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### PAPER

# Complexes of aryl-substituted porphyrins and naphthalenediimide (NDI): investigations by synchrotron X-ray diffraction and NMR spectroscopy<sup>†</sup>

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New donor-acceptor hybrids of Zn(II)-metallated 5,15-diaryl porphyrins have been designed and synthesised via the porphyrin interactions with an electron acceptor molecule, di-n-hexyl N-substituted 1,2,4,8-naphthalenetetracarboxylic diimide (NDI). Binding interactions within these supramolecular complexes were investigated in the solid state by synchrotron X-ray diffraction and probed in solution by <sup>1</sup>H NMR spectroscopy. The systematic modulation of the porphyrin  $\pi$ -density was achieved, for the first time as multiple methoxy and fluorine groups were introduced as substituents to the 5,15-diaryls of the porphyrin. For these, the variation of the porphyrin–NDI binding strengths determined by <sup>1</sup>H NMR titrations was shown, using the Swain's type dual parameter approach, to be closely linked with the peripheral substitution pattern of the diaryl porphyrins validated by crystallography. The new 1:1 donor-acceptor complexes formed display characteristic features of the aromatic-stacked systems, i.e. the parallel arrangement and short interplanar separation between the substituted porphyrin and NDI. Synthetic modification of electron-density on the porphyrin surface by introducing substituents at peripheral sites of functionalised porphyrins represent a general solution towards electronically tunable aromatic surfaces: an understanding of their solution and solid state behaviour will significantly improve the rational design of new functional donor-acceptor supramolecular materials with potential applications ranging from new energy materials to dye-sensitised solar cells, photovoltaics and future drug delivery devices.

#### Introduction

Attractive interactions between aromatic molecules play significant roles in biological and molecular recognition<sup>1</sup> and in material science.<sup>2</sup> Recently, composites incorporating aromatic systems such as porphyrins and naphthalenediimides have become of importance due to their potential role in organic electronics, dye-sensitised solar cells and photovoltaic applications.<sup>3</sup> Naphthalenediimides and related materials are emerging as electron acceptors and electron-transporting materials that have been explored for applications as components for new materials with interesting optical properties in the solid state.<sup>4</sup> An understanding of their ability to form tunable donor–acceptor complexes with



**Scheme 1** Synthesis of 5,15-diaryl porphyrins. Reagents and conditions: (i)  $H_2$ , Pd/C, THF, 2%  $Et_3N$ , 2h, r.t.; (ii) TFA; (iii) MeOH, r.t.; (iv) DDQ; (v)  $Zn(OAc)_2$ , MeOH-CHCl<sub>3</sub>. ( $R_1$  = various substituents).

porphyrins should be of significant importance towards the rational design of the new generation of hybrid materials for optoelectronics.

The electronic nature and geometrical requirements for intermolecular interactions of simple aromatics can be rationalised by simple quadrupolar models,<sup>5-7</sup> but this is still a lively area of exploration.<sup>8</sup> Strong interactions are observed between porphyrin

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Fig. 1 (a) Schematic representations and substitution pattern of the 5,15-diaryl substituted porphyrins (1–16); (b) Structures of the *N*-disubstituted diimides (I–III) employed in the complexation studies. ( $^{P}$ Pr = *iso*-propyl).

planes due to their large and planar conjugated structure, giving rise to self aggregates in solution and offset packing arrangements in the solid state. Although the use of porphyrins to construct molecular tweezers for  $\pi$ -complexation of aromatic electron poor species has been demonstrated,9 the first solid state evidence for  $\pi$ -complexes of porphyrins with aromatic acceptors was only recently reported.<sup>10</sup> Earlier work has been concerned with the determination of solution structures of  $\pi$ -complexes, including those of several metallated porphyrins with aromatic substrates. Porphyrins have been under intense investigation because of their unique properties leading to catalytic roles in photochemical to organic transformations. It has been demonstrated that the variation of the electronic properties on the peripheral sites alters the properties of the macrocycles, but only a couple of reports on the factors affecting the strength of aromatic interactions have been published and only brief discussions on the factors affecting the strength of these interactions have been reported.<sup>11,12</sup> Importantly, only the electronic effects of peripheral substituents on the porphyrin metal centre have received attention thus far. The electronic effect of peripheral substituents on the porphyrin metal centre has received intensive attention: Walker and coworkers showed that the coordination of the metal centre by free-base porphyrins is sensitive to the substitution pattern at the periphery.13

Despite the fact that the peripheral substituents have been used to probe the properties of porphyrin macrocycles, the, electronic effects on the thermodynamic stabilities of the donor-acceptor complexes involving porphyrins have received only limited attention, and to the best of our knowledge only one such report was published to date.<sup>14</sup> Here we describe for the first time combined solution and solid state investigations of the effect of the systematic modulation of the  $\pi$ -density in a series of symmetrically substituted 5,15-diaryl porphyrins in their interactions with electron deficient molecules such as di-n-hexyl N-substituted 1,2,4,8-naphthalenetetracarboxylic diimide (NDI). Our work aims to validate a new, entirely accessible route towards tuning the  $\pi$ -surface of porphyrins and was undertaken to demonstrate that the electronic structures of the zinc porphyrin, and therefore the association properties in solution and in the solid state, can be tuned as required by applications with significance in biological, materials science and future photovoltaics. This could provide a general solution for constructing electronically controllable donor-acceptor hybrids, and aims to enhance our understanding of the attractive interactions between aromatic molecules.

An understanding of such effects is crucial in the quest for new energy-harvesting composites incorporating porphyrins and organic electronics and the rational design of new donor– acceptor synthetic precursors for energy materials. Substituent effects in other  $\pi$ -complexations, such as in recognition of 2,4,7-trinitrofluorenone within the tweezer-like cavity of two co-facially substituted acridine units, have been applied in the effective separation of nitro-substituted polycyclic aromatic compounds.<sup>15</sup> Establishing a reliable way to vary the  $\pi$ -electronic density of porphyrins can be beneficial to the rational design of porphyrin-based systems for separation of aromatic compounds *via* aromatic interactions such as selective extraction of higher fullerenes<sup>16</sup> and in the design and synthesis of new materials with optoelectronic properties for dye-sensitised solar cell applications.<sup>17</sup>

We now report the formation of new porphyrin–NDI composites in solution and their solid state structures. Explorations into the substituent effects of the 5,15-diaryl symmetrically substituted porphyrins on the strength of  $\pi$ -complexation with a dialkyl *N*substituted naphthalenediimide (NDI) are also discussed. Due to the highly conjugated nature of the porphyrin ring systems, the presence of electron-donating or withdrawing substituents on the peripheral *meso*-phenyls can affect the physical and chemical properties of the macrocycle, hence the strength of the interactions within the donor–acceptor complex in solution and the nature of the aromatic stacking within the resulting complex in the solid state. An understanding of these effects will significantly improve the rational design of new donor–acceptor hybrid materials.

#### **Results and discussions**

#### Experimental design and syntheses

To investigate the peripheral substituent effects on aromatic interactions between electron-rich porphyrins and electron-poor acceptors, di-N-substituted naphthalenediimide I and related electron deficient molecules II and III were selected and their complexations in CHCl<sub>3</sub> solutions with porphyrins 1–16 were examined (Fig. 1).

Free base, zinc- and nickel-metallated 5,15-diaryl symmetrically substituted porphyrins 1–16 were synthesised in high yield *via* modification of established procedures.<sup>18</sup> With the exception of 6,<sup>19</sup>  $7^{20}$  and  $16^{21}$  all porphyrin donors used are new and have been synthesised as described in Scheme 1. The optimum reaction time for the acid catalysed condensation between deprotected 5,5'-dibenzyl-3-3'-di-(*n*-hexyl)-4,4'-dimethyl-dipyrromethane and substituted benzaldehyde varied from 4 to 16 h depending on the reactivity of the individual aromatic aldehyde. The di-*n*-hexyl substituted NDII and related acceptor molecule II (di-2,6-<sup>i</sup>PrC<sub>6</sub>H<sub>3</sub> *N*-substituted NDI) and III (di-*n*-hexyl *N*-substituted pyromellitic diimide) were prepared following published procedures<sup>22</sup> or *via* adapted synthetic methods.

For 1-16, multiple substituents were introduced onto the peripheral aryl rings to alter the electronic properties of the porphyrin  $\pi$ density. An increasingly depleted electron density in the porphyrin  $\pi$ -system was gained by increasing the number of electronwithdrawing groups. The opposite electronic effect was achieved using electron-donating methoxy substituents. Methoxylated (1-4) and fluorinated (8-13) porphyrins bear various numbers of methoxy groups and fluorines respectively. Free-base porphyrin 6 and its zinc- and nickel-metallated analogues (5 and 7 respectively) possess no peripheral substitutions but phenyl rings at the meso positions. For porphyrins 14, 15 and 16 each of the peripheral sites are substituted with one 3-allyloxy or 4-nitro groups or two 3,5-di-*tert*-butyl groups respectively, but synthetic challenges did not allow any further functionalisation for tuning the electron density. For all porphyrins 1-16, four flexible hexyl side chains were incorporated into the  $\beta$ -pyrrolic positions of the porphyrin framework to enhance the solubility and minimise aggregation in common solvents.

Aromatic aldehydes bearing electron-donating methoxy groups required longer reaction times than their fluorinated analogues. The subsequent oxidation with DDQ followed by zinc insertion using  $Zn(OAc)_2$  in a  $CHCl_3$ -MeOH mixture yielded the corresponding zinc metallated porphyrin. Free-base porphyrin 6 was obtained in high yield by reacting the zinc counterpart 5 with dilute hydrochloric acid. Treatment of 6 with Ni(OAc)\_2 afforded the corresponding nickel-metallated porphyrin 7.

Full characterisation of the porphyrins and acceptor molecules was obtained by <sup>1</sup>H, <sup>13</sup>C NMR and UV-Vis spectroscopies, high resolution mass spectrometry (HRMS) or MALDI-TOF and elemental analysis. Additionally, characterisation of the fluorine-containing porphyrins **8–13** was obtained by <sup>19</sup>F NMR spectroscopy. In all cases, the symmetric structures gave rise to simple <sup>1</sup>H NMR spectra with a well resolved *meso* proton singlet resonance in the 10 ppm region of the spectrum. The position of this resonance allowed its use as a probe to monitor the titration experiment (*vide infra*) and as a diagnostic tool for the electron density in the porphyrin  $\pi$ -system.

Due to the structural similarities within each of the fluorineor methoxy-substituted series investigated, and within the experimental timescale of the <sup>1</sup>H NMR experiments, we propose that, all compounds are similarly solvated and that any changes in solvation upon complex formation are likely to be similar throughout the series. The electron-poor character of di-*n*-hexyl substituted NDI I should render it an effective acceptor, as demonstrated in earlier studies.<sup>23</sup> Its complementary geometrical dimensions with the substituted porphyrins under investigations were expected to provide suitable  $\pi$ -surfaces for aromatic interactions with the porphyrins.

#### Investigations in the solid state by X-ray diffraction

The molecular structures of six of the zinc porphyrins (**2**, **8**, **10**, **12**, **13** and **16**) were determined in the solid state by single-crystal X-ray diffraction after using high-intensity synchrotron radiation (ESI†). Typically, extremely small and weakly diffracting single crystals suitable for X-ray analysis were grown by slow diffusion of methanol into a chloroform or dichloromethane solution of porphyrins. The porphyrin frameworks in these compounds are all essentially flat, with slight deviations from the molecular plane through core atoms of the porphyrins in the range of up to 0.1 Å. The internal dimensions of the zinc metallated porphyrins fall within the normal ranges.<sup>24</sup> The substituted diaryl units lie close to perpendicular to the molecular plane as observed previously in the free-base 5,15-diaryl porphyrins.<sup>20</sup>

Four new donor-acceptor complexes (or co-crystallites) **A–D**, incorporating naphthalenediimide **I** and porphyrins **5**, **6**, **14** and **15** respectively, were isolated and characterised by X-ray diffraction. X-ray quality single crystals were grown by the slow diffusion of MeOH into a mixture of equimolar ratio of porphyrin and NDI in  $CH_2Cl_2$ . In each case the 1:1 porphyrin: acceptor molecule stacking was observed in the solid state with the NDI surface appears to stack over the porphyrin plane. The main feature in these co-crystallites is the offset arrangement of the components, which seems most prominent in the case of complex **A** (Fig. 2). The mean plane separation between the porphyrin and the diimide molecules is 3.23 Å, suggesting the aromatic stacking interactions between the molecules. The closest approach of a neighbouring atom in the NDI molecule to the zinc atom (*i.e.* the Zn(1)–N(5) distance) is 3.31 Å. The tilt between the planes of



Fig. 2 (a) The molecular structure of complex A. The asymmetric unit contains only half of the acceptor and the porphyrin molecules, the other half was generated by symmetry (NDI is symmetric with respect to an inversion centre); (b) Projection of NDI onto the zinc porphyrin 5 (hexyl chains of both components are not shown); (c) Packing arrangement along b axis (hexyl chains of both components are not shown). Hydrogen atoms and solvated molecules are omitted for clarity. (Key: grey, carbon; blue, nitrogen; purple, zinc; red, oxygen).

these two molecules (*i.e.* porphyrin **5** and acceptor molecule **I**) is 1.28°. The overall packing arrangement in complex A is shown in Fig. 2c. This structure showed no major distortions of the geometry of the individual molecular components indicating that this is a complex held together by weak noncovalent interactions. Internal dimensions of the porphyrin such as zinc-nitrogen bond lengths fall within expected ranges.<sup>24</sup> In the diimide molecules the mean deviation from the plane for all atoms is only 0.03 Å (excluding hexyl chains). However, the porphyrin plane appears to be slightly concave towards the NDI molecule. The metal centre Zn(1) is protruding away from the porphyrin core, being displaced from the porphyrin plane by 0.15 Å. As a consequence, the mean deviation of any of the core porphyrin atoms, excluding the aliphatic side groups, from the plane of this core is 0.11 Å. Outof-plane deformations of the phenyl rings are observed. The phenyl rings lie approximately perpendicular to the porphyrin plane and adopt a syn orientation, with relatively large displacements of 0.48 Å of the *ipso* carbons above the molecular plane. This deformation results in a substantial angle between the porphyrin plane and the para hydrogen.

The structure of complex **B** displays a strong resemblance to that of **A** (Fig. 3). These complexes are isostructural and crystallise in the same space group ( $P\overline{I}$ ). The structures have almost identical unit cells and they differ only in the presence/absence of zinc and the replacement of CHCl<sub>3</sub> by CH<sub>2</sub>Cl<sub>2</sub> as the solvate. The *n*-hexyl substituents in both cases are found to adopt an 'up–up' orientation on one side and a 'down–down' orientation on the opposite side. The complex formed between NDI with porphyrin **14** also showed the equimolar ratio of porphyrins and acceptor molecule. In contrast to co-crystallites **A** and **B**, where discrete pairs of porphyrin-acceptor units were observed, the solid



**Fig. 3** (a) The molecular structure of complex **B**; (b) Projection of NDI onto the free-base porphyrin **6** (hexyl chains of both components are not shown); (NDI is symmetric with respect to an inversion centre) (c) Packing arrangement along b axis (hexyl chains of both components are not shown). Hydrogen atoms and solvated molecules are omitted for clarity. (Key: grey, carbon; blue, nitrogen; red, oxygen).

state structure of co-crystallite C shows polymer-like columns containing alternating molecules of diimide and porphyrin stacked along the crystallographic *b* axis (Fig. 4). Within these stacks the porphyrin and acceptor molecular make close face-to-face contacts.



Fig. 4 (a) The molecular structure of complex C; (b) Projection of NDI onto the zinc porphyrin 14 (hexyl chains of both components are not shown); (Both components, porphyrin and NDI, are symmetric with respect to independent inversion centres) (c) Packing arrangement along b axis (hexyl chains of both components are not shown). Hydrogen atoms are omitted for clarity. (Key: grey, carbon; blue, nitrogen; purple, zinc; red, oxygen).

The mean plane separation between the porphyrin and the diimide molecules in co-crystallite C is 3.30 Å and the tilt between these planes is  $2.4^{\circ}$ . The position of the NDI molecule in C is laterally displaced away from the centre such that the closest contact between the metal centre labelled Zn(1) and the nearest atom in the adjacent diimide is 3.31 Å, to the carbonyl carbon C(38). Instead of the discrete pair of porphyrin-acceptor observed in A and B, and similar to the supramolecular structure of C, the solid state structure of **D** shows columns that contain alternating molecules of diimide and porphyrin that are stacked along the crystallographic b axis (Fig. 5). Within these stacks the porphyrin and acceptor molecules show close face-to-face contacts and the position of the diimide molecule is laterally displaced away from the porphyrin centre. The zinc porphyrin and NDI molecules are held apart by a Zn–O bond of 2.326(18) Å. As before, the structural parameters of individual molecules and the interplanar distances between the donor and acceptor component fall within the normal range and are very close to those found for the complex C.



**Fig. 5** (a) The molecular structure of complex **D**; (b) Projection of NDI onto the zinc porphyrin **15** (hexyl chains of both components are not shown); Connectivity and structure have been established: full details are in the CIF.<sup>†</sup> (c) Packing arrangement along *a* axis (hexyl chains of both components are not shown). Hydrogen atoms are omitted for clarity. (Key: grey, carbon; blue, nitrogen; purple, zinc; red, oxygen).

Interestingly, for all complexes A–D, a "staircase-like" arrangement of the hexyl groups present either side of the porphyrin molecules was 'followed' by the hexyl groups in the diimide. This may allow a more efficient packing in solid state. Additional Van der Waals interactions between the chains may help stabilise these structures. The formation of porphyrin–NDI complexes was therefore established *via* X-ray structure determinations. The structures show characteristic features of the  $\pi$ – $\pi$  stacked systems, such as the parallel arrangement of the acceptor and the short interplanar spacing between the two components. The porphyrin– acceptor contacts seen in these complexes are comparable to previously reported cases where 7,7',8,8'-tetracyanoquinodimethane (TCNQ) molecules interact with metallated octaethylporphyrins (OEP).<sup>10</sup> For example, in TCNQ–Cu<sup>II</sup>(OEP), the interplanar spacing between the components is 3.19 Å while in TCNQ– $Zn^{II}(OEP)$  it is 3.16 Å.

#### Solution studies by <sup>1</sup>H NMR spectroscopy

Aromatic interactions between porphyrins and acceptor molecules I-III were probed in solution by <sup>1</sup>H NMR titrations in CDCl<sub>3</sub> at 298 K. <sup>1</sup>H NMR dilution studies tested the aggregation behaviour of the porphyrins alone: dilution curves from 15 to 1 mM were constructed for the two most highly substituted porphyrins, 1 and 13, which showed the greatest differences between these structures (ESI<sup>†</sup>). Throughout the series, dilution experiments showed only very small variations of meso shifts (<0.01 ppm), suggesting that the level of aggregation of porphyrins is rather low in this concentration range. Under the dilute experimental conditions used we approximate that the degree of aggregation for all porphyrins 1-16 would be similar. We expect that the absolute magnitude of the binding strengths might be affected by approximately the same amount but this factor is not large enough to alter the overall outcomes and trends resulting from these binding studies. A dilute concentration of porphyrin (5 mM) proved to be optimum for <sup>1</sup>H NMR studies on the entire series, and this was used throughout to minimise the extent of porphyrin aggregation during the experiment.

For the titration experiment, aliquots of the acceptor in chloroform were sequentially added to the chloroform solution of the substituted porphyrins. The addition of the acceptor molecule I caused increasing upfield shifts to the *meso* resonance of the zinc porphyrins. All other porphyrin resonances remained essentially unaffected by the complexation process. Chemical exchange of the aromatic substrate between the complexed and un-complexed form is rapid on the chemical shift timescale and only the exchange-averaged observed shift was observed.

For metalloporphyrins studied, the chemical shift of the meso protons at each acceptor concentration composed a data point and a data set of 20 points was collected from each titration study (Fig. 6). The data sets were analysed by EQNMR<sup>25</sup> and the fitting to a 1:1 binding isotherm afforded values of association constant  $K_{meso}$  using initial meso chemical shifts ( $\delta_0$ ) and the limiting complexation-induced *meso* shifts of the porphyrins ( $\delta_{\text{complex}}$ ). Evidence for the formation of 1:1 adducts in solution comes from Job plot analysis. A typical plot between porphyrin 1 and NDI molecule (acceptor I) is shown in Fig. 7. The plot of the mole fraction ( $\chi$ ) multiplied by the complexation-induced shift of the *meso* proton ( $\Delta\delta$ ) *versus* the mole fraction  $\chi$  shows a maximum at  $\chi = 0.5$ . The use of EQNMR gave a good fit for the 1:1 donor-acceptor stoichiometry. Porphyrin and dihexyl substituted naphthalenediimide I are therefore in equilibrium with the 1:1 donor-acceptor complex (eqn (1)), with the association constant  $K_{meso}$  (eqn (2)).

Porphyrin + NDI 
$$\rightleftharpoons$$
 Complex (1)

$$K_{meso} = \frac{[\text{Complex}]}{[\text{Porphyrin}][\text{NDI}]}$$
(2)

The association constants of Zn(II) porphyrins with NDI (I) are given in Table 1. A typical plot of complexation-induced chemical shift of *meso* protons of porphyrin 1 *versus* the addition



Fig. 6 The complexation of a 5,15-diaryl substituted porphyrin (R = H, F and OMe groups) and a dihexyl substituted NDI. Protons coloured in pink indicate the <sup>1</sup>H NMR probe used to follow the complex formation in solution.



Fig. 7 Typical plot (Job) of mole fraction ( $\chi$ ) against mole fraction multiplied by complexation-induced shift of the *meso* proton ( $\chi \times \Delta \delta$ ) of the complexation of porphyrin 1 and acceptor molecule I. Similar plots were obtained for all zinc porphyrins studied here.

of acceptor I is given in the ESI.<sup>†</sup> The complexation-induced shift  $(\Delta \delta)$  for porphyrins 1–5 and 8–13 is in the range 0.30 to 0.43 ppm indicating essentially identical geometries for the resulting donor-acceptor complexes. These similarities are maintained in the solid state for complexes A–C as confirmed by X-ray diffraction.

The binding strengths between acceptor I and Zn(II)-porphyrins 5, 14–16 were first examined. The association constant between I and the dinitro-substituted porphyrin 15 ( $K_{meso} = 47 \pm 1.4 \text{ M}^{-1}$ ) appears to be smaller than that between I and "unsubstituted" porphyrin 5 ( $K_{meso} = 58 \pm 1.1 \text{ M}^{-1}$  respectively), but those between I and allyloxy- and tert-butyl substituted porphyrins 14 and 16 ( $K_{meso} = 67 \pm 1.3$  and 70  $\pm 4.9$  M<sup>-1</sup> respectively) were found to be somewhat larger. This prompted an investigation of the substituent effects operating on the binding strength due to differences in electronic demands of the substituents at peripheral aryl sites. The association constants listed in Table 1 appear to be strongly dependent on the electron withdrawing or releasing characteristics of the peripheral substituents: porphyrins with donating groups show enhanced binding, whereas those bearing electronegative fluorines display reduced affinities. Since the systematic modulation of electron density by altering the

**Table 1** Association constants ( $K_{mew}$ , inclusive of standard deviation errors from the data fitting calculated by EQNMR), *meso* chemical shifts ( $\delta_0$ ) and maximum limiting complexation-induced <sup>1</sup>H NMR shifts of the *meso* protons ( $\Delta \delta = \delta_0 - \delta_{complex}$ ) for the complexation reactions between zinc porphyrins and the acceptor molecule I (5 mM, CDCl<sub>3</sub>, 298 K, 500 MHz)

Porphyrin	$K_{meso}$ (M <sup>-1</sup> )	$\delta_{\scriptscriptstyle 0}({ m ppm})$	$\Delta\delta$ (ppm)	Number/type of non- hydrogen substituents
1	$110 \pm 4.2$	10.256	0.351	6/OMe
2	$79 \pm 1.7$	10.236	0.346	4/OMe
3	$67 \pm 1.2$	10.218	0.352	2/OMe
4	$61 \pm 1.6$	10.176	0.350	2/OMe
5	$58 \pm 1.1$	10.187	0.340	0
8	$54 \pm 1.0$	10.172	0.318	2/F
9	$42 \pm 1.3$	10.176	0.320	2/F
10	$24 \pm 1.0$	10.151	0.302	4/F
11	$13 \pm 1.9$	10.128	0.324	6/F
12	$19 \pm 0.5$	10.263	0.427	8/F
13	$18 \pm 0.3$	10.268	0.412	10/F
14	$67 \pm 1.3$	10.194	0.312	$2/OCH_2CH=CH_2$
15	$47 \pm 1.4$	10.215	0.355	$2/NO_2$
16	$70\pm4.9$	10.200	0.285	4/C(CH <sub>3</sub> ) <sub>3</sub>

number of nitro, allyloxy and tert-butyl substituents could not be achieved synthetically thus far, only the binding strengths within the methoxylated (1-4) and fluorinated (8-13) porphyrin series with the acceptor I were analysed further. The chemical shifts of meso protons of the 5,15-diaryl substituted porphyrins appear to correlate with the extent of substitution with fluorines and methoxy groups. The substitution-free porphyrin 5 may be considered as a "reference" in the peripheral substitution study as it binds stronger to I than the fluorinated porphyrins but weaker than the methoxylated porphyrins. As evident from Table 1, the meso <sup>1</sup>H NMR chemical shifts showed a general upfield shift with increasing number of electron-donating groups (except for the case of 4) while the opposite trend is observed with increasing number of fluorines (except 12 and 13). The observed variations of the meso chemical shifts seem to point towards the long distance and systematic influences through substitutions on the meso aryl rings. Overall, a noticeably weaker binding of NDI with the fluorinated porphyrins (8-13) was observed compared with the methoxy-substituted ones (1-4). It appears that electronic effects of both substituents operate generally in a cumulative manner, with some exceptions (vide infra). The binding strength increases slightly with increasing number of methoxy groups. The opposite trend with a general decrease in association constant was observed upon progressive incorporation of fluorine. The cumulative argument may apply to account for the gradual decrease in affinity, from substitution-free porphyrin 5 to *bis*-(3,4,5-trifluorophenyl) substituted porphyrin 11 ( $K_{meso}$  =  $13 \pm 1.9 \text{ M}^{-1}$ ). Incorporation of further fluorine substituents showed insignificant effect on the binding strength. However, the possibility that the fluorine ortho-substituted porphyrins 12 and 13 can exhibit an electron donating character in these systems cannot be ignored. Such an unusual property has been previously observed and proposed to be arising from the overlap between the electron clouds of the fluorines and the  $\pi$  system of the porphyrin.13i

The use of Hammett type linear free energy analysis treatment was initially attempted to account for the trend of the binding strengths observed in the complexation studies for all systems in the selected set, with the exception of porphyrins 12 and 13, since Hammett constant for *ortho* fluorine was unavailable. The fact that a trend line could not be deduced from the Hammett plot suggested that this model is not suitable for analysing the peripheral substituent effects on the binding strengths for these donor–acceptor complexes (ESI†). This may be due to the fact that substituents are not directly attached to the porphyrin core, but placed at the aryl rings where the electronic 'information' can only be transmitted indirectly through the *meso*-aryl bonds.

The dual parameter approach developed by Swain,<sup>26</sup> which analyses the resonance and inductive contributions separately, was applied to the data to probe whether this approximation constitutes a more suitable model for the interpretation of the binding results. Here, the sigma ( $\sigma$ ) values for the substituents used in the Hammett approach may be separated into two components,  $\sigma_1$  (inductive) and  $\sigma_R$  (resonance), as given by eqn (3) (also see Table S3, ESI†). To take into account the possible positional dependence of the resonance contribution, two parameters sigma *meta*-( $\sigma_m$ ) and sigma-*para* ( $\sigma_p$ ) are introduced. For a given porphyrin donor *j*, the overall electronic contribution from the peripheral substituents depends also on the total number of *meta* substituents ( $N_{jm}$ ) and *para* substituents ( $N_{jp}$ ). The Swain eqn (4) was derived as described in the ESI,

$$\sigma = a\sigma_{\rm I} + b\sigma_{\rm R} \tag{3}$$

1.0

).5

1.5

$$\log \frac{K_j}{K_H} = \rho \Big[ N_{jm} (\sigma_{\rm I} + \beta_m \sigma_{\rm R}) + N_{jp} (\sigma_{\rm I} + \beta_p \sigma_{\rm R}) \Big]$$
(4)

and used in the fitting of the experimental data (see Table S4, ESI and Fig. 8). The values for sigma-I ( $\sigma_1$ ) and sigma-R ( $\sigma_R$ ) of fluorine and methoxy groups have been reported.<sup>27</sup> The Zn(II) porphyrins considered for the fitting of Swain eqn (4) are listed in Table S4 (ESI†) together with the relevant parameters used. From the data, it is noted the resonance contribution to the substituent parameter sigma-*meta* ( $\sigma_m$ ) is 0.65, while the inductive contribution is 1 by definition (*i.e.*  $\sigma_m = \sigma_1 + 0.65\sigma_R$ ). The same applies to the sigma-*para* ( $\sigma_p$ ) (*i.e.*  $\sigma_p = \sigma_1 + 0.73\sigma_R$ ). With the beta values in hand, the overall substituent parameter, *i.e.* the sum over all the electronic contributions for all the substituents in the *meso* phenyl rings can be computed (Fig. 8) (the actual plot). The linear

0.4

0.2

0

-0.2

-0.4

-0.6

 $\log(K_j/K_H)$ 

00

-0.5

Njm (or + 0.65or) + Njp (or + 0.73or)

-1.0



fit gives  $\rho$  the value of  $-0.43 \pm 0.04$  with a correlation factor ( $R^2$ ) of 0.94. The different sigma-R values for meta and para substituents may reflect possible differences in efficiency for the resonance effect to be transmitted to the porphyrin core. These values are only apparently different, because the error associated with beta-para  $(\beta_n)$  renders this value very close to that of beta-meta  $(\beta_m)$ , *i.e.* 0.65  $\pm 0.04$  versus  $0.73 \pm 0.11$ . It appears that the substituents introduced into the peripheral phenyls exert their influence somewhat more effectively through the inductive than the resonance route. The resonance communication between the porphyrin core and the periphery may be hindered by the perpendicular geometry of the aryl rings. The correlation obtained in the fitting process seems close to linear both for the methoxylated (1-4) and fluorinated series (8-11), and therefore consistent with a simple electrostatic explanation: the stacking interactions seem to reflect the electrostatic potential on the surface of the porphyrins and are sensitive to the nature and peripheral substitution patterns.

Metallation effects on solution binding constants remain unpredictable within the experimental error. For example, the binding strength of the free-base and substitution-free porphyrin 6 to I (e.g.  $K_{meso} = 55 \pm 1.5 \text{ M}^{-1}$ ) is very close to that of its zincmetallated analogue 5 ( $K_{meso} = 58 \pm 1.1 \text{ M}^{-1}$ ). Here, comparable binding strengths found for porphyrins 5 and 6 may be due to the structurally similar, flat, frameworks yielding isostructural complexes A and B, as confirmed by X-ray diffraction (Fig. 2 and 3). Steric effects appear to play a role in the binding interactions. The crystal structure of 7 shows a non-planar ruffled conformation of the nickel porphyrin (ESI<sup>†</sup>),<sup>20</sup> in strong contrast to the largely undistorted flat porphyrin surface observed in the structure of its zinc counterpart 5 (Fig. 2) or free base analogue 6 (Fig. 3). In solution, only a very small induced chemical shift difference ( $\Delta\delta$ ) was detected by <sup>1</sup>H NMR spectroscopy at the complexation between acceptor I and substitution-free nickel porphyrin 7, suggesting that the binding interactions within this donor-acceptor system are negligible (ESI<sup>†</sup>). The electronic contributions by Zn(II) and Ni(II) to the  $\pi$ -electron clouds are not fully understood but their structural effects on the porphyrin framework are evident from the X-ray structure determination. Such differences could explain the ineffective overlapping of the  $\pi$ -systems in the intermolecular binding process for the Ni(II) porphyrins.

The binding experiment between porphyrin **5** and the peripherally crowded *bis-N-(2',6'-di-iso-*propylphenyl)naphthalenediimide **II** showed no complexation induced shifts by <sup>1</sup>H NMR. In fact, the perpendicular orientation adopted by the 2,6-di-*iso-*propylphenyl groups in the crystal structure (*i.e.* giving an average distance between the plane of the aromatic core and the further methyl hydrogens of *ca.* 4.10 Å yields a sterically isolated NDI acceptor unit (ESI, Fig. S8<sup>†</sup>). This strengthens the argument that the donor–acceptor interactions are mediated by steric factors. A similar geometrical arrangement for a substituted aryl groups was proposed to originate from the unfavourable clashes between the sterically demanding isopropyl groups and the carbonyl groups.<sup>28</sup>

The binding of the *bis*-(3,4,5-trimethoxyphenyl) substituted porphyrin 1 to di-*n*-hexyl *N*-substituted pyromellitic diimide III  $(K_{meso} = 10 \pm 0.7 \text{ M}^{-1})$  was found to be significantly weaker than that of NDI I  $(K_{meso} = 110 \pm 4.2 \text{ M}^{-1})$ . On the other hand, the binding strength between the *bis*-(2,3,4,5,6- pentafluorophenyl)

substituted porphyrin 13 and the acceptor III and  $(K_{meso} = 9 \pm$ 0.8 M<sup>-1</sup>) is comparable to that of NDI I ( $K_{meso} = 18 \pm 0.3 \text{ M}^{-1}$ ). It was expected that the more effective electron-accepting nature of III with respect to I would result in a stronger binding to the porphyrin donors.<sup>29</sup> The binding strengths of 1 and 13 with pyromellitic diimide III showed negligible differences. This is in sharp contrast to that observed with naphthalenediimide (NDI) I  $(\approx 100 \text{ M}^{-1})$  and suggests that acceptor molecule III is less sensitive to the electronic changes of the porphyrin core than acceptor I.<sup>‡</sup> Such a decrease in the binding strength can be attributed to the smaller size of the pyromellitic diimide acceptor III.<sup>30</sup> Thus, an acceptor molecule bearing a large and unshielded surface area such as I constitutes the ideal design for sensing the variations of  $\pi$ -density in Zn(II) metallated porphyrins and for probing the effect of the substituent on the strength of donor-acceptor interactions in solution.

#### Conclusions

Systematic modulation of the  $\pi$ -density of the aromatic surface of 5,15-diaryl substituted Zn(II) porphyrins was achieved by variation of the number of substituents at peripheral positions. Up to six substituents (i.e. F or OMe groups) were introduced gradually at the periphery of the porphyrin. Comparison of the binding strength in solutions of porphyrin donors with dihexyl substituted naphthalenediimide allowed the investigation of substituent effect on electronic properties of the porphyrins. The binding in solutions led to 1:1 donor-acceptor complexes and their structures were confirmed by X-ray diffraction studies. In solution, the binding strengths of NDI are primarily governed by the intrinsic electronic properties of the peripheral substituent and the total number of substituents present in a given porphyrin, although steric factors seem to influence the binding strengths too. Incorporation of increasing numbers of electron-donating groups produces more electron-rich aromatic surfaces, as indicated by the progressively enhanced binding affinities, while the opposite cumulative electronic effect is observed with the electron-withdrawing fluorine atoms. An almost linear correlation is obtained for the binding strength and the peripheral substitution pattern in the Swain's type dual parameter model: this suggests an overestimation of the resonance contribution in the Hammett constants in this alternative approach. This might indicate that the presence of a largely undistorted zinc porphyrin core is crucial for measurable interactions in solutions to be achieved. Synthetic modification of electron-density on the porphyrin surface by introducing substituents at peripheral sites of large, flat and sterically unhindered aromatics may represent a general solution towards electronically tuneable aromatic surfaces. Such an approach may be extended to other related planar systems, for example, expanded porphyrins with larger aromatic surfaces<sup>31</sup> and lead to the rational design of new supramolecular hybrids, with applications ranging from new energy materials for dye-sensitised solar cells and photovoltaic applications to future sensors and drug delivery devices.

Air sensitive reactions were performed using standard vacuum line and Schlenk techniques and were carried out under an inert environment (argon or nitrogen). All solvents were distilled prior to use and obtained from solvent stills (Et<sub>3</sub>N ex. CaH<sub>2</sub>, THF ex. Na). 3-Allyloxybenzaldehyde,<sup>32</sup> 5,5'-dibenzyl-3-3'-di-(*n*-hexyl)-4,4'-dimethyldipyrromethane,<sup>18</sup> 5,15-bis(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-tetramethylzincporphyrin 16,<sup>21</sup> N, N'-di-*n*-hexylnaphthalene-1,4,5,8-tetracarboxylic diimide<sup>22</sup> I and N, N'-di-*n*-hexylpyromellitic diimide<sup>22</sup> III were prepared according to the published procedures. All other chemicals were purchased from Aldrich, Avocado or Strem in reagent grade quality or better and used without further purification. Screw-cap NMR tubes with disposable non-absorbing septa for NMR titrations were purchased from Fluorochem. Micro-volume gastight syringes for fluid measurements were obtained from Hamilton.

All <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR measurements were carried out in chloroform-d at room temperature (298 K) and recorded on a Brucker DPX-400 or DRX-500 instrument at 400.13 and 500.20 MHz respectively. Chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) and are expressed relative to TMS (<sup>1</sup>H, <sup>13</sup>C). The downfield direction is taken as positive. Fluorine chemical shifts were referenced to an external CFCl<sub>3</sub> reference. High Resolution Mass Spectra (HRMS) were performed on ABI/Sciex Q-Star pulsar. The spectra were run in positive ion and the parts per million (ppm) values were worked out using the analyst software. HRMS MALDI-TOF analyses were carried out at the EPSRC Mass Spectrometry service at Swansea. UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array spectrometer using a 10 mm path quartz cell versus a pure-solvent reference. Elemental analyses were performed in the University of Cambridge, UK. Column chromatography was performed on Merck 60 silica gel (230-400 mesh).

### General procedure for co-crystallisations between porphyrins and naphthalenediimides

Equimolar ratio of porphyrin 5 (2.10 mg, 2.00 mmol) and di*n*-hexyl substituted naphthalenediimide I (0.90 mg, 2.00 mmol) was mixed and dissolved in a minimum amount of  $CH_2Cl_2$ . Slow diffusion of MeOH into the solution mixture afforded extremely small, but well-formed crystals of complex **A**. The other porphyrin–NDI complexes, **B** (between 6 and I), **C** (between 14 and I) and **D** (between 15 and I) were prepared by a similar co-crystallisation procedure from their respective components mixed in equimolar ratio in CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

#### <sup>1</sup>H NMR dilution experiments

A concentrated porphyrin solution (1 and 13) of known concentration (2 ml, 30 mM) was prepared in CDCl<sub>3</sub>. Aliquots of this solution were sequentially added to 0.5 mL of CDCl<sub>3</sub> in an NMR tube and the <sup>1</sup>H spectra were recorded at 500 MHz, 298 K. A total of 9 data points were obtained for each dilution experiment.

<sup>&</sup>lt;sup>‡</sup> When 1,3,5-trifluorobenzene was used as the acceptor molecule, no detectable changes in the *meso* chemical shift were observed with either porphyrins **1** and **13**. Binding studies with di-*n*-hexyl *N*-substituted perylene diimide and cyano-containing aromatics (*e.g.* 1,3,5-tricyanobenzene and TCNQ) were hampered by their limited solubility in chlorinated solvents.

#### <sup>1</sup>H NMR titrations and curve fitting procedure

All binding studies were performed using solutions derived from crystalline materials. Any solvated methanol present in the materials was removed under reduced pressure prior to use in order to eliminate a possible MeOH-Zinc(II) coordination. Titrations to estimate the strengths of binding interactions in solution were performed maintaining constant porphyrin concentrations (similar to the method described in Reference 2f): each titration was carried out using 5 mM solutions of the porphyrin 'host' (1 mL) in CDCl<sub>3</sub>. To this porphyrin 'host' solution, aliquots of the 'guest' solution (containing a mixture of the 'guest' acceptor, 200 mM and the porphyrin 'host', 5 mM) in CDCl<sub>3</sub> were added directly into the NMR tube. The sample was then shaken well and the <sup>1</sup>H NMR spectrum was recorded immediately (500 MHz, 298 K). Aliquots were added in a 2.5 µL interval (i.e. 0.1 eq.) until reaching the 1:1 ratio. Further additions were made at a 25 µL interval and therefore a total of 20 data points for each titration were obtained. The association constant for each titration was evaluated based on the observed change in chemical shift of the meso protons, except free-base porphyrin 7 where variation of the NH protons was also used. Shifts from corresponding peaks were measured and fitted using a 1:1 binding model. Titration experiments were carried out at least 2 times and the errors have been estimated by the fitting programme as standard deviations from the mean. Titration data were converted to association constants by using EQNMR.<sup>25</sup> The fitting of eqn (4) was performed using the software MicroMath<sup>®</sup> Scientist<sup>®</sup> for Windows<sup>™</sup>, Version 2.01 (MicroMath, Inc.) implementing a least squares algorithm.

#### General procedure for porphyrin synthesis<sup>18</sup>

Palladium on carbon (10%, typically 0.1 g for every 1 g of dipyrromethane used) was added to a solution of 5,5'-dibenzyl-3,3'-di(n-hexyl)-4,4'-dimethyldipyrromethane (2.00 g, 3.27 mmol) (1 eq.) in THF (100 mL, containing 1% Et<sub>3</sub>N), the resulting black suspension was placed under hydrogen for 2 h. The catalyst was filtered off through a plug of Celite and the filtrate concentrated to give an off-white solid which was dried under vacuum. To this cold degassed trifluoroacetic acid (20 mL) was added by cannula under argon at 0 °C. After 1 h a degassed methanolic solution of substituted aromatic aldehyde was cannulated into the mixture at -25 °C. The reaction was allowed to warm up with stirring over a period of time depending on the reactivity of individual the aldehyde, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.89 g, 3.93 mmol) was then added and stirring continued overnight. Et<sub>3</sub>N (40 mL) was added and the solvent removed by evaporation. The crude free-base porphyrin product was redissolved in  $CH_2Cl_2$  (300 mL) and washed with  $H_2O$  (4 × 400 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Excess of  $Zn(OAc)_2 \cdot 2H_2O$  (*ca.* 5 eq.) was added to a stirred solution of the appropriate free-base porphyrin (1 eq.) in CHCl<sub>3</sub>-MeOH solution (10% MeOH) and the mixture was refluxed for 20 min. The solution was washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and passed through a plug of silica gel. The solvent was removed under reduced pressure. The desired product was typically purified by column chromatography over silica gel (as described in the ESI<sup>†</sup>). Recrystallisation using a combination of solvents (as described in the ESI) in a layered fashion yielded the desired materials of high purity and with moderate yields.

#### X-ray diffraction experiment

Crystallographic data of extremely small crystals of co-crystallites were collected using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer. The structures were solved by direct methods using the program SIR92.<sup>33</sup> The refinement and graphical calculations were performed using the CRYSTALS<sup>34</sup> program suite. Crystallographic and refinement data of porphyrins **2**, **8**, **10**, **12**, **13** and **16**, as well as the diimide **III** are given in the ESI.<sup>†</sup>

**Crystal data A.**  $C_{147}H_{184}N_{10}O_4Zn_2Cl_2$ , M = 2356.72, Z = 1, triclinic space group  $P\bar{1}$ , a = 13.629(2) Å, b = 16.504(3) Å, c = 16.554(3) Å,  $\alpha = 112.529(2)^\circ$ ,  $\beta = 96.328(2)^\circ$ ,  $\gamma = 104.184(2)^\circ$ , V = 3246.8(10) Å<sup>3</sup>, T = 120(2) K,  $\mu = 0.468$  mm<sup>-1</sup>. Of 24 110 reflections measured, 11 363 were independent ( $R_{int} = 0.033$ ). Final R = 0.0615 (6579 reflections with  $I > 3\sigma(I)$ ) and wR = 0.0621.

**Crystal data B.**  $C_{147}H_{187}N_{10}O_4Cl_3$ , M = 2264.42, Z = 1, triclinic space group  $P\bar{1}$ , a = 13.465(2) Å, b = 16.552(3) Å, c = 16.697(3) Å,  $\alpha = 112.645(2)^\circ$ ,  $\beta = 95.228(2)^\circ$ ,  $\gamma = 103.286(2)^\circ$ , V = 3275.0(10) Å<sup>3</sup>, T = 120(2) K,  $\mu = 0.127$  mm<sup>-1</sup>. Of 24 342 reflections measured, 11 417 were independent ( $R_{int} = 0.028$ ). Final R = 0.1088 (5490 reflections with  $I > 3\sigma(I)$ ) and wR = 0.1160.

**Crystal data C.**  $C_{92}H_{114}N_6O_6Zn$ , M = 1465.28, Z = 1, triclinic space group  $P\bar{1}$ , a = 9.207(1) Å, b = 12.543(1) Å, c = 17.287(1) Å,  $\alpha = 88.83(2)^\circ$ ,  $\beta = 86.38(3)^\circ$ ,  $\gamma = 87.52(3)^\circ$ , V = 1990.2(3) Å<sup>3</sup>, T = 150(2) K,  $\mu = 0.367$  mm<sup>-1</sup>. Of 11 416 reflections measured, 4720 were independent ( $R_{int} = 0.07$ ). Final R = 0.0348 (3440 reflections with  $I > 3\sigma(I)$ ) and wR = 0.0396.

**Crystal data D.**  $C_{87}H_{106}Cl_2N_8O_9Zn$ , M = 1544.73, Z = 2, monoclinic space group P21, a = 15.952(6) Å, b = 9.578(4) Å, c = 27.437(10) Å,  $\beta = 93.065(6)^\circ$ , V = 4186(3) Å<sup>3</sup>, T = 150(2)K,  $\mu = 0.352$  mm<sup>-1</sup>. Of 13 163 reflections measured, 4843 were independent ( $R_{int} = 0.044$ ). Final R = 0.1264 (3771 reflections with  $I > 3\sigma(I)$ ) and wR = 0.1390.

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