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Aromaticity versus regioisomeric effect of b-substituents in porphyrinoids†

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The photophysical properties of naturally occurring chlorophylls depend on the regioisomeric nature of the b-pyrrolic substituents. Such systems are the ‘‘gold standard’’ by which such effects are judged. However, simple extrapolations from what has been learned with chlorophylls may not be appropriate for other partially reduced porphyrinoids. Here we report the synthesis of a series of cis/trans-porphodilactones (cis/trans-1) and related derivatives (cis/trans 2–5) designed to probe the effect of regioisomeric substitution in porphyrinoids that incorporate degrees of unsaturation through the b-pyrrolic periphery that exceed those of chlorophyll. These test systems were obtained through b-pyrrolic modifications of the tetrapyrrolic core, which included reduction of b-diazalone to the corresponding dilactol moieties and 1,3-dipolar cycloadditions. In the case of cis- vs. trans-3 bearing two pyrrolidine-fused b-rings we found an unprecedented DQ_L up to ca. 71 nm (2086 cm^{1}), where DQ_L (Q_L means the lowest energy transfer band, also the S_0 - S_1 transition band, which is often assigned as Q_y(0,0) band) refers to the transition energy difference between the corresponding cis/trans-isomers. The DQ_L values for these and other systems reported here were found to depend on the differences in the HOMO–LUMO energy gap and to be tied to the degeneracy and energy level splitting of the FMOs, as inferred from a combination of MCD spectral studies and DFT calculations. The aromaticity, estimated from the chemical shifts of the N–H protons and supported by theoretical calculations (e.g., AICD plots and NICS(1) values), was found to correlate with the extent of porphyrin periphery saturation resulting from the specific b-modifications. The aromaticity proved inversely proportional to the degree to which the regioisomerism affected the photophysical properties as noted from plots of DQ_Ls in cm^{1} vs. the average NICS(1) values for 1–5. Such a finding is not something that can be easily interpolated from prior work and thus reveals how aromaticity may be used to fine-tune photophysical effects in reduced porphyrinoids.

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Introduction

Regioisomeric effects, specifically where carbonyl substituents are placed on the b-pyrrolic periphery of unsaturated porphyrin derivatives, can have a profound effect on the electronic structures, photophysical properties, and intermolecular interactions of these quintessential p-conjugated chromophores.[1] The impact of these effects has recently come to be recognized in the context of organic optoelectronics.[2] They are also appreciated for the role they play in regulating the optical features of natural occurring tetrapyrroles. Likely, regioisomeric substitution effects play a key role in fine-tuning the biological features of these ‘‘life pigments’’, as exemplified by chlorophylls, such as chl b, d, and f, isolated from both the sea and the land.[1b,1e,3] For example, the lowest energy absorption difference, DQ_L, where DQ_L (Q_L means the lowest energy transfer band, also the S_0 S_1 transition band, which is often assigned as Q_y(0,0) band) refers to the transition energy difference between the corresponding cis/trans-isomers, between chl d and f is 9 nm (183 cm^{1}, Fig. 1).[3f,4] The origin of this difference is ascribed to the relative orientations of the formyl or vinyl substituents on the porphyrin periphery, and is viewed as a phenomenon that is well understood in the case of chlorophyll derivatives.[3] In fact, the effect could be

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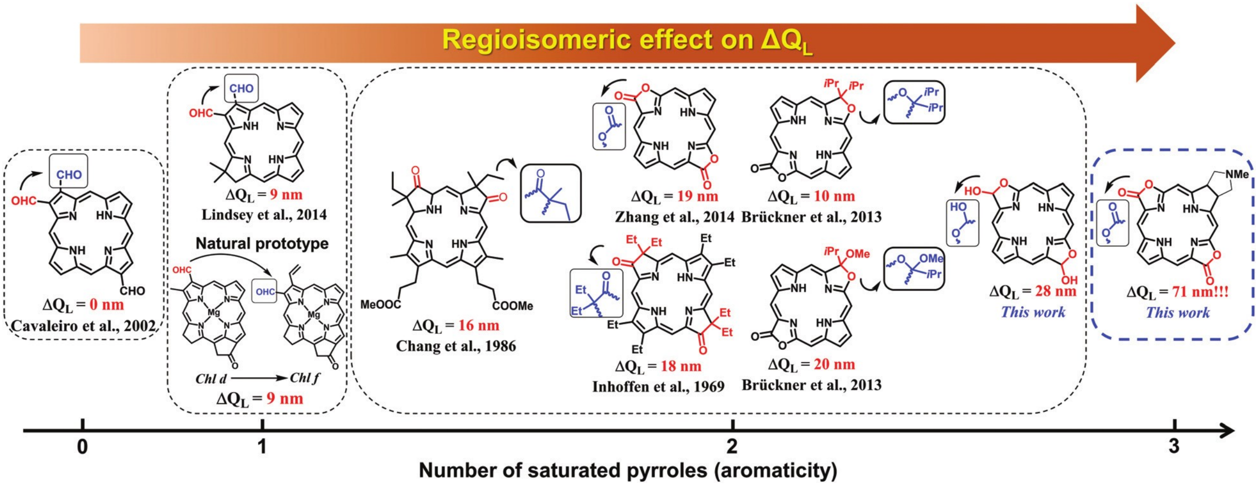


Fig. 1 Families of porphyrinoid isomers grouped so as to show the how effect of substitution depends on the degree of aromaticity as reflected in the extent of b-pyrrolic saturation (meso-aryl groups omitted for clarity). The substitutions drawn by red and blue indicate the cis and trans isomers respectively, the lowest energy absorption difference (DQ$_L$) are listed, and the authors with the years of literature are also presented below the structures.

recapitulated by Lindsey and co-workers through preparative work involving chlorins.[5] However, the regioisomeric consequences of b-pyrrolic substitution have been much less studied in the case of other porphyrinoids and seemingly contradictory findings have been reported in the literatures. For instance, as early as 1969 Inhoffen and co-workers reported the orientation of b-dioxo groups influenced the absorptions of dioxobacteriochlorin isomers (DQ$_L$ = 18 nm, or 387 cm^{1}, Fig. 1).[6] In 1986, Chang et al. synthesized isomeric porphyrindiones with ketone groups in different orientations in adjacent pyrroles and found a DQ$_L$ of 16 nm (403 cm^{1}) between the isomers in their free-base forms.[7] In 1991, the same group reported that the DQ$_L$ increased up to 71 nm (2086 cm^{1}) upon coordination of copper(II) ion.[8] In a sharp contrast, in 2002 Cavaleiro, et al. observed, however, no difference in the absorption features of isomers that differed in terms of the orientation of two b-formyl groups on the periphery.[9] Later Brückner and we found that the cis/trans-porphodilactone isomers (cis/trans-1) and their derivatives, characterized by different orientations of the constituent b-diazalone moieties, displayed distinctively different absorption (DQ$_L$ = 10–20 nm) and emission features.[10] This latter regioisomeric effect was reflected in the respective triplet energies.

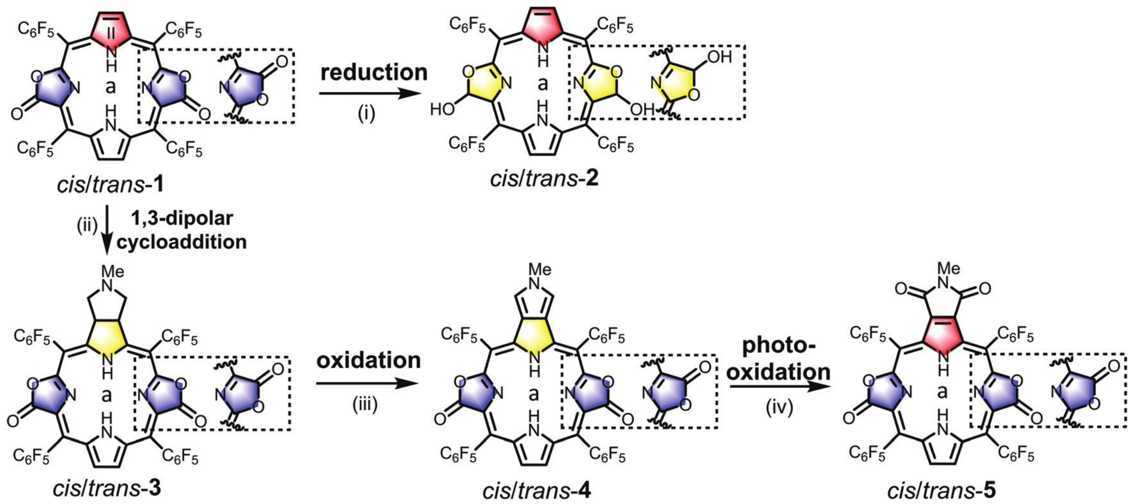
Being able to fine-tune the electronic features through control of regioisomeric effects may allow for the production of chromophores optimized for a certain applications or better control over NIR lanthanide sensitization and triplet annihilation-based upconversion.[10a,11] However, currently a clear understanding of the fundamental relationship between regioisomeric substitution effects and the photophysical properties of highly reduced tetrapyrrolic chromophores is lacking. The present study was instigated with the goal of obtaining such fundamental structure–function insights.

As a first step, we analysed the differences in the lowest energy absorption spectral maxima using sets of previously reported congeneric porphyrinoid regioisomers.[4–6,9,10,12] Although isomeric copper porphyrindiones showed the pronounced regioisomeric effect,[8] the unknown role of copper coordination renders difficult comparison with the most reported porphyrinoid free bases and thus we focused on the porphyrinoid free bases in the context. We noticed a possible inverse relationship between DQ$_L$ and degree of saturation represented by the number of the saturated pyrroles (cf. Fig. 1). Specifically, DQ$_L$ was found to increase as the number of saturated b-pyrroles increased from 0 to 2. In an effort to confirm or refute the validity of this observation, we have prepared several new derivatives of the cis/trans-porphodilactones 1, namely the isomeric lactols, cis/trans-2, the further tri-substituted pyrrole system cis/trans-3, and oxidized forms of the latter, viz. cis/trans-4 and cis/trans-5. In accord with our preliminary expectations, the DQ$_L$ values were found to increase as the saturation level of the b-periphery increased. In fact, an unprecedented DQ$_L$ was observed (up to ca. 71 nm; 2086 cm^{1}) for cis- vs. trans-3. To our best of knowledge, this DQ$_L$ is the largest in the porphyrinoid free base system. The present study was thus undertaken with a goal to understanding the effects of macrocyclic structure on the optical feature of porphyrinoid regioisomers. We note that pyrrocorphins and related corphinoids with three hydrogenated or saturated pyrroles were reported early on by Eschenmoser, Chang, and Cavaleiro and co-workers.[7,13] However, their photophysical properties were not investigated in detail. Thus, an ancillary objective was to carry out fundamental studies that might provide further insights into these classic systems.

Results and discussion

Synthesis and characterization

The synthesis of cis/trans-2–5 is summarised in Scheme 1. Starting from cis/trans-1 and following Cavaleiro's procedure with slight modification,[13d,14] cis- and trans-3 were obtained in yields of 57 and 66%, respectively, through 1,3-dipolar cycloaddition of azomethine ylides. cis/trans-4 were then obtained by



Scheme 1 Synthesis of cis/trans-2–5. Reagents and conditions: (i) DIBAL-H, THF, 78 1C; (ii) sarcosine, paraformaldehyde, 105 1C, toluene, 12 h; (iii) DDQ, toluene, reflux for 4 h; (iv) O_2, $CHCl_3$, irradiated under white light for 4 h.

subjecting cis/trans-3 to oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene.[15] Further oxidation of cis/trans-4 by oxygen under conditions of photo-irradiation produced cis/trans-5 in 16 and 18% yield, respectively.[16] Separately, cis/trans-1 was subject to diisobutylaluminium hydride (DIBAL-H) reduction in THF, according to Brückner's procedure; this allowed us to obtain cis/trans-2 both in the yield of 90%.[10b,17] However, attempts to reduce cis/trans-3 to the corresponding porphodilactols proved unsuccessful. For instance, 3 was found to decompose in the presence of DIBAL-H. In addition, we only isolated one form of cis isomer in 3–5, and this was analysed in the ESI† (Scheme S7).

The chemical shifts of the inner N–H signals seen in the ^1H NMR spectra of cis/trans-1–5 were found to vary from 1.64 to 6.53 ppm. This was taken as evidence that there are significant differences in the ring currents within this series as a function of b-modification. It also provided an initial hint that aromaticity effects would prove important in terms of analysing the optical features (see discussion below). Detailed synthetic procedures and full characterization data are listed in the ESI† (Schemes S1–S6 and Fig. S1–S40). All new compounds were fully characterized using ^1H, ^{13}C and ^{19}F NMR spectroscopies, mass spectrometry (MS), and infrared (IR) spectroscopy. In addition, 2D-NMR (COSY and NOESY) experiments revealed clean cross-peaks between the b-H and N–H proton signals leading us to suggest that, in accord with the predictions by Gouterman et al.,[18] compounds 1–5 exist in one tautomeric form (Fig. S41–S50, ESI†).

X-ray crystallography

Slow diffusion of n-hexane into $CHCl_3$ or CH_2Cl_2 solutions of cis/trans 3–5 provided single crystals suitable for X-ray diffraction analysis. The resulting crystal structures of cis/trans-3 (CCDC: 1568750 and 1568751), cis/trans-4 (CCDC: 1841552 and 1841553) and cis/trans-5 (CCDC: 1851807 and 1851808),† respectively, are shown in Fig. 2. Collectively, these structures provide support for the chemical assignments made initially on the basis of the spectroscopic and mass spectrometric analyses (vide supra), in particular the presence of a fused five-member ring on porphodilactone b-periphery in all six compounds (Tables S1–S3 and Fig. S51–S56, ESI†). In 3, the N–CH_3 moiety was found slanted towards the porphyrin ring in the cis isomer, while it was found to point in the opposite direction in the case of the trans isomer. The pyrrole-fused b-rings of cis/trans-4 and the pyrrolidine-2,5-dione-fused b-rings of cis/trans-5 were found to be coplanar with the porphyrin ring. The average C–N and C–C bond lengths are similar in cis/trans-3–5 (Tables S4–S6, ESI†), a finding we take as meaning that are apart from the position of the substituents there are relatively small structural differences between the cis and trans-isomers. Across the series, both the cis and trans forms of 3–5 display relatively planar core porphyrinoid structures (RMSD = 0.072 and 0.104 Å for cis/trans-3, 0.085 and 0.161 Å for cis/trans-4, and 0.153 and 0.168 Å for cis/trans-5, respectively. Fig. 2).[12a,19] Again, this is consistent with the suggestion that the key 1,3-dipolar cycloaddition that provides an entry into this series of porphyrinoids affects only slightly the planarity and configuration of the central macrocycle.

Photophysical properties

The absorption and emission spectra of cis/trans 2–5 were recorded in CH_2Cl_2 at room temperature (Fig. 3). The corresponding photophysical data are summarized in Table S7 and Fig. S57–S76 (ESI†)As can been seen from an inspection of Fig. 3, all members of the cis/trans 2–5 series display intense Soret bands in the 350–450 nm spectral region, as well as several weak and broad Q bands at lower energy (between 450 and 780 nm). Compared with cis/trans-1, which displays typical bacteriochlorin absorption features,[3a,3b] the lowest Q band of cis/trans-2 are bathochromically shifted (by ca. 65 and 74 nm for the cis and trans isomers, respectively; cf. Table S7, ESI†). cis-3 is characterized by a large hypsochromic shift in its Q bands (by ca. 108 nm) relative to cis-1, while only a smaller

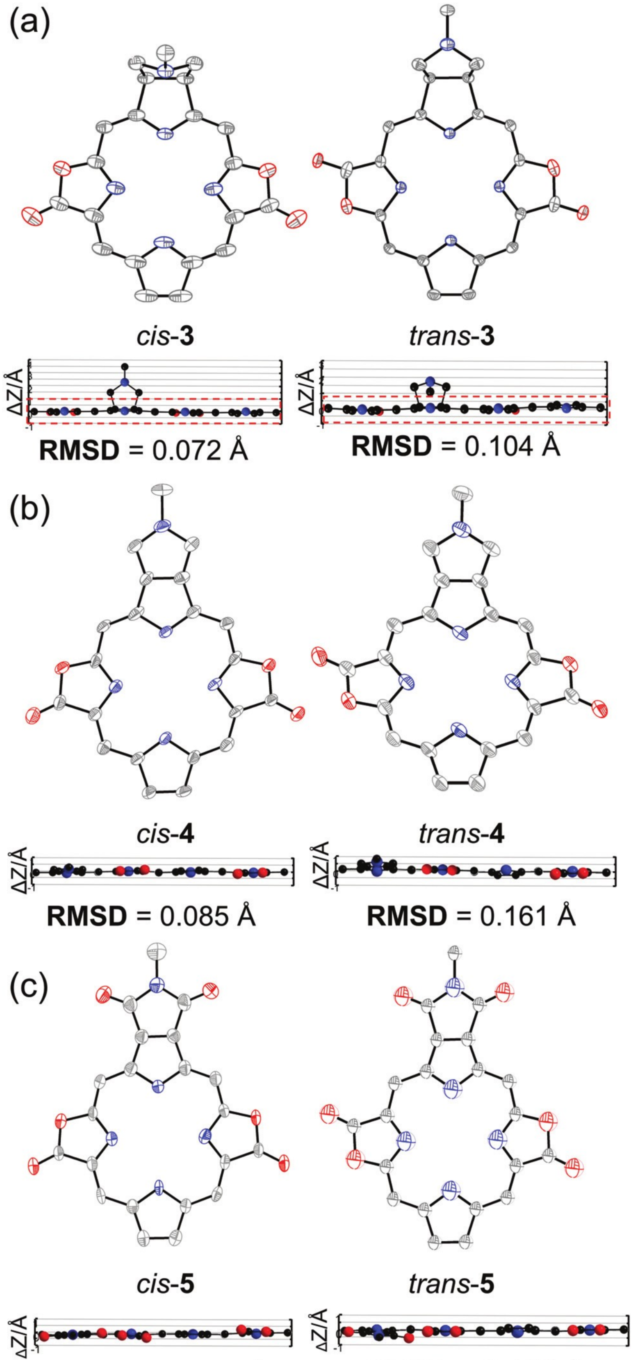


Fig. 2 ORTEP structures of (a) cis/trans-3, (b) 4, and (c) 5 (50% probability) showing the deviations of the skeletal atoms from the N_4 mean plane defined by the four pyrrolic nitrogen atoms. The RMSD values listed are of the $C_{18}O_4N_4$ ring (selected atoms shown within the red dashed line box for cis/trans-3). Hydrogen atoms, solvent molecules, and meso-aryl groups are omitted for clarity.

hypsochromic shift (by ca. 56 nm) is seen in the case of trans-3 relatives to trans-1. cis and trans-4 both display bathochromically shifted Q-band features as compared to 1. In contrast to the general trend of the trans-isomers showing red-shifted Q bands to their cis counterparts (as seen in 1–4), cis-5 is characterized by

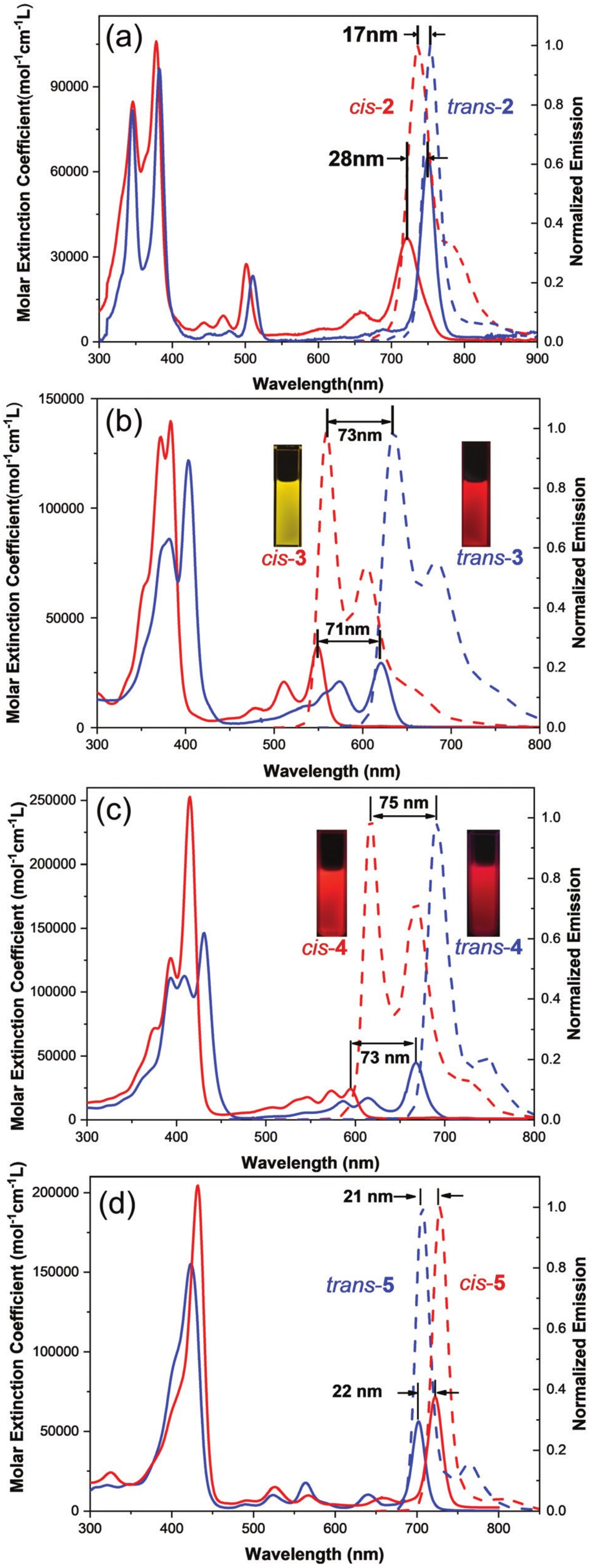


Fig. 3 Electronic absorption (solid lines) and emission (dashed lines) spectra of (a) cis-2 (red) and trans-2 (blue), (b) cis-3 (red) and trans-3 (blue), (c) cis-4 (red) and trans-4 (blue) and (d) cis-5 (red) and trans-5 (blue) in CH_2Cl_2. Photographs of solutions of 3 and 4 taken under a 365 nm UV lamp are provided as inserts.

Q bands that are red-shifted relative to those seen in trans-5 (Fig. 3d). Taken in concert, the observed spectroscopic features, including the presence of prominent Soret and Q bands, leads us to suggest that aromaticity is retained in cis/trans-1–5 in spite of the obvious structural modifications.[13d,20] The increase in the value of DQ_Ls for the two isomers follows the trend: 1 (19 nm)[10a] E 5 (20 nm) o 2 (28 nm) o 3 (71 nm) E 4 (73 nm). This leads us to conclude that increasing from two to three the number of saturated pyrroles in otherwise similar porphyrinoids leads to an enhanced regioisomeric effect on the absorption features. In other words, moving from a cis to a trans isomer has a relatively greater effect in the case of more highly reduced porphyrinoids. This trend is underscored by the fact unprecedentedly large DQ_Ls of ca. 71 and 73 nm were seen in the case of cis/trans-3 and 4, respectively. In addition, the absorption difference between the lowest Soret bands for the cis and trans isomers follows a similar trend, namely 1 (2 nm) o 2 (4 nm) and 5 (9 nm) (both with two saturated pyrroles) o 4 (16 nm) and 3 (20 nm) (three saturated pyrroles).

A regioisomeric effect on the fluorescence emission spectra was seen. The underlying photophysical data measured in CH_2Cl_2 are summarized in Fig. 3 and in Table S7 (ESI†). The trends were found to parallel what was seen in the case of the absorption spectral studies. For instance, cis/trans-2 were characterized by fluorescence emission features centred at 737 and 754 nm with a shoulder at 784 and 828 nm, respectively. These values are bathochromically shifted relative to cis/trans-1. Quantum yields (F) of 6.1% and 5.3% and lifetimes (t) of 2.1 ns and 2.6 ns were obtained for, cis-2 and trans-2, respectively. cis-3 displays an emission maximum at 559 nm with a shoulder at 604 nm (F = 35.1%, t = 5.5 ns), while the emission maximum of trans-3 is red-shifted to 635 nm with a shoulder at 683 nm (F = 24.5%, t = 5.1 ns). Thus, the difference in the emission maxima is 76 nm. cis- and trans-4 display fluorescence maxima centred at 617 and 692 nm with quantum yields of 36.3% and 15.2% and lifetime of 8.34 ns and 3.29 ns, respectively. cis/trans-5 display NIR fluorescence features centred at 728 nm and 707 nm with quantum yields of 20.9% and 28.0%, respectively. Thus, as true for the corresponding absorption spectra, a relatively small difference in the emission maxima of 21 nm was seen for these two isomers. On the basis of the crystal structures of 1, and 3–5, the regioisomeric effects on the fluorescence emission features are not considered to arise from distortions of the respective porphyrin planes since all species have relatively planar structures.[12a,19]

The redox properties of cis/trans 2–5 were examined in CH_2Cl_2 by cyclic voltammetry (CV) using tetra-n-butylammonium hexafluoro-phosphate (n-Bu_4NPF_6) as the supporting electrolyte. As shown in Table S7 and Fig. S77–S80 (ESI†), the CVs of cis/trans-2–4 are each characterized by two quasi-reversible reduction waves and one quasi-reversible oxidation wave. In contrast, three quasi-reversible reduction waves are seen in the CVs of cis/trans-5 and no oxidation waves were observed in CH_2Cl_2. The use of slower scan rate in the CV measurement studies failed to improve the reversibility of the redox waves (Fig. S81 and Table S8, ESI†), which was taken to indicate that the lack of reversibility is inherent to these tetrapyrroles, rather than the result of slow electron transfer kinetics at the electrode/electrolyte interface.

Modulating the regioisomeric effect by aromaticity

Porphyrinoids 1–5 are expected to be aromatic compounds. Experimental support for this assumption comes from the observed the spectroscopic features, including the strong Soret bands, low field chemical shifts observed for the outer b-H protons (7.23–8.85 ppm), and the upfield shift seen for the inner pyrrole N–H protons (2.12 to 6.53 ppm). However, the extent of aromaticity was expected to depend on the degree of unsaturation. Thus, we sought to test whether the optical features could be correlated with indicators of aromaticity. To the extent this proved true, it would provide an indication that differences in aromaticity could explain the large disparities in photophysical properties induced by ostensibly similar regioisomeric effects across the series of porphyrin analogues embodied in Fig. 1.

Anisotropy of the induced current density (AICD) is a magnetic indicator of aromaticity that allows ring-currents and electron delocalization effects to be easily visualised.[21] As shown in Fig. 4, AICD plots constructed at the B3LYP[22]/6-31+G(d) level[23] disclose ring circulation patterns typical of aromaticity across the series 1–5. Reduction of 1 to 2 does not change the macrocyclic circulation within the porphyrin core but does reduce the ring current at the b-dilactol moieties. The 1,3-dipolar cycloaddition that serves to convert 1 into 3 acts to interrupt the circulation of one pyrrole ring and thus weaken the extent of aromaticity. In 3, the lone pair of the pyrrollic N atom still participates in the p-conjugation pathway; thus 3 retains aromaticity. Oxidation of the pyrrolidine-fused b-rings in 3 to produce the pyrrole-fused b-rings present in cis/trans-4 serves to restore partly the original level of aromaticity present in 1. Presumably, this is due to the creation of a more extended p system but with a partially ''broken'' circulation. Photooxidation of 4 to 5 can completely restore the macrocyclic circulation as well as the aromaticity within the porphyrin rings. Thus, the AICD plots constructed at an isosurface value of 0.06 for 1–5 clearly show the changes of macrocyclic and local p circulation that result from b-modification. However, it is important to appreciate that in our hands this technique does not provide insights into the regioisomeric effect on macrocyclic p-conjugation.

In light of the above limitations, the isotropic nucleus-independent chemical shift (NICS)[24] values were calculated at the B3LYP/6-31+G(d) level so as to compare more quantitatively the aromaticity of cis/trans-1–5. In particular, the NICS(1) values of the ring a (Scheme 1) were determined, with the resulting findings being summarized in Table 1 and Table S9 (ESI†). On this basis, it was concluded that within this matched set, whether considering the cis- or trans-isomer, the order of the NICS(1) values increases in the order 1–5 o 2 o 4 o 3. This trend is in the line with what is seen for the chemical shifts of the inner N–H protons (2.12 to 6.53 ppm) or those of the outer b-H signals (7.23–8.85 ppm).

To verify the validity of computational work, we correlated the chemical shifts of the N–H proton signals for all compounds

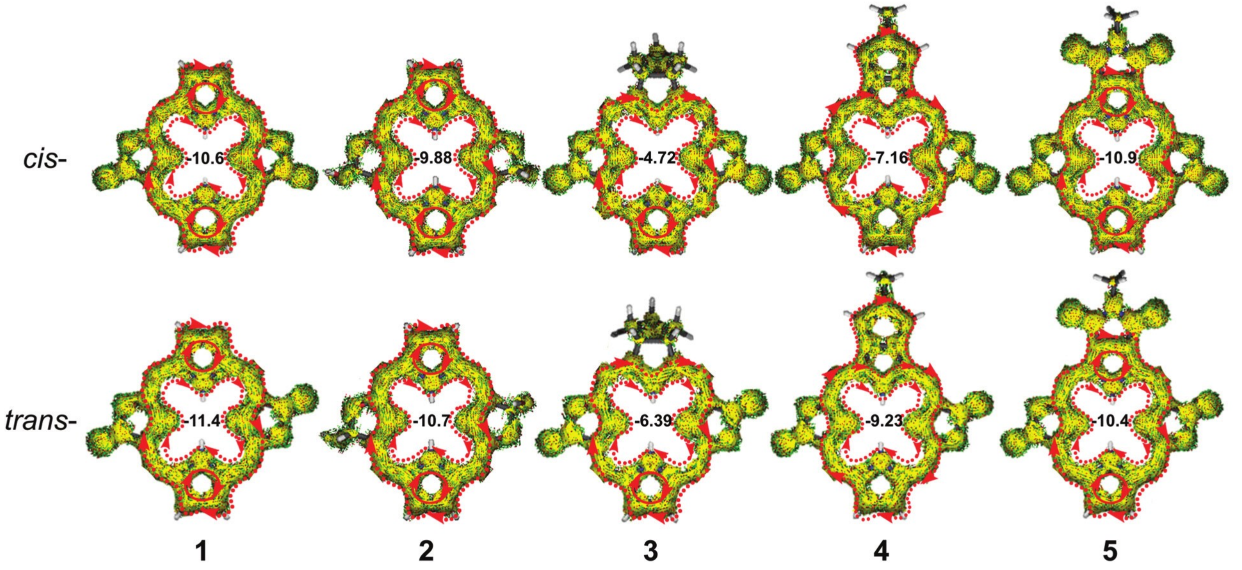


Fig. 4 AICD plots at isosurface values of 0.06 and NICS(1) values (black number in the middle of molecules) calculated for cis/trans 1–5.

Table 1 N–H pyrrolic proton chemical shifts, NICS(1) values and DQ$_L$ of cis/trans-1–5

Comp.		d$_{N–H}$/ppm	Avg. d$_{N–H}$^{a}/ppm	NICS(1)/ppm	Avg. NICS(1)^{b}/ppm	DQ$_L$/cm ^{1}
1	cis	0.95, 0.33	1.38	10.61	10.99	428
	trans	2.12		11.37		
2	cis	0.79, 1.26	0.16	9.88	10.29	517
	trans	1.35		10.71		
3	cis	5.45, 6.53	4.90	4.72	5.56	2086
	trans	3.48, 4.13		6.39		
4	cis	2.39, 3.51	1.72	7.16	8.19	1837
	trans	0.19, 0.79		9.23		
5	cis	1.05, 1.64	1.01	10.93	10.65	395
	trans	0.66, 0.69		10.36		

[a] Avg. $d_{N–H} = [n_{cis}*(d_{N–H})_{cis} + n_{trans}*(d_{N–H})_{trans}]/(n_{cis} + n_{trans})$, where n is the integrated value of the N–H proton signal in the ^{1}H NMR spectra. [b] Avg. NICS(1) = [NICS(1)$_{cis}$ + NICS(1)$_{trans}$]/2.

in the study, as well as their average value for each isomeric pair, with the corresponding NICS(1) values.[25] Interestingly, plotting the NICS(1) values vs. the chemical shifts of the pyrrole N–H proton signals produced a positive correlation (Fig. 5a). Moreover, the NICS(1) values were found to be inversely correlated with the chemical shifts of the b-H protons (Fig. S82, ESI†). On the other hand, with the exception of 5, the trans-isomers are characterized by more negative NICS(1) values than the cis-isomers.

To probe a possible relationship between the regioisomeric effect and the aromaticity of porphyrinoids, we correlated DQ$_L$s in units of energy (cm ^{1}) vs. the aromaticity represented by the average NICS(1) values for 1–5. As shown in Fig. 5b, we obtained a positive correlation. In addition, we also plotted DQ$_L$ values vs. the average chemical shifts of the N–H (Fig. S83, ESI†) and the b-H proton signals (Fig. S84, ESI†), as well as the D(Soret band) values vs. the average NICS(1) values for 1–5 (Fig. S85 and Table S10, ESI†); the same trend was observed. Again, these plots help underscore the fact that the regioisomeric substitution effects that are well appreciated for chlorophylls can be enhanced significant in the case of more highly unsaturated systems. For example, on passing from 3 to 5 via the chemistry outlined in Scheme 1, a significant change in the magnitude of the regioisomeric effect on DQ$_L$ is seen. Moreover, the nearly linear plotting of regioisomeric effect (Q$_L$(cis)–Q$_L$(trans)) vs. aromaticity difference between cis and trans isomers (NICS(1)$_{cis}$–NICS(1)$_{trans}$) for compounds 1–5 and seven other previously reported isomeric pairs (Fig. 5c) further indicates that the enlarged regioisomeric effects on photophysical properties originate from the increased aromaticity difference between isomers.

Electronic structures

To investigate the regioisomeric effect on the electronic structures of 1–5, density functional theory (DFT) calculations were performed at the B3LYP/6-31+G(d) level. Based on the 2D NMR spectroscopic studies noted above, we discounted the possibility of tautomerism involving the N–H protons within the N$_4$ cavity and considered only the tautomers where these protons were located on the pyrrolic moieties.[18] The nodal patterns of the frontier molecular orbitals (FMOs) and the corresponding energy diagrams were then derived in accord with Gouterman's four-orbitals model.[26] The results are shown in Fig. 6. From 5,10,15,20-tetrakis(perfluorophenyl)-porphyrin (F20-porphyrin)

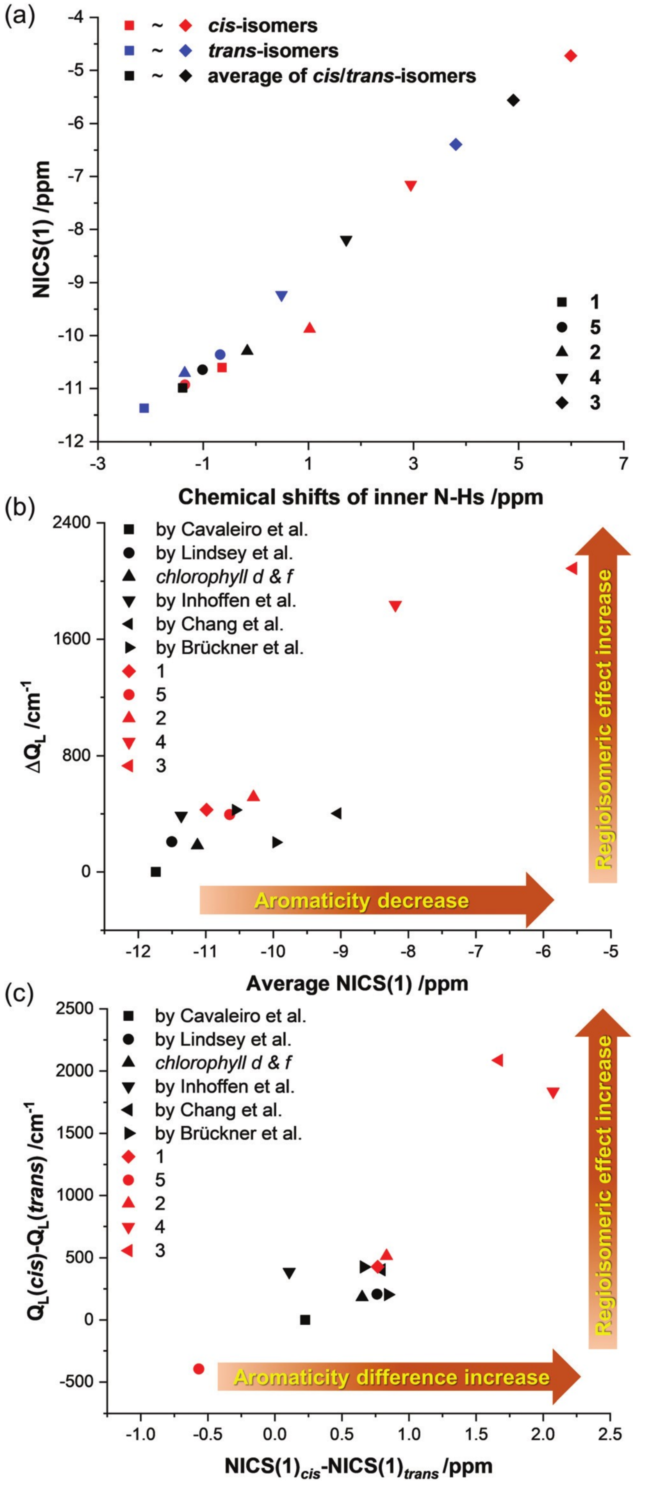


Fig. 5 (a) Relationship between the calculated NICS(1) values vs. chemical shifts of the inner N–H proton signals observed in the ^{1}H NMR spectra of 1–5. (b) Plot of a key photophysical parameter (DQ$_L$) vs. aromaticity as inferred from the NICS(1) values and (c) plot of regioisomeric effect (Q$_L$(cis)–Q$_L$(trans)) vs.aromaticity difference between cis and trans isomers (NICS(1)$_{cis}$–NICS(1)$_{trans}$) for compounds 1–5 (red) and seven other previously reported isomeric pairs (black) discussed in the Introduction.

to 1–5, the energy levels of the HOMOs and LUMOs decrease, as expected given the strong electron-withdrawing nature of the b-diazalone moiety. As a result, the HOMO–LUMO gap (HL gap) decreases from 2.80 eV in F20-porphyrin to 2.46 and 2.34 eV in cis- and trans-1, respectively. From 1 to 2, the HOMO–LUMO gap (HL gap) of the cis- and trans isomers decreases further to 2.09 and 2.01 eV, respectively, presumably due to the further decrease in the orbital degeneracy that occurs upon reduction of the b-diazalone to the corresponding dilactol moieties. This reduction in the HL gap is also in accord with the bathochromic shifted Q$_L$ bands seen for 2 relatives to 1 and the other systems under study. For cis-3, the energy of LUMO increases more than that of HOMO, leading to an increased HL energy gap (2.64 eV) compared with cis-1 (2.46 eV).[10a] In contrast, the HL energy gap of trans-3 (2.35 eV) is almost the same as that of trans-1 (2.34 eV).[10a] Therefore, it is not surprising that a much larger DQ$_L$ between the cis/trans isomers is seen in the case of 3 than in 1. The HL gap is almost the same for cis-3 (2.64 V) and cis-4 (2.67 eV), a finding that reflects the nearly identical energy changes in the HOMO and LUMO energies for these two systems. The HOMO energy of trans-3 is higher in energy level than that of trans-4; this is reflected in a decrease in the HL energy gap (from 2.35 to 2.26 eV) upon conversion of 3 to 4. The HOMO energies of cis/trans-5 are the lowest within the series 1–5. Such a finding is consistent with the relatively anodic oxidation waves seen in the electrochemical measurements. The nearly linear relationship of HL gap vs. observed Q band, calculated Q band vs. experimental Q band and DHOMO vs. oscillator strengths in TDDFT calculations validate our calculation results according Martin J. Stillman et al. (Fig. S86–S88ESI†).[27] Thus, overall the HL gaps seen for 1–5 follow the trend for the Q$_L$(0,0) bands discussed above (Fig. S89, ESI†). They thus provide another indicator of the effect of porphyrin periphery saturation on the electronic structure of these reduced porphyrinoids.This correspondence between theory and experimentalso serves to validate our DFT calculations.

As shown in Fig. 6b, the HOMO 1 frontier orbitals in 1–5 resemble the Gouterman a_{1u} orbitals modified for the presence of strongly electron-withdrawing diazalone moieties. Likewise, the HOMO frontier orbitals in 1–5 resemble the Gouterman a_{2u} orbitals. In contrast, the HOMO 1 and HOMO orbitals of 1–5 are different from the corresponding orbitals in F20-porphyrin.[26a,28] The LUMO and LUMO+1 orbitals for 1–5 resemble Gouterman's e_g orbitals oriented along two opposite pyrrolic fragments.[26a,28] For F20-porphyrin,as well as 1–2 and 5, the lower energy LUMO is oriented along the axis of the pyrrolic ring containing the inner N–H bonds. In the case of 3 and 4, the lower energy LUMO within the Gouterman e_g set is oriented toward the b-diazalone moieties. Thus, b-modification significantly decreases the degeneracy of the FMOs in 1–5, presumably due to the reduction in symmetry (from D_{2h} to C_{2v} for the cis isomers, and from D_{2h} to C_{2h} or C_s for the trans isomers) compared with the control F20-porphyrin system.[28]

Magnetic circular dichroism (MCD) spectroscopy can provide information about molecular electronic structure and electronic transitions that complements that obtained from absorption and emission spectroscopy.[29] Therefore, the MCD spectra of 1–5 were recorded as shown in Fig. 7. The nodal patterns of the frontier p-MOs are maintained even after substantial structural

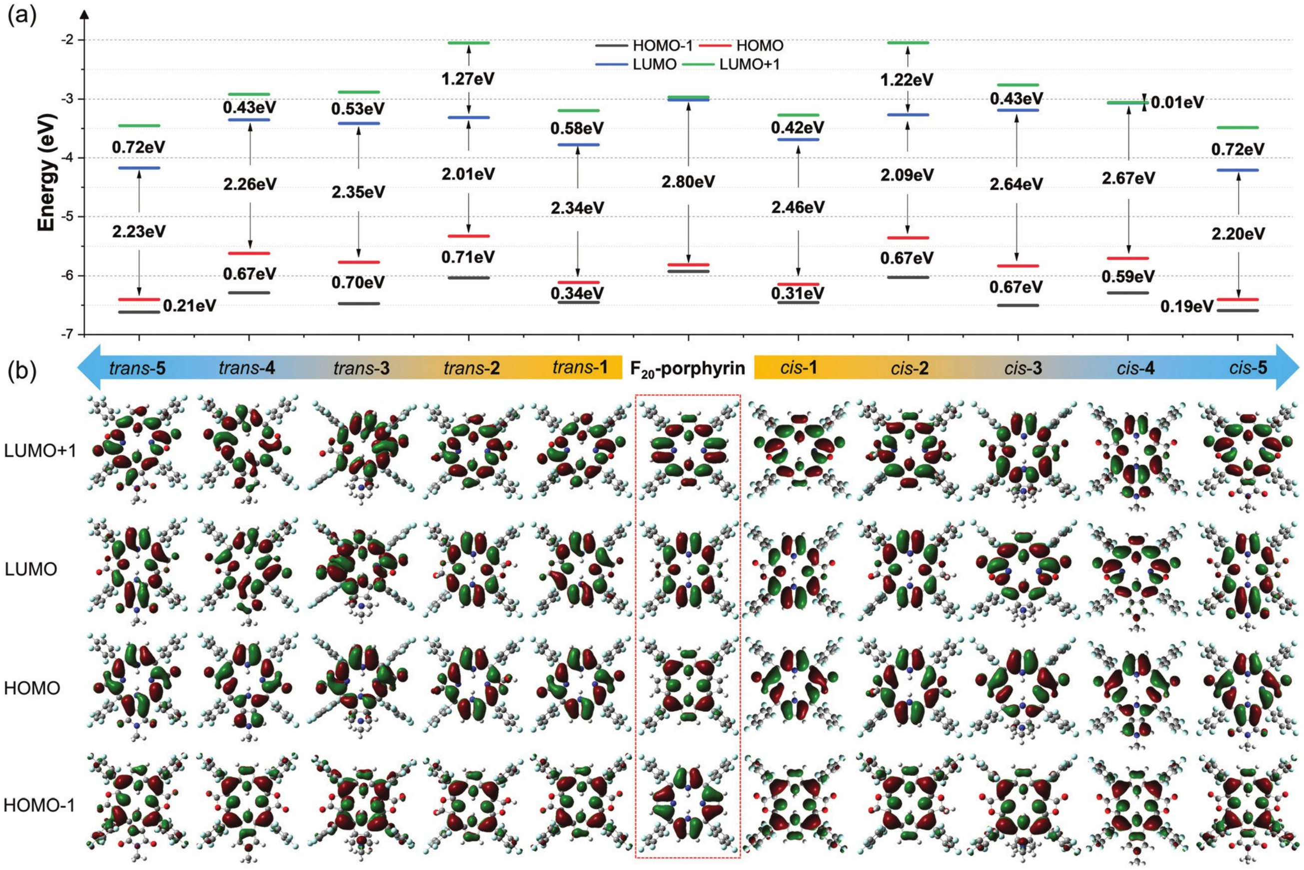


Fig. 6 (a) Energies of selected molecular orbitals of cis/trans-1–5 as determined by DFT calculations carried out at the B3LYP/6-31+G(d) level. (b) Nodal patterns of the frontier p-MOs of cis/trans-1–5 calculated using the optimized S_0 geometries.

perturbations as shown in Fig. 6b and can, therefore, be related back to those of an ideal high symmetry parent hydrocarbon ($C_{18}H_{18}$ for free base compounds).[29a] According to Michl's perimeter model,[29a,30] in high symmetry cyclic polyenes, the p-MOs associated with the perimeter retain orbital degeneracy described by the Faraday A_1, B_0 and C_0 terms. Typically, positive Faraday A_1 terms are the dominant spectral feature since the orbital angular momentum associated with the LUMO is usually higher than that associated with the HOMO.[29a] When the symmetry of the cyclic perimeter is modified, a lifting of the orbital degeneracy of the HOMOs or the LUMOs occurs and the A_1 terms of high symmetry complexes are replaced by coupled oppositely signed B_0 terms with the same basic ve/+ve or +ve/ve sign sequence.[29a] In reduced symmetry porphyrinoids, the Q band (DM$_L$ = 1) and B band (DM $_L$ = 9) transitions tend to have the strongest magnetic transition dipole moments and, therefore, are most extensively mixed by the applied field.[29a,30] Consequently, the alignment of the magnetic moment is determined by the relative energy separations of the frontier p-MOs derived from the HOMO and LUMO (DHOMO, DLUMO) of the parent hydrocarbon perimeter.[30b] In porphyrinoids with DHOMO E DLUMO, systems referred to as soft MCD chromophores by Michl,[29a] small structural changes can reverse the direction of the induced magnetic dipole excited states. When DHOMO 4 DLUMO, the orbital angular momentum associated with the excited electron predominates and there is a ve/+ve/ ve/+ve intensity pattern (manifest as a '' , +, , +'' ordering in signal signs for the Q and B bands) with an ascending energy for the Faraday B_0 terms associated with Platt's L(Q) and B bands.[29a,31] When DLUMO 4 DHOMO, the sign sequence for the Faraday B_0 terms in ascending energy becomes +ve/ve/+ve/ ve (i.e., an ordering of '' +, , +, '' in the signal signs for the Q and B bands).[29a,31b] As shown in Fig. 7, an ordering of ''+, , +, '' is seen in the MCD spectra of cis/trans-2 and 5 in accord with the calculated DHOMO o DLUMO. Likewise, the observed ordering of '' , +, , +'' in the MCD spectra of 3 and 4 is also consistent with the calculations, namely DHOMO 4 DLUMO. The fact that the sign sequences observed in the MCD spectra for the B_0 terms associated with the Q and B bands are broadly consistent with the trends that would be anticipated based on the MO energies predicted in the B3LYP geometry optimizations is taken as further validation of the theoretical descriptions used to define the electronic structures of cis/trans-2–5.

As may be inferred from Fig. 6 and in accord with Gouterman's four orbital model,[26] the regioisomeric effect on the electronic structures has its origins in the energy level splitting of the FMOs associated with each given pair of regioisomers. Within the series 1–5, the trans-isomers stabilize a_{1u} orbitals and destabilize a_{2u} orbitals to a greater extent than the cis-isomers. Therefore, the DHOMOs for the trans-isomer are generally larger

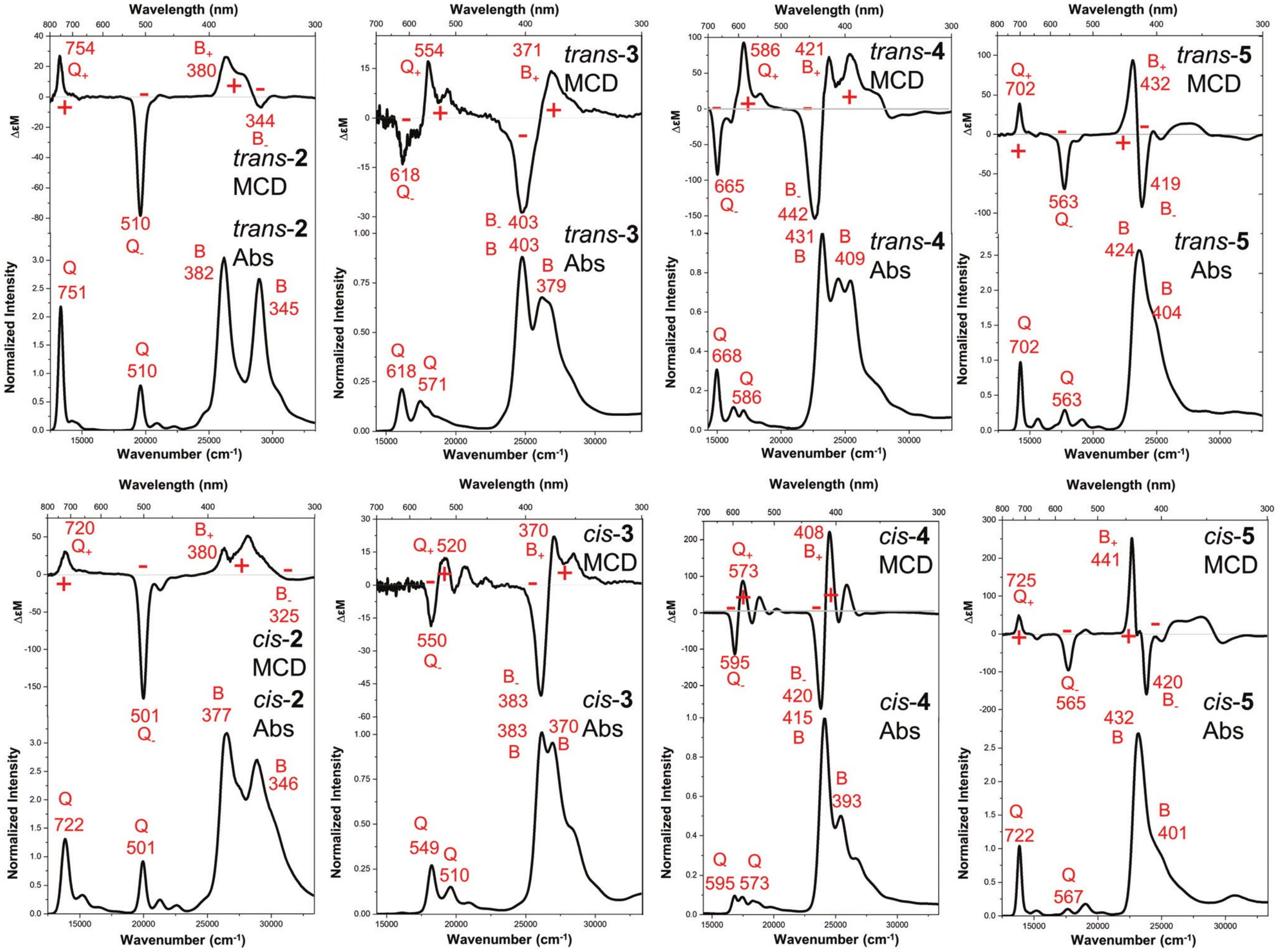


Fig. 7 MCD (top) and normalized electronic absorption (bottom) of cis/trans 2–5 in CH_2Cl_2 at room temperature.

than those for the corresponding cis-isomers. Similarly, the trans-isomers are characterized by LUMO energies that are relatively lowered more than the corresponding LUMO+1 orbitals. They thus have larger DLUMOs than their cis-counterparts (note, however, that the DLUMOs of cis/trans-5 are the same). On this basis, we conclude that the observed regioisomeric effects on the photophysical properties, including the DQ$_L$s, are dependent on the HL gaps but are essentially tied to the degeneracy and energy level splitting of the FMOs.

Conclusions

Reported here is a series of porphodilactones derivatives (cis/trans-2–5) that differ in terms of the extent and nature of the saturation associated with porphyrin periphery. Specifically, by means of b-diazalone reduction or 1,3-dipolar cycloaddition, a congruent set of relatively reduced regioisomers was obtained. The regioisomeric effect of substitution was readily apparent in terms of readily measured spectroscopic features. For instance, the DQ$_L$ values vs. were found to follow the trend cis/trans-1 (19 nm)[10a] E cis/trans-5 (22 nm) o 2 (28 nm) o 3 (71 nm) E 4 (73 nm) for DQ$_L$s. Importantly, the degree of modulation within this series was much larger than what might be interpolated from corresponding studies with chlorophyll derivatives. AICD plots at iso-surface values of 0.06 and the calculated NICS (1) values revealed a correlation between the specifics of the porphyrin periphery and the global aromaticity of the system in question. The chemical shift values of the inner N–H protons in the ^{1}H NMR spectrum also proved well correlated with the calculated NICS (1) values. Experimental (MCD and ^{1}H NMR spectra) and theoretic studies based on DFT calculation on the level of B3LYP/6-31+G(d) allowed the effect of saturation around the porphyrin periphery to be correlated to the degree of frontier molecular orbital (FMO) splitting.

On the basis of the observed effects and the strong interplay between structure and optical effects, we suggest that in porphyrinoids, a close relationship is expected to exist between the degree of b-pyrrolic saturation and aromaticity just as it can for meso-substitution.[32] The effect of b-pyrrolic saturation further depends on regioisomeric differences as illustrated by the present analysis of the photophysical properties of a set of reduced, aromatic porphyrinoids, namely cis/trans-1–5, as well as consideration of four previously reported isomeric systems introduced by Chang and Brückner.[7,10b] Specifically, an effect that is barely noticeable in the case of porphyrins, discernible but small in the case of chlorophylls and related systems, becomes exceptionally large as the degree of b-pyrrolic saturation (and hence global aromaticity) is further reduced (cf. Fig. 1). This unexpected finding sets the stage for the design of new porphyrinoid-based functional materials whose photophysical features are fine-tuned via subtle structural changes.

Conflicts of interest

No competing financial interests have been declared.

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