b_{1u}^*$ ) and MLCT2 ( $e_g$  ( $d_\pi$ )  $\rightarrow 1b_{2u}^*$ ) transitions were predicted at 279 and 268 nm, respectively, which is very close to the energies predicted for  $[Pc(2-)Co^{III}(Br)_2]^-$  (Table S1†). TDDFT-predicted LMCT transitions can be separated into two groups. The first group consists of the non-degenerate transitions. These are dominated by the  $1b_{2u} \rightarrow b_{1g}^*$  ( $d_{x^2-y^2}$ ),  $1a_{2u} \rightarrow a_{1g}^*$  ( $d_{z^2}$ ), and  $2a_{2u} \rightarrow a_{1g}^*$  ( $d_{z^2}$ ) single-electron excitations predicted at 311, 310, and 264 nm (Table S1†) and should result in MCD B-terms. The second group consists of two degenerate excited states that are dominated by the  $1e_u \rightarrow b_{1g}^*$  ( $d_{x^2-y^2}$ ) and  $2e_u$  (CN/Pc)  $\rightarrow b_{1g}^*$  ( $d_{x^2-y^2}$ ) single-electron excitations predicted at 264 and 250 nm. These excited states should be associated with MCD A-terms and are LMCT in nature. Only one symmetry-forbidden LMCT band was predicted between phthalocyanine-centered Q- and B1-bands. It has pure  $1a_{1u} \rightarrow b_{1g}^*$  ( $d_{x^2-y^2}$ ) nature and was predicted at 541 nm. The following phthalocyanine-centered degenerate excited states were predicted by TDDFT calculations: Q- ( $1a_{1u} \rightarrow 1e_g^*$ , 671 nm), B1- ( $1a_{2u} \rightarrow 1e_g^*$ , 443 nm), B2- ( $1b_{2u} \rightarrow 1e_g^*$ , 379 nm),  $2a_{2u} \rightarrow 1e_g^*$  (361 nm), B3- ( $1b_{1u} \rightarrow 1e_g^*$ , 354 nm), L-bands ( $1a_{1u} \rightarrow 2e_g^*$ , 339 nm),  $2a_{1u} \rightarrow 1e_g^*$  (306 nm),  $3a_{2u} \rightarrow 1e_g^*$  (271 nm), and  $1a_{2u} \rightarrow 2e_g^*$  (260 nm). Thus, it seems that the 390–500 nm spectral region should only have the B1 band (which is unlikely judging from the MCD spectrum of  $[Pc(2-)Co^{III}(CN)_2]^-$ ), while the other  $\pi$ – $\pi^*$  transitions should be located between 250 and 390 nm. Considering typical TDDFT calculation errors (0.1–0.2 eV), we

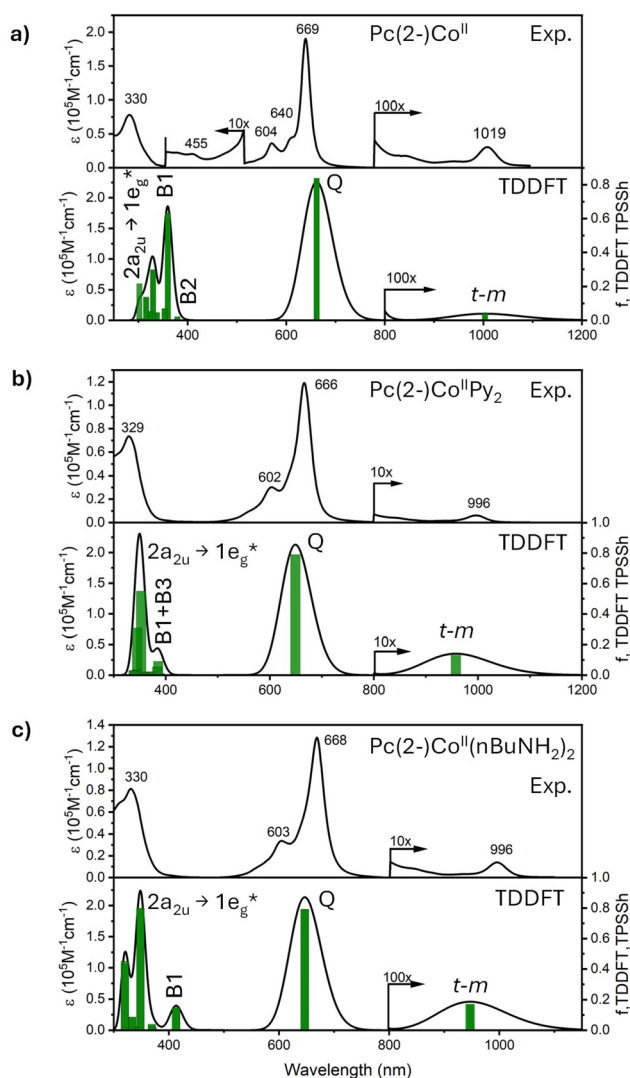


speculate that the B2-band can also contribute to this spectral envelope (Fig. 13).

For  $\text{Pc}(2-)\text{Co}^{\text{II}}$ , one might expect that the energies of the  $d_{\pi}$  orbitals will be between those predicted for cobalt(III) and cobalt(I) species. Indeed, DFT predicts that the HOMO in  $\text{Pc}(2-)\text{Co}^{\text{II}}$  has  $1a_{1u}$  symmetry, and the HOMO-1 and HOMO-2 are cobalt  $d_{\pi}$  orbitals (Table 3). Cobalt-centered  $d_{\pi}$  orbitals are  $\sim 0.9$  eV more stable than the phthalocyanine-centered HOMO. In addition, the unoccupied  $d_{x^2-y^2}$  orbital is  $\sim 1.4$  eV higher in energy compared to the  $d_{z^2}$  orbital ( $\beta$ -set). The LUMO and LUMO+1 in this complex are classic Gouterman  $1e_g^*$  orbitals.<sup>132-134</sup> The lowest energy symmetry allowed LMCT transition should originate from the  $1a_{2u} \rightarrow a_{1g}$  ( $d_{z^2}$ ) single-electron excitation. The  $1a_{1u}$ - $1a_{2u}$  energy gap ( $\beta$ -set) is  $\sim 1.7$  eV and the  $1e_g^* \rightarrow d_{z^2}^*$  energy separation is  $\sim 0.5$  eV. Such electronic structure precludes observation of the low-energy LMCT and MLCT transitions. Indeed, the energies of the MLCT1 ( $e_g$

( $d_{\pi} \rightarrow 1b_{1u}^*$ ) and MLCT2 ( $e_g$  ( $d_{\pi} \rightarrow 1b_{2u}^*$ ) transitions were predicted at 323 and 316 nm, respectively, while the LMCT transition was predicted at 329 nm (Table S2†). These should be observed in the B-band region. TDDFT calculations predict phthalocyanine-centered degenerate excited states at 662 nm (Q-band,  $1a_{1u} \rightarrow 1e_g^*$ ), 379 nm (B2-band,  $1b_{2u} \rightarrow 1e_g^*$ ), 360 nm (B1-band,  $1a_{2u} \rightarrow 1e_g^*$ ), 353 nm (B3-band,  $1b_{1u} \rightarrow 1e_g^*$ ), 338 nm (L-band  $1a_{1u} \rightarrow 2e_g^*$ ), and 330 nm ( $\pi$ - $\pi^*$ ,  $2a_{2u} \rightarrow 1e_g^*$ , Fig. 14). Again, except for the Q-band, all of these bands should be observed in the B-band region. Additionally, the mixed  $\pi$ - $\pi^*$ /MLCT (56% of  $2a_{1u} \rightarrow 1e_g^*$  and 25%  $d_{\pi} \rightarrow 1b_{1u}^*$ ) band was predicted at 302 nm. TDDFT also correctly predicts the presence of a t-m transition in the NIR region of the  $\text{Pc}(2-)\text{Co}^{\text{II}}$  complex (predicted at 1003 nm, Table S2†). The presence of such transitions in the experimental NIR spectra of the open-shell transition-metal phthalocyanines was pointed out by Lever and co-workers,<sup>90</sup> while theoretical aspects for such excitations were provided by Zerner and Cory.<sup>91</sup> In short, the metal-ligand exchange coupling in paramagnetic transition-metal phthalocyanines should result in a non-zero intensity to the t-m transitions and should give rise to the Q-band-like absorption that originates from the spin-forbidden  $1a_{1u}$  ( $^1\text{Pc}$ )  $\rightarrow 1e_g^*$  ( $^3\text{Pc}$ ) single-electron excitation that brings the phthalocyanine chromophore from a singlet to a triplet state (Fig. 2). Considering that the single-electron excitations in the  $1a_{1u}$  ( $^1\text{Pc}$ )  $\rightarrow 1e_g^*$  ( $^1\text{Pc}$ ) (Q-band) and the  $1a_{1u}$  ( $^1\text{Pc}$ )  $\rightarrow 1e_g^*$  ( $^3\text{Pc}$ ) (t-m transition) are the same, we expect that the observed t-m transition will have a vibronic profile close to that observed for a regular Q-band. By analogy, the MCD spectra of the t-m band should resemble (at least for 0-0 transitions) the MCD signature of the spin-allowed Q-band. Next, since ligand-metal exchange integrals  $K_{\text{im}}$  and  $K_{\text{am}}$  should be small, the energies of the  $^4\Psi_{\text{II}}$  and  $^2\Psi_{\text{II}}$  states are expected to be close to each other (Fig. 2), leading to contamination of the doublet state by the quartet state. Indeed, TDDFT-predicted  $\langle S^2 \rangle$  values for the t-m transitions in  $\text{PcCo}^{\text{II}}$  are significantly higher than those expected for the transitions in a simple  $s = 1/2$  system (Table S2†). TDDFT calculations also correctly predict a greatly decreased oscillator strength for the t-m transition compared to the  $Q_{0-0}$  band. Overall, TDDFT predictions for the  $\text{Pc}(2-)\text{Co}^{\text{II}}$  complex are in good agreement with the experimental data and indicate the presence of the NIR t-m transitions, Q-bands, number of the excited states in the B-band region, and the window between 400 and 550 nm.

Although the effective symmetry of the  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$  complexes is  $D_{4h}$ , the highest symmetry that can be used in the DFT calculations of this compound is  $D_{2d}$  (for obvious reasons). Elimination of the inversion center in DFT geometry leads to heavier mixing of the excited state expansion vectors and allows some transitions forbidden under  $D_{4h}$  point group restrictions. Adding axial pyridine ligands to  $\text{Pc}(2-)\text{Co}^{\text{II}}$  has several consequences for its electronic structure. First, the axial coordination significantly destabilizes the energy of the  $d_{z^2}$  orbital relative to the Gouterman<sup>132-134</sup> LUMO/LUMO+1 pair ( $\Delta 1e_g^* - d_{z^2}$  is  $\sim 0.5$  eV in  $\text{Pc}(2-)\text{Co}^{\text{II}}$  and  $\sim 1.9$  eV in  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$ , respectively; we will keep  $D_{4h}$  point group notation in



**Fig. 14** Experimental (top) versus TDDFT-predicted (bottom) UV-Vis spectra of  $\text{Pc}(2-)\text{Co}^{\text{II}}$  (a),  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$  (b), and  $\text{Pc}(2-)\text{Co}^{\text{II}}(\text{nBuNH}_2)_2$  (c).

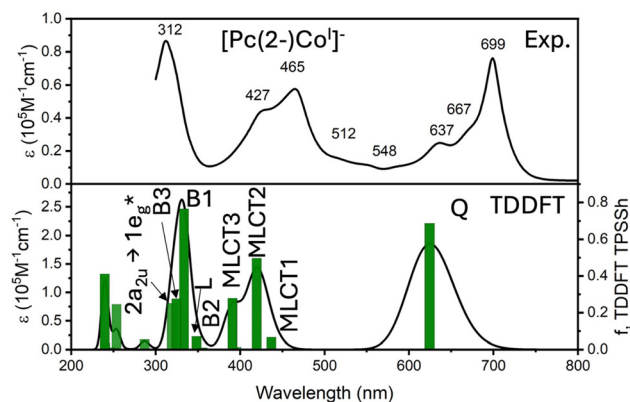


Fig. 15 Experimental (top) versus TDDFT-predicted (bottom) UV-Vis spectra of  $[\text{Pc}(2-)\text{Co}]^-$ .

the discussion part, while actual  $D_{2d}$  point group notation for  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$  in Tables 3 and 8), while the energy gap between the phthalocyanine-centered  $1a_{1u}$  HOMO and  $d_\pi$  orbitals gets smaller ( $\sim 0.8$ – $1.0$  eV for  $\text{Pc}(2-)\text{Co}^{\text{II}}$  versus  $\sim 0.4$ – $0.8$  eV for  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$ ). Third, a pair of degenerate, unoccupied, pyridine-centered orbitals were predicted at  $\sim 1.5$  eV above the Gouterman LUMO/LUMO+1  $1e_g^*$  pair. Pyridine ligand lone pairs also mix with the cobalt  $d_{z^2}$  orbital. Thus, pyridine coordination adds metal-to-axial ligand and phthalocyanine-to-axial ligand charge transfer transitions to the overall picture (Fig. 11 and Table S2†). Indeed, several such transitions were predicted by the TDDFT calculations although their intensities remain low. Out of the two most intense, one is dominated by the  $1a_{1u}(\text{Pc}) \rightarrow e_g^*(\text{Py})$  single-electron excitation ( $f = 0.0542$ , 384 nm) and should result in a MCD A-term, while the other one originates from the  $d_\pi(\text{Co}) \rightarrow e_g^*(\text{Py})$  single-electron excitation ( $f = 0.0196$ , 352 nm) and should lead to a MCD B-term (this transition is forbidden in  $D_{4h}$  but allowed in  $D_{2d}$  point group). The t–m transition in  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$  was predicted at 958 nm and correlates well with the experimental data. TDDFT calculations predicted the phthalocyanine-centered degenerate excited states at 649 nm (Q-band,  $1a_{1u} \rightarrow 1e_g^*$ ), 385 nm (B1 + B3-band, 35% of  $1a_{2u} \rightarrow 1e_g^*$  and 28% of  $1b_{1u} \rightarrow 1e_g^*$ ), 370 nm (B2-band,  $1b_{2u} \rightarrow 1e_g^*$ ), 353 nm ( $\pi$ – $\pi^*$ ,  $2a_{2u} \rightarrow 1e_g^*$ ), 345 nm (B3-band,  $1b_{1u} \rightarrow 1e_g^*$ ), 339 nm ( $\pi$ – $\pi^*$ ,  $2a_{1u} \rightarrow 1e_g^*$ ), and 338 nm (L-band  $1a_{1u} \rightarrow 2e_g^*$ ). In addition, the MLCT1 ( $d_\pi \rightarrow 1b_{1u}^*$ ) and MLCT2 ( $d_\pi \rightarrow 1b_{2u}^*$ ) bands were predicted at 358 and 345 nm. Again, TDDFT calculations correctly predict the window between Q- and B-band regions (Fig. 14).

Lowering the point group symmetry in  $\text{Pc}(2-)\text{Co}^{\text{II}}(\text{nBuNH}_2)_2$  to  $C_i$  results in the complete removal of degeneracy in the DFT orbitals, which complicated the analysis of the DFT and TDDFT results. Nevertheless, we can still recognize and assign the major transitions in this compound predicted by TDDFT. In general, the electronic structure of the  $\text{Pc}(2-)\text{Co}^{\text{II}}(\text{nBuNH}_2)_2$  complex resembles that of  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$ . Since butylamine is a stronger  $\sigma$ -donor compared to pyridine, it is not surprising to see a further destabilization of the unoccupied ( $\beta$ -set) cobalt-

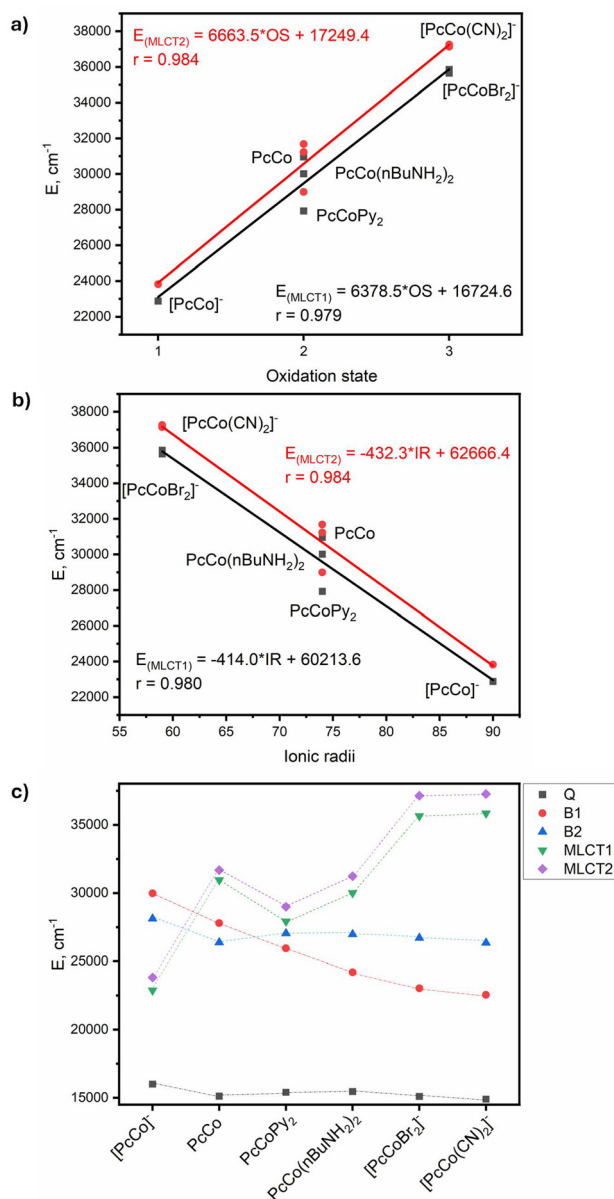
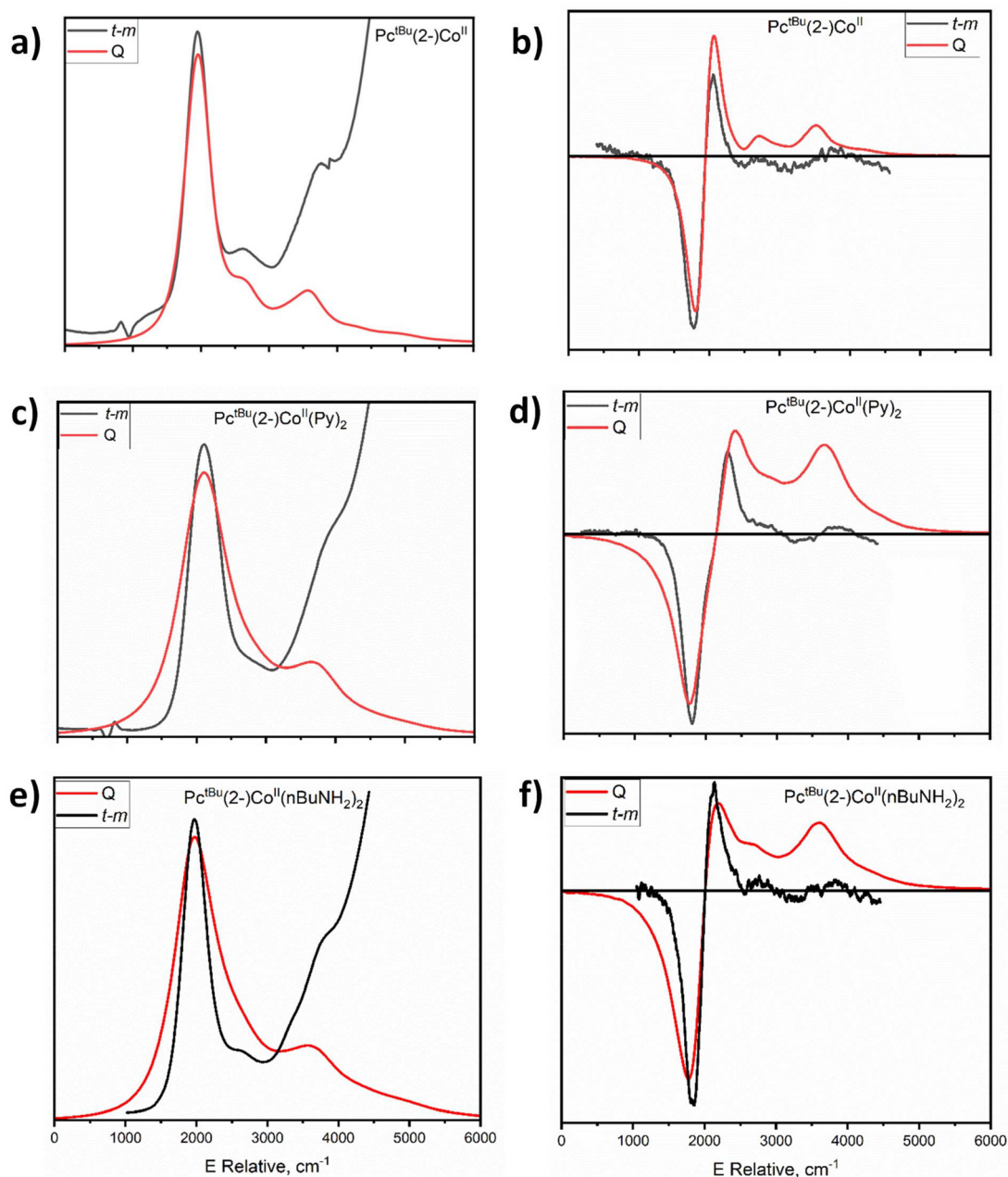


Fig. 16 TDDFT-predicted energies of the MLCT1 and MLCT2 transitions versus cobalt oxidation state (a) and cobalt ionic radii (b). Selected transition energies of  $\pi$ – $\pi^*$  and charge-transfer transitions in cobalt phthalocyanines predicted by TDDFT calculations (c).

centered  $d_{z^2}$  orbital relative to the Gouterman<sup>132–134</sup>  $1e_g^*$  pair ( $\sim 2.1$  eV in  $\text{Pc}(2-)\text{Co}^{\text{II}}(\text{nBuNH}_2)_2$  versus  $\sim 1.9$  eV in  $\text{Pc}(2-)\text{Co}^{\text{II}}\text{Py}_2$ ). No predominantly axial ligand-centered unoccupied orbitals are expected close to the frontier orbital energy envelope. However, nitrogen lone pairs from the axial ligands contribute significantly to the phthalocyanine-centered  $1a_{2u}$  and cobalt  $d_{z^2}$  orbitals (Table 3). The degenerate t–m transition in  $\text{Pc}(2-)\text{Co}^{\text{II}}(\text{nBuNH}_2)_2$  was predicted at  $\sim 947$  nm and correlates well with the experimental data, in particular the MCD A-term. TDDFT calculations predicted the phthalocyanine-centered nearly degenerate excited states at  $\sim 647$  nm (Q-band,  $1a_{1u} \rightarrow$



**Fig. 17** Overlays of absorption and MCD spectra in Q- and t-m bands regions:  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  complex (a and b),  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}\text{Py}_2$  complex (c and d), and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(\text{nBuNH}_2)_2$  (e and f).

$1\text{e}_\text{g}^*$ ,  $\sim 414$  nm (B1-band,  $1\text{a}_{2\text{u}} \rightarrow 1\text{e}_\text{g}^*$ ),  $\sim 349$  nm ( $\pi-\pi^*$ ,  $2\text{a}_{2\text{u}} \rightarrow 1\text{e}_\text{g}^*$ ), and  $\sim 339$  nm (B3-band,  $1\text{b}_{1\text{u}} \rightarrow 1\text{e}_\text{g}^*$ ). The B2-band is heavily mixed with MLCT components, which were predicted at 371 and 369 nm (Table S2†). In addition, the almost pure MLCT1 ( $\text{d}_\pi \rightarrow 1\text{b}_{1\text{u}}^*$ ) and MLCT2 ( $\text{d}_\pi \rightarrow 1\text{b}_{2\text{u}}^*$ ) bands were predicted at 333 and 321 nm (Fig. 14). Similar to the other cobalt (II) complexes, TDDFT calculations predict a spectral window between Q- and B-band regions.

In the case of  $[\text{Pc}(2-)\text{Co}]^-$ , one might expect that the occupied metal-centered orbitals will be strongly destabilized and located above or close to the phthalocyanine-centered  $1\text{a}_{1\text{u}}$

orbital. Indeed, DFT predicts that the cobalt-centered  $\text{d}_\pi$  orbitals are HOMO and HOMO-1 in the  $[\text{Pc}(2-)\text{Co}]^-$  anion, which are located in close proximity to the  $\text{d}_{z^2}$  and  $1\text{a}_{1\text{u}}$  orbitals (Fig. 8 and Table 2). These orbitals are  $\sim 1$  eV less stable than the  $\text{d}_{xy}$  MO. The DFT-predicted LUMO and LUMO+1 are the classic Gouterman  $1\text{e}_\text{g}^*$  pair,<sup>132–134</sup> which follows phthalocyanine-centered  $1\text{b}_{1\text{u}}^*$ ,  $1\text{b}_{2\text{u}}^*$ , and  $1\text{a}_{2\text{u}}^*$  orbitals. The energy difference between the LUMO/LUMO+1 pair and the cobalt-centered  $\text{b}_{1\text{g}}^*$  ( $\text{d}_{x^2-y^2}$ ) orbital is  $\sim 2$  eV, which excludes any symmetry-allowed LMCT transitions observed in the UV-Vis region. Such an electronic structure resembles  $\text{Pc}(2-)\text{Fe}^{\text{II}}\text{L}_2$

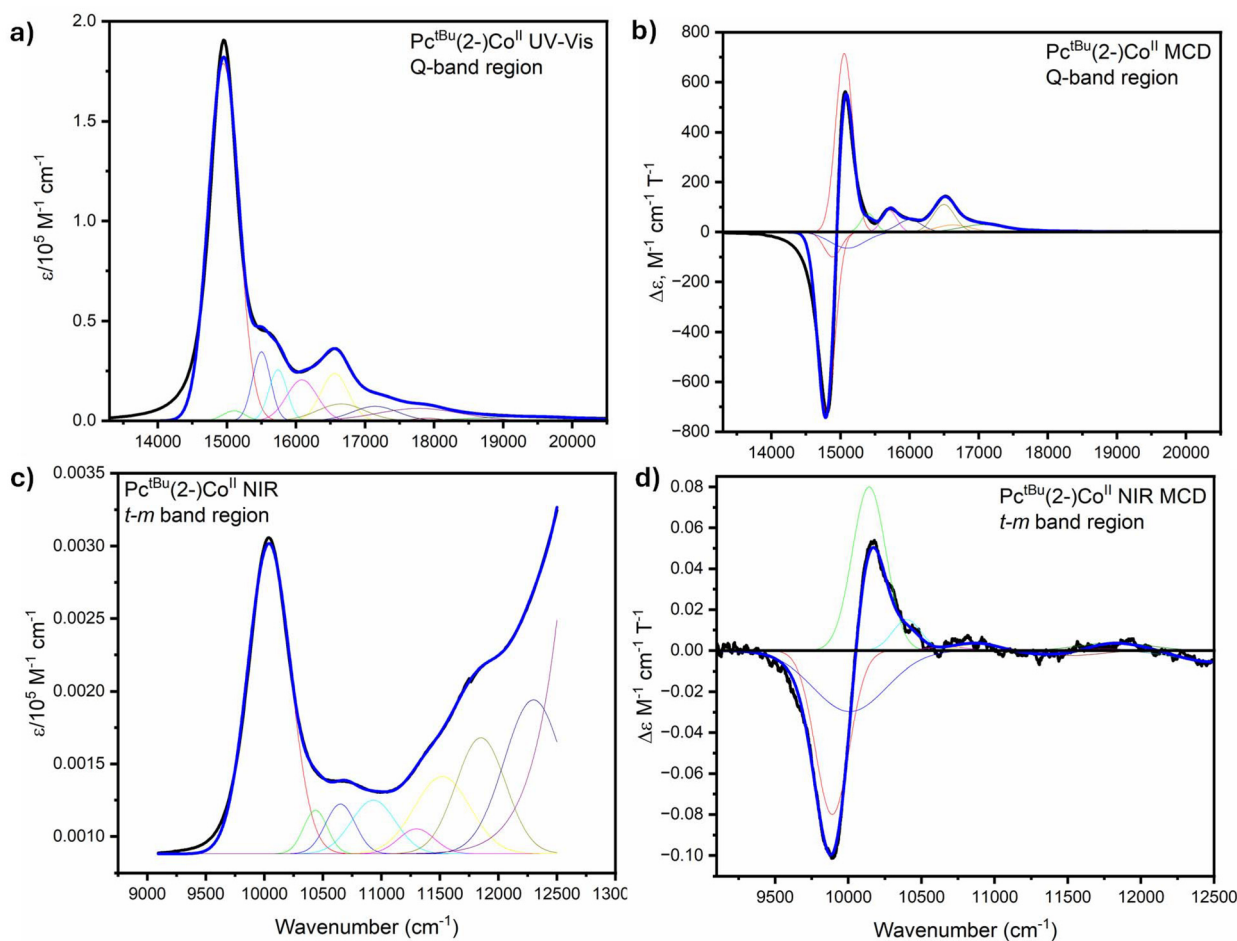


Fig. 18 Band deconvolution of UV-Vis (a and c) and MCD (b and d) spectra of  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  in Q- (a and b) and t-m (c and d) spectral regions.

complexes<sup>112</sup> to a large extent and implies the possibility of low-energy, symmetry-allowed MLCT transitions between cobalt-centered  $d_{\pi}$  orbitals and phthalocyanine-centered  $1b_{1u}^*$ ,  $1b_{2u}^*$ , and  $1a_{2u}^*$  orbitals. Indeed, these were predicted by Lever in 1985 based on his electrochemical potential approach.<sup>113</sup> TDDFT predicts the energies of the  $d_{\pi} \rightarrow 1b_{1u}^*$ ,  $1b_{2u}^*$ , and  $1a_{2u}^*$  MLCT1–3 transitions at 437, 420, and 391 nm respectively (Fig. 15 and Table S3<sup>†</sup>). An additional MLCT transition dominated by the  $d_{z^2} \rightarrow 1a_{2u}^*$  single-electron excitation was predicted at 396 nm. Unlike the previously mentioned MLCT1–3, which should lead to three observable Faraday A-terms in the MCD spectrum of  $[\text{Pc}(2-)\text{Co}^{\text{I}}]^-$ , the latter MLCT transition is non-degenerate and should result in the observation of a MCD B-term. The MCD spectrum in the 400–550 nm region has at least three visible Faraday A-terms that could be associated with the TDDFT-predicted MLCT1–3 transitions. The last degenerate MLCT transition predicted by our TDDFT calculations was predicted at 240 nm and is dominated by the  $d_{\pi} \rightarrow 2b_{2u}^*$  single-electron excitation. The phthalocyanine-centered  $\pi-\pi^*$  transitions were predicted at 625 nm (Q-band, 98%  $1a_{1u} \rightarrow 1e_g^*$ ), 356 nm (B2-band, 87%  $1b_{2u} \rightarrow 1e_g^*$ ), 348 nm (L-band, 89%  $1a_{1u} \rightarrow 2e_g^*$ ), 334 nm (B1-

Table 7 MCD band centers for Q-band and t-m band spectral envelopes from band deconvolution analysis of the UV-Vis-NIR and MCD spectra of  $\text{Pc}^{\text{tBu}}\text{Co}$  in toluene

Q-band region		t-m band region	
$E$ , $\text{cm}^{-1}$	$\lambda$ , nm	$E$ , $\text{cm}^{-1}$	$\lambda$ , nm
14 949 <sup>a</sup>	669	10 039 <sup>a</sup>	996
15 100	662	10 437	958
15 500	645	10 650	939
15 739	635	10 932	915
16 086	622	11 300 <sup>a</sup>	885
16 553	604	11 520	868
16 559	604	11 850	849
17 144	583	12 300	813
17 780	562		

<sup>a</sup> Associated with MCD A-term.

band, 77%  $1a_{2u} \rightarrow 1e_g^*$ ), 324 nm (B3-band, 75%  $1b_{1u} \rightarrow 1e_g^*$ ), 319 nm ( $\pi-\pi^*$ , 59%  $2a_{2u} \rightarrow 1e_g^*$ ), 287 nm ( $\pi-\pi^*$ , 59%  $2a_{1u} \rightarrow 1e_g^*$ ), 252 nm ( $\pi-\pi^*$ , 79%  $1a_{1u} \rightarrow 3e_g^*$ ), 246 nm ( $\pi-\pi^*$ , 72%  $1e_g \rightarrow 1b_{1u}^*$ ), and 240 nm ( $\pi-\pi^*$ , 84%  $2e_g \rightarrow 1b_{1u}^*$ , Table S3<sup>†</sup>). In general, our TDDFT calculations suggest that the



~380–550 nm spectral envelope should be dominated by MCLT transitions. Again, our TDDFT calculations predicted no symmetry-allowed transitions in the Q-band region except the Q-band. Thus, it is quite likely that the relatively strong MCD signal with positive amplitude observed at ~620 nm is reflective of the H-aggregation of the phthalocyanine chromophore.

The overall agreement between theoretically predicted and experimental UV-Vis-NIR spectra of cobalt phthalocyanines discussed in this report is very good (Fig. 13–15). Indeed, TDDFT calculations correctly predicted the lack of intense transitions between the Q- and B-bands for cobalt(II) complexes and explained the nature of such transitions for cobalt(I) and cobalt(III) systems. They also predicted the presence of t-m transitions in the NIR region for cobalt(II) systems. The systematic increase of the B1-band energy from cobalt(I) to cobalt(III) systems is also correctly predicted by TDDFT calculations and reflects the systematic decrease of the  $1a_{1u}$ – $1a_{2u}$  energy gap with increasing oxidation state of the central metal ion. TDDFT calculations also predicted oxidation state (or ionic radii) dependence on the energies of the MLCT1 and MLCT2 transitions in all cobalt complexes (Fig. 16). Indeed, one might expect that upon increase of metal oxidation state, the cobalt-centered  $d_\pi$  orbitals will become more stable, and the relative energies of the phthalocyanine core will remain nearly constant. In this case, the energies of the MLCT1 and MLCT2 transitions will increase with increasing oxidation state. Analysis of the profiles of the Q- and t-m transitions is also interesting (Fig. 17). In all cases, a close resemblance in the absorption spectra envelopes was observed, with the best match coming from the UV-Vis-NIR spectra of  $\text{Pc}^{\text{tBu}}(2)\text{-Co}^{\text{II}}$ . The  $Q_{0-0}$  and  $t\text{-}m_{0-0}$  transitions are clearly associated with a MCD A-term. The presence of a second A-term for the  $t\text{-}m_{0-2}$  transition was previously observed in copper phthalocyanine complexes.<sup>94</sup> The overlap of the UV-Vis-NIR and MCD spectra also suggests that the only difference upon axial ligand coordination is the broadening of the  $Q_{0-0}$  band, which likely reflects the  $\text{Pc}(2)\text{-Co}^{\text{II}}\text{L}_2 \rightleftharpoons \text{Pc}(2)\text{-Co}^{\text{II}}\text{L} + \text{L} \rightleftharpoons \text{Pc}(2)\text{-Co} + \text{L}$  equilibria.

Band deconvolution analysis of the Q- and t-m spectral envelopes of  $\text{Pc}^{\text{tBu}}(2)\text{-Co}^{\text{II}}$  is shown in Fig. 18. Similar to the copper(II) phthalocyanine complexes, it seems that the vibronic intervals for Q- and t-m sets are closely related (Table 7). The  $Q_{0-0}$ – $t\text{-}m_{0-0}$  energy difference for cobalt(II) phthalocyanines ranges between 4869 and 5134  $\text{cm}^{-1}$ , which is slightly smaller than that observed in copper(II) phthalocyanines (5470–5585  $\text{cm}^{-1}$ ).<sup>94</sup> There has been a controversial discussion on the nature of the NIR bands in cobalt(II) phthalocyanines. Indeed, in a series of reports, Cariati and co-workers assigned these bands to d-d transition,<sup>86–89</sup> while later Lever and co-workers assigned them as t-m bands.<sup>90</sup> Based on the discussion above and below, we are confident that the NIR bands observed in cobalt(II) phthalocyanines belong to the t-m transition and its vibronic components. First, as shown in Fig. 17, the Q- and t-m-band region profiles are very similar, indicative of the close energy intervals for the vibronic components. Next, the molar extinction coefficients of the  $t\text{-}m_{0-0}$  transitions ( $\epsilon = 306\text{--}1443 \text{ M}^{-1} \text{ cm}^{-1}$ ) are significantly higher than those

expected for d-d transitions in centrosymmetric tetragonal cobalt complexes. Third, the energies of  $t\text{-}m_{0-0}$  bands in both hexa- and tetra-coordinated cobalt(II) phthalocyanines range between 9815 and 10 310  $\text{cm}^{-1}$  (~500  $\text{cm}^{-1}$  difference) for all complexes studied in this work. This range is even smaller for *tert*-butyl substituted compounds (9814–10 040  $\text{cm}^{-1}$ ; ~240  $\text{cm}^{-1}$  difference). Based on simple ligand-field theory considerations (which are obviously oversimplified but can be used to illustrate our point), one might expect a significantly larger energy difference for d-d transitions in tetra- and hexa-coordinate compounds. Indeed, following Lever<sup>135</sup> and Kida,<sup>136</sup> one might expect the state diagram shown in Fig. 19 for cobalt(II) ion in systems with  $D_{4h}$  symmetry. According to this diagram (ignoring quartet excited states, which should give negligible intensities of d-d transitions), three excited states might, potentially, be observed in the low-energy region. These are  ${}^2B_{1g}$  ( $d_{z^2} \rightarrow d_{x^2-y^2}$  transition),  ${}^2E_g$  ( $d_\pi \rightarrow d_{z^2}$  transition), and  ${}^2B_{2g}$  ( $d_{xy} \rightarrow d_{z^2}$  transition) states. Out of these, only the  ${}^2E_g$  excited state is degenerate and can lead to the observation of MCD C- or A-terms (a MCD A-term was always observed for the lowest energy NIR band in cobalt phthalocyanines). It is expected that the energy of the  $d_{z^2}$  orbital will vary significantly in tetra- and hexa-coordinated cobalt(II) phthalocyanines. Its energy should also vary in hexa-coordinated complexes because of the differences in  $\sigma$ -donor strength between pyridine and *n*-butyl amine axial ligands. Indeed, it is clear from Table 3 that  $d_{z^2}$  orbital has the largest energy influence by the axial ligands in cobalt(II) phthalocyanines compared to any other d-orbitals. Not surprisingly, the largest variation of the TDDFT-predicted energies of d-d transitions among  $\text{Pc}(2)\text{-Co}^{\text{II}}$ ,  $\text{Pc}(2)\text{-Co}^{\text{II}}\text{Py}_2$ , and  $\text{Pc}(2)\text{-Co}^{\text{II}}(n\text{BuNH}_2)_2$  were observed when the electron was transferred from or to the  $d_{z^2}$  orbital (Table 8). For instance, TDDFT-predicted energies of the  ${}^2E_g$  ( $d_\pi \rightarrow d_{z^2}$  transition) state are 5968, 16 035, and 16 776  $\text{cm}^{-1}$  for  $\text{Pc}(2)\text{-Co}^{\text{II}}$ ,  $\text{Pc}(2)\text{-Co}^{\text{II}}\text{Py}_2$ , and  $\text{Pc}(2)\text{-Co}^{\text{II}}(n\text{BuNH}_2)_2$  com-

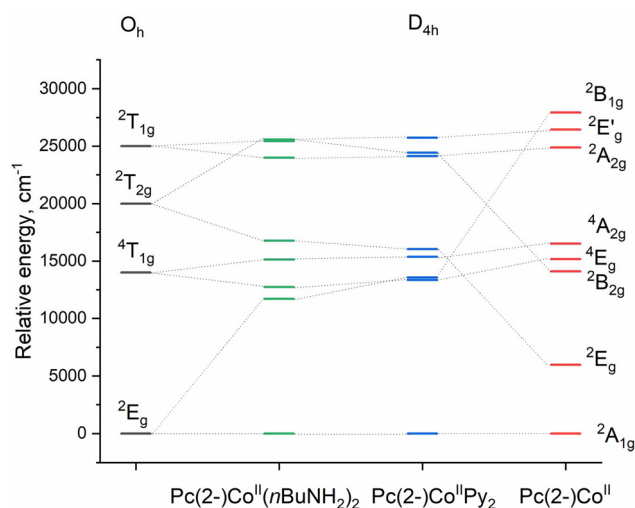


Fig. 19 Term splitting diagram and TDDFT-predicted low-energy d-d transitions in cobalt(II) phthalocyanines in  $D_{4h}$  effective symmetry.

**Table 8** TDDFT-predicted predominant d–d transitions in cobalt(II) phthalocyanines<sup>a</sup>

ES symm	Pc(2-)Co <sup>II</sup>			Pc(2-)Co <sup>II</sup> Py <sub>2</sub>			Pc(2-)Co <sup>II</sup> ( <i>n</i> BuNH <sub>2</sub> ) <sub>2</sub>		
	<i>E</i> , cm <sup>-1</sup> (λ, nm)	⟨ <i>S</i> <sup>2</sup> ⟩	Composition <sup>b</sup>	<i>E</i> , cm <sup>-1</sup> (λ, nm)	⟨ <i>S</i> <sup>2</sup> ⟩	Composition <sup>b</sup>	<i>E</i> , cm <sup>-1</sup> (λ, nm)	⟨ <i>S</i> <sup>2</sup> ⟩	Composition <sup>b</sup>
<sup>2</sup> E <sub>g</sub>	5968 (1676)	0.771	92.0% H–2(β) → L+2(β)	16 035 (623)	0.831	76.6% H–1(β) → L+9(β)	16 743 (597) <sup>c</sup>	0.823	76.5% H–1(β) → L+7(β)
	5968 (1676)	0.771	92.0% H–1(β) → L+2(β)	16 035 (623)	0.831	76.6% H–2(β) → L+9(β)	16 810 (595) <sup>c</sup>	0.822	76.0% H–2(β) → L+7(β)
<sup>2</sup> B <sub>2g</sub>	14 106 (709)	0.901	73.6% H–3(β) → L+2(β), 10.2% H–12(β) → L+2(β)	24 422 (409)	0.831	79.9% H–3(β) → L+9(β)	25 569 (391)	0.941	68.0% H–3(β) → L+7(β)
	15 164 (659)	2.696	50.7% H–1(α) → L+2(α), 31.2% H–1(β) → L+5(β), 13.7% H–11(α) → L+2(α)	13 346 (749)	2.422	44.2% H–2(α) → L+2(α), 21.5% H–1(β) → L+12(β), 16.2% H–1(α) → L+1(α), 11.0% H–1(β) → L+10(β)	12 690 (788) <sup>c</sup>	2.552	32.7% H–2(α) → L+2(α), 25.0% H–1(β) → L+8(β), 14.1% H–1(β) → LUMO(β), 13.4% H–2(β) → L+1(β)
<sup>4</sup> E <sub>g</sub>	15 164 (659)	2.696	50.7% H–2(α) → L+2(α), 31.2% H–2(β) → L+5(β), 13.7% H–12(α) → L+2(α)	13 346 (749)	2.422	44.2% H–3(α) → L+2(α), 21.5% H–2(β) → L+12(β), 16.2% H–1(α) → LUMO(α), 11.0% H–2(β) → L+10(β)	12 765 (783) <sup>c</sup>	2.690	50.3% H–3(α) → L+2(α), 38.8% H–2(β) → L+8(β)
	16 513 (606)	2.748	45.0% H–3(β) → L+5(β), 28.5% H–4(α) → L+2(α), 21.9% H–16(α) → L+2(α)	15 361 (737)	2.742	32.0% H–3(β) → L+12(β), 28.0% H–4(α) → L+2(α), 16.2% H–18(α) → L+2(α), 16.1% H–3(β) → L+10(β)	15 120 (661)	2.751	48.7% H–3(β) → L+8(β), 36.8% H–5(α) → L+2(α)
<sup>2</sup> A <sub>2g</sub> <sup>d</sup>	24 879 (402)	0.768	42.1% H–3(β) → L+5(β), 36.3% H–4(α) → L+2(α), 15.5% H–16(α) → L+2(α)	24 117 (415)	0.776	32.5% H–4(α) → L+2(α), 29.2% H–3(β) → L+12(β), 15.8% H–3(β) → L+10(β), 11.5% H–18(α) → L+2(α)	23 982 (417)	0.767	45.0% H–3(β) → L+8(β), 40.5% H–5(α) → L+2(α), 10.4% H–16(α) → L+2(α)
<sup>2</sup> E' <sub>g</sub>	26 434 (378)	0.816	48.7% H–2(β) → L+5(β), 32.3% H–2(α) → L+2(α)	25 727 (389)	0.839	25.9% H–2(α) → L+2(α), 25.9% H–1(β) → L+12(β), 16.3% H–1(β) → L+10(β)	25 410 (394) <sup>c</sup>	0.819	41.7% H–1(β) → L+8(β), 24.9% H–2(α) → L+2(α)
	26 434 (378)	0.816	48.7% H–1(β) → L+5(β), 32.3% H–1(α) → L+2(α)	25 727 (389)	0.839	25.9% H–3(α) → L+2(α), 25.9% H–2(β) → L+12(β), 16.3% H–2(β) → L+10(β)	25 456 (393) <sup>c</sup>	0.815	42.5% H–2(β) → L+8(β), 25.5% H–3(α) → L+2(α)
<sup>2</sup> B <sub>1g</sub>	27 925 (358)	0.778	83.0% H–10(α) → L+2(α)	13 572 (736)	1.091	57.0% H–1(α) → L+2(α), 20.1% H–1(β) → L+1(β), 20.1% H–2(β) → LUMO(β)	11 710 (854)	0.834	81.0% HOMO(α) → L+2(α)

<sup>a</sup> Effective *D*<sub>4h</sub> symmetries are used for Pc(2-)Co<sup>II</sup>Py<sub>2</sub> and Pc(2-)Co<sup>II</sup>(*n*BuNH<sub>2</sub>)<sub>2</sub> complexes. <sup>b</sup> Only expansion coefficients with more than 10% contribution are shown. <sup>c</sup> Nearly degenerate states in C<sub>i</sub> symmetry. <sup>d</sup> 10Dq = 3.08, 2.99, and 2.97 eV for Pc(2-)Co<sup>II</sup>, Pc(2-)Co<sup>II</sup>Py<sub>2</sub>, and Pc(2-)Co<sup>II</sup>(*n*BuNH<sub>2</sub>)<sub>2</sub>, respectively. Experimentally observed 10Dq for Pc(2-)Co<sup>II</sup> complex are: 3.09 and 2.8 eV.<sup>137,138</sup>

plexes, respectively. Thus, TDDFT-predicted energies of this state vary significantly and are inconsistent with the nearly constant position of the lowest energy NIR band observed in cobalt(II) phthalocyanines. Similarly, TDDFT-predicted energies of the <sup>2</sup>B<sub>1g</sub> (d<sub>z<sup>2</sup></sub> → d<sub>x<sup>2</sup>-y<sup>2</sup></sub> transition) excited state are 27 925, 13 572, and 11 710 cm<sup>-1</sup> for Pc(2-)Co<sup>II</sup>, Pc(2-)Co<sup>II</sup>Py<sub>2</sub>, and Pc(2-)Co<sup>II</sup>(*n*BuNH<sub>2</sub>)<sub>2</sub>, respectively. According to TDDFT calculations, the <sup>4</sup>E<sub>g</sub> state should be observed close to the NIR region. However, it cannot be assigned to the NIR transitions observed in this region in cobalt(II) phthalocyanines because: (i) predicted energies for three different complexes still vary significantly (2474 cm<sup>-1</sup>; ~0.3 eV); (ii) intensities of the quartet states should be negligibly small, while the observed intensities of the NIR transitions in cobalt(II) phthalocyanines were found between 306 and 1443 M<sup>-1</sup> cm<sup>-1</sup>. Finally, TDDFT-predicted energies for the <sup>2</sup>E'<sub>g</sub> state are between 25 410 and 26 434 cm<sup>-1</sup>, ~2 eV higher in energy than the NIR bands observed in the cobalt(II) phthalocyanines. Although it is obvious that the TDDFT calculations have some errors and the predicted ener-

gies will have exchange–correlation functional dependency (TPSSH exchange–correlation functional is a good compromise for the accurate predictions of the π–π\* and charge-transfer transitions), it is difficult to see that TDDFT calculations can result in ~2 eV errors for d–d transitions. Indeed, TDDFT-predicted 10Dq values for cobalt(II) phthalocyanines (Table 8) are in excellent agreement with the 10Dq values determined experimentally for Pc(2-)Co<sup>II</sup>.<sup>137,138</sup> If our calculations are within the expected TDDFT errors (0.1–0.2 eV), then some d–d transitions should be located in the NIR region with energies lower than the Q-band. However, taking into consideration the expected molar extinction coefficients for d–d transitions in centrosymmetric molecules (*ε* ~ 1–10 M<sup>-1</sup> cm<sup>-1</sup>; all cobalt(II) phthalocyanines discussed here have effective *D*<sub>4h</sub> symmetry) versus the molar extinction coefficients for the Q-band (*ε* ~ 100 000–200 000 M<sup>-1</sup> cm<sup>-1</sup>) and t–m transitions (*ε* ~ 300–1450 M<sup>-1</sup> cm<sup>-1</sup>), it is difficult to believe that such weak bands would be clearly observable. In addition, TDDFT predicts only one excited state of <sup>2</sup>E<sub>g</sub> symmetry for Pc(2-)Co<sup>II</sup> complex in the

NIR region and no excited states of  $^2E_g$  symmetry in this region for the axially coordinated systems. This contradicts the observation of the MCD A-term at  $\sim 1000$  nm for  $Pc^{R^4}(2-)Co^{II}$ ,  $Pc^{R^4}(2-)Co^{II}Py_2$ , and  $Pc^{R^4}(2-)Co^{II}(nBuNH_2)_2$ . Of course, because of covalency, d-orbitals in cobalt phthalocyanines have significant contributions from the ligand and thus, TDDFT-predicted d-d transitions are not classic crystal field transitions. Nevertheless, overall, the data and discussion above suggest that the NIR bands observed in cobalt(II) phthalocyanines are t-m in nature and cannot be assigned to d-d transitions.

The EPR  $g_{||}$  and  $g_{\perp}$  values in cobalt(II) complexes with  $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^1$  configuration can be estimated from ligand-field theory using eqn (1) and (2):<sup>136,139–141</sup>

$$g_{||} = 2.0 \quad (1)$$

$$g_{\perp} = 2 - 6(\xi/\Delta E_{d_{xz,yz} \rightarrow d_{z^2}}) \quad (2)$$

Here,  $\xi$  is a spin-orbit coupling constant for cobalt(II) ion in coordination compound and  $\Delta E_{d_{xz,yz} \rightarrow d_{z^2}}$  is the experimental or theoretically predicted energy of the  $^2E_g \leftarrow ^2A_{1g} (d_{xz,yz} \rightarrow d_{z^2})$  d-d transition. Following Kida,<sup>136</sup> we used  $\xi = -510$  cm<sup>-1</sup>. TDDFT-predicted energies listed in Table 8 for  $^2E_g \leftarrow ^2A_{1g} (d_{xz,yz} \rightarrow d_{z^2})$  d-d transitions for  $Pc(2-)Co^{II}$ ,  $Pc(2-)Co^{II}Py_2$ , and  $Pc(2-)Co^{II}(nBuNH_2)_2$ . The calculated values for  $g_{\perp}$  (2.51, 2.19, and 2.18 for  $Pc(2-)Co^{II}$ ,  $Pc(2-)Co^{II}Py_2$ , and  $Pc(2-)Co^{II}(nBuNH_2)_2$ , respectively) follow the experimental trend for  $g_{\perp}$  values observed in  $Pc^{tBu}(2-)Co^{II}$ ,  $Pc^{tBu}(2-)Co^{II}Py_2$ , and  $Pc^{tBu}(2-)Co^{II}(nBuNH_2)_2$  and are in reasonable agreement with the experimental data. This, again, suggests that the energies of the  $^2E_g \leftarrow ^2A_{1g} (d_{xz,yz} \rightarrow d_{z^2})$  d-d transitions in  $Pc(2-)Co^{II}$ ,  $Pc(2-)Co^{II}Py_2$ , and  $Pc(2-)Co^{II}(nBuNH_2)_2$  should be quite different and thus NIR bands observed in cobalt(II) phthalocyanines cannot be assigned as d-d in nature. We also calculated the EPR parameters of  $Pc(2-)Co^{II}$ ,  $Pc(2-)Co^{II}Py_2$ , and  $Pc(2-)Co^{II}(nBuNH_2)_2$  using DFT methodology, with results shown in Table 1 and ESI Table S4.† Since EPR spectroscopy is used in this report only for confirmation of the low-spin ( $s = 1/2$ ) electronic structure of the cobalt(II) systems, detailed discussion on the influence of the exchange-correlation functionals<sup>142</sup> and basis sets<sup>143</sup> is relegated to the ESI.† In short, as one can see from Table 1 and ESI Table S4,† we obtained good agreement between theory and experiment for  $g$ -values. Trends in  $A$ -values are also correct for most tested functionals, although their absolute values differ significantly, indicating that a new computational protocol should be developed to accurately predict both,  $g$ - and  $A$ -values in phthalocyanine cobalt(II) systems. Nevertheless, our DFT calculations on the EPR parameters solidify our assumption that these compounds have low-spin configurations and the  $d_{z^2}$  orbital in the EPR active space (ESI Fig. S12†).

## Conclusions

In this report, we provided combined experimental (UV-Vis-NIR and MCD) and theoretical (DFT and TDDFT) analyses of

the optical and magneto-optical properties of cobalt(I), cobalt(II), and cobalt(III) phthalocyanines between 250 and 1200 nm. Two cobalt(I), five cobalt(II), and two cobalt(III) complexes were studied. It was shown that diamagnetic systems have no activity in the NIR spectral envelope, while paramagnetic low-spin cobalt(II) phthalocyanines have an easily detectable set of NIR bands. The NIR t-m bands in  $Pc^{R^4}(2-)Co^{II}L_2$  ( $L = \text{nil}, Py$ , or  $nBuNH_2$ ;  $R = H$  or *tert*-Bu) complexes were studied by MCD spectroscopy for the first time and compared to those reported earlier by us in  $Pc^{R^4}(2-)Cu$  ( $R = \text{tert}$ -Bu or  $SO_3Na$ ) compounds. In all cases, the Faraday MCD A-term was observed for the lowest energy NIR transition. Based on their profile similarities with the Q-band, degeneracy of the lowest energy MCD signal, intensities, TDDFT calculations, and ligand-field theory considerations, the NIR transitions can be assigned to t-m transitions with a high degree of confidence. We also showed that the MLCT bands in cobalt phthalocyanine complexes increase in energy going from cobalt(I) to cobalt(III) systems in a step-wise fashion. DFT and TDDFT calculations also confirm and explain changes in energies of the B1-band going from cobalt(I) to cobalt(III) complexes. Additional absorption bands observed in the 370–530 nm spectral envelope in  $[Pc^{R^4}(2-)Co^{III}X_2]^-$  complexes ( $X = Br^-$  or  $CN^-$ ) were also assigned with a high level of confidence for the first time. This work provides the first combined systematic experimental and theoretical study that highlights similarities and differences in (magneto) optical spectroscopy of cobalt phthalocyanines spanned over three oxidation states at the central metal ion.

## Experimental section

### Materials and instrumentation

All solvents were purified using standard procedures.  $Pc(2-)Co^{II}$  was purchased from Alfa Aesar. Pyridine,  $[NBu_4]Br$ , and  $[NBu_4](CN)$  were purchased from Aldrich. *N*-Butylamine and bromine were purchased from Thermo Fisher Scientific.  $Pc^{tBu}(2-)Co^{II}$  was synthesized as previously described.<sup>102</sup> Reduction of  $Pc(2-)Co^{II}$  to  $[Pc(2-)Co^I]^-$  was carried out in DMF following the previously published procedures.<sup>100,106</sup> Formation of  $(NBu_4)[Pc(2-)Co^{III}(CN)_2]^-$  was performed in DMF using excess  $[NBu_4](CN)$ .<sup>103</sup>  $Pc^{Rn}(2-)Co^{II}(nBuNH_2)_2$  complexes were synthesized by dissolving  $Pc^{Rn}(2-)Co^{II}$  complexes in benzene or DMF in the presence of a large ( $\sim 1000$  times) of *n*-butylamine.  $Pc^{Rn}(2-)Co^{II}(Py)_2$  complexes were formed by dissolving  $Pc^{Rn}(2-)Co^{II}$  in pyridine, benzene/pyridine, or DMF/pyridine.  $(NBu_4)[Pc^{tBu}(2-)Co^{III}Br_2]$  complex was prepared by adding 1.1 eq. of the  $Br_2$  in DCM to the solution of the  $Pc^{tBu}(2-)Co^{II}$  in 0.1 M of  $[NBu_4]Br$ . In all cases, the UV-Vis-NIR spectra of the target compounds were identical to those reported earlier.

All spectra were collected using a Q-3 quartz cell purchased from Labomed Inc. UV-Vis data were collected on a JASCO V-770 spectrometer and MCD data were recorded using a JASCO V-1500 spectropolarimeter with a permanent 1.6 T magnet. Each MCD sample was recorded three times each

with a parallel and anti-parallel field. All intensities of MCD data are expressed in molar ellipticity per tesla. Origin Pro 8.0<sup>144</sup> was used for simultaneous band deconvolution analysis of the UV-Vis-NIR and MCD spectra of  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$ . EPR spectra were collected on a Bruker X-band ELEXSYS E-500 instrument at 150 K. Samples were prepared and frozen under a nitrogen atmosphere. Toluene was used for  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}$  and toluene/axial ligand (95/5 v/v) was used for  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(\text{Py})_2$  and  $\text{Pc}^{\text{tBu}}(2-)\text{Co}^{\text{II}}(n\text{BuNH}_2)_2$ .

### DFT and TDDFT calculations

All calculations were performed using Gaussian 16.<sup>145</sup> TPSSH<sup>146,147</sup> (hybrid functional with 10% of Hartree-Fock exchange) was used for all geometry optimizations, TDDFT, and single-point DFT calculations to better describe charge-transfer transitions compared to GGA exchange–correlation functionals. Wachter's full-electron basis set<sup>148</sup> for cobalt and the 6-311G(d) basis set<sup>149</sup> for all other atoms were used. PCM<sup>150</sup> using the dielectric constant of DMF was used to mimic solvent effects in the systems. Geometries of  $\text{PcCo}^{\text{II}}$ ,  $[\text{PcCo}^{\text{I}}]^-$ ,  $[\text{PcCo}^{\text{III}}\text{Br}_2]^-$ , and  $[\text{PcCo}^{\text{III}}(\text{CN})_2]^-$  converged to the  $D_{4h}$  point group,  $\text{PcCo}^{\text{II}}\text{Py}_2$  converged to the  $D_{2d}$  point group, and  $\text{PcCo}^{\text{II}}(n\text{BuNH}_2)_2$  converged to the  $C_i$  point group. Frequencies were calculated for each converged structure to ensure that the structure converged to a minimum. GaussView 6.0 was used for MO visualization and QMForge<sup>151</sup> for orbital composition analysis.

### Data availability

Additional data are available on request from the corresponding authors.

### Conflicts of interest

The authors declare no competing financial interest.

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