Synthesis and near-infrared luminescence of a deuterated conjugated porphyrin dimer for probing the mechanism of non-radiative deactivation

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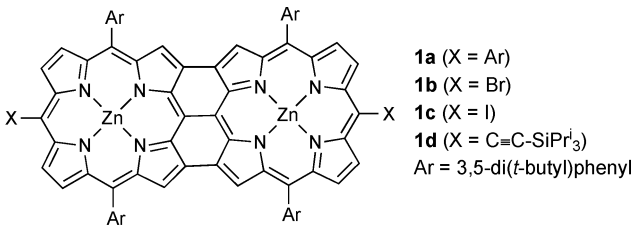
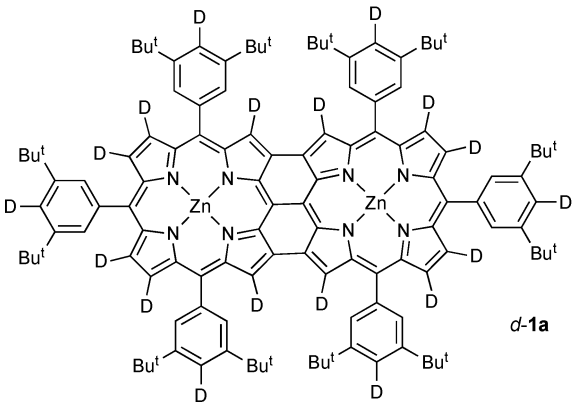
β,meso,β-Fused porphyrin oligomers have many attractive photophysical features such as strong absorption in the near-IR at wavelengths greater than 1000 nm, and high two-photon cross sections. However their ultrafast S_1–S_0 deactivation ($k_d > 10^{11}$ s^{-1}) limits potential applications. We have synthesised a deuterated fused porphyrin dimer to test whether deuteration influences the rate of non-radiative deactivation. An efficient synthetic strategy was developed, starting with deuteration of dipyrromethane. Deuteration of the zinc porphyrin dimer does not affect its fluorescence quantum yield in CD_2Cl_2 ($\Phi_{fD}/\Phi_{fH} = 1.00 \pm 0.05$). This implies that the ultrafast non-radiative deactivation is not simply a consequence of the small S_1–S_0 energy gap. Comparison with other conjugated porphyrin oligomers confirms that the deactivation rate in the edge-fused oligomers is faster than would be expected from the energy gap law. This result indicates that it should be possible to create near-IR dyes with similar S_1–S_0 energy gaps to the *β,meso,β*-fused porphyrin oligomers but with slower rates of S_1–S_0 decay.

Introduction

The synthesis of *β,meso,β*-fused porphyrin dimers, such as **1a**, and longer tape-like oligomers of this type, pioneered by Osuka and coworkers,[1–5] is probably the most revolutionary development in the field of porphyrin chemistry during the last 10 years. The strong porphyrin–porphyrin π-conjugation in these oligomers shifts their absorption far into the infrared and results in strong two-photon absorption.[6] For example dimer **1a** exhibits an absorption maximum at 1068 nm (in $CHCl_3$)[1,2] and a two-photon cross-section of 14000 GM at 800 nm (in toluene);[6] longer oligomers take this absorption to even longer wavelengths. The rate of S_1–S_0 deactivation (k_d) is amazingly fast in these molecules, occurring in 4.5 ps in dimer **1a** (from transient absorption measurements).[7–11] Thus neither fluorescence nor S_1–T_1 intersystem crossing compete with deactivation to the ground state, and fluorescence quantum yields are very low ($\Phi_f < 10^{-3}$).[9] Accordingly, the overall rate of S_1 deactivation is dominated by the S_1–S_0 internal conversion process ($k_d \approx k_{nr} \approx k_{ic}$, where k_{nr} and k_{ic} denote the rates of non-radiative and internal conversion processes, respectively).





The usefulness of these chromophores is limited by the negligible fluorescence quantum yield and triplet formation,[9] precluding applications in near-infrared light emitting diodes (NIR LEDs) and fluorescence imaging or in reverse-saturable absorption (RSA).[12] The short S_1 lifetimes also preclude all applications involving photochemistry, such as photoinduced energy- and electron-transfer, photoinitiated polymerisation (*e.g.* for microfabrication)[13] or photochromism (*e.g.* for optical data storage). We have shown that the attachment of heavy atoms to the periphery of the π-system accelerates intersystem crossing in

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1b and **1c**, bringing the triplet yield up to $\Phi_T = 0.2$ in **1c** and leading to substantial RSA in the spectral region 800–1000 nm ($\sigma_{ex}/\sigma_{gr} = 8.2$ at 870 nm).[14] This work led to some promising NIR RSA materials, but there is still a strong motivation for learning to curtail the ultrafast deactivation of the lowest electronic singlet excited state (S_1) in these systems.

The ultrafast S_1–S_0 decay in chromophores such as **1a–d** has generally been attributed[7–10] to the energy gap law.[15,16] In other words, it is assumed that in such rigid molecular systems the S_1 and S_0 states have very similar geometries so that their potential energy surfaces do not intersect (Fig. 1a) and that the overall deactivation rate (corresponding to k_{ic}, see above) is determined by the Frank–Condon factor, f_v, which in turn is determined by the S_1–S_0 energy gap, ΔE, according to eqn (1) and (2):

$$k_{ic} = f_0 f_v \quad (1)$$

$$f_v = e^{-\alpha \Delta E} \quad (2)$$

where f_0 is the maximum possible decay rate ($f_0 \approx 10^{13}$ s^{-1} in most chromophores with C–H bonds) and α is a constant of proportionality. High frequency C–H stretch vibrations ($\nu \approx 3000$ cm^{-1}) make a dominant contribution to the Frank–Condon factor, f_0, so replacing C–H for C–D bonds ($\nu \approx 2200$ cm^{-1}) generally reduces the rate of non-radiative deactivation.[15–18] We decided to test this idea by synthesising a deuterated dimer *d*-**1a** and comparing its fluorescence quantum yield with that of **1a**. We intended only to deuterate the β-positions of **1a**, because these protons are closest to the π-system, but during the synthesis deuteration also occurred on the aryl substituents, mainly *para* to the porphyrin.

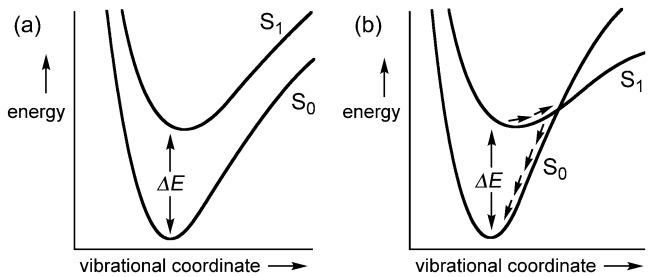
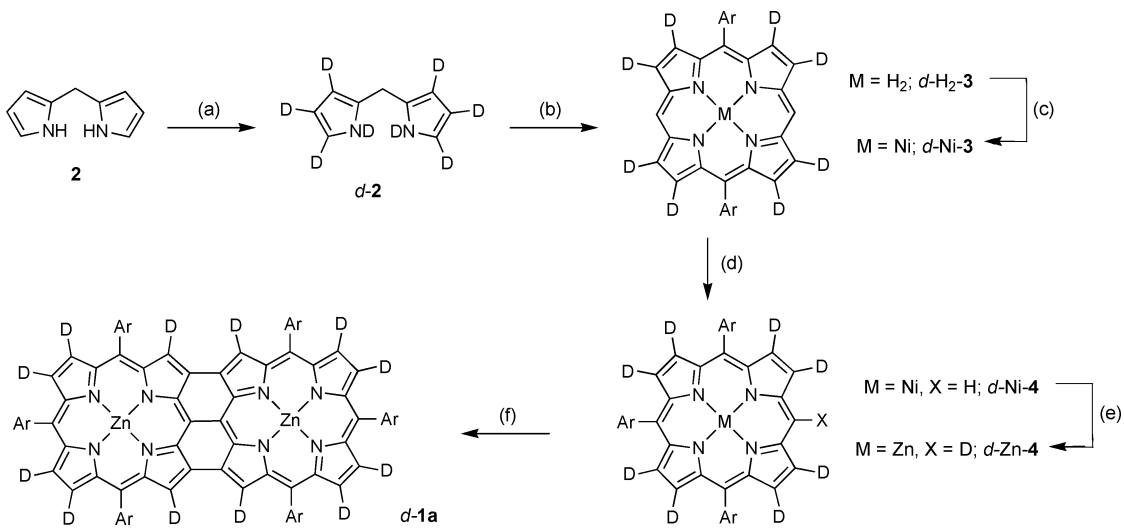


Fig. 1 Internal conversion (a) between matching adiabatic surfaces and (b) between intersecting surfaces.

We found that deuteration has no effect on the fluorescence quantum yield, even in a deuterated solvent (CD_2Cl_2). This implies that the ultrafast internal conversion in **1a** is not simply a consequence of the energy gap law, but reflects the presence of a readily accessible intersection of the S_1 and S_0 surfaces (Fig. 1b). In the course of this work we have developed new chemistry for the synthesis of deuterated porphyrins, and to the best of our knowledge this is the first time that a deuterated porphyrin dimer has been synthesised.

Results and discussion

The deuterated fused dimer *d*-**1a** was synthesised as summarised in Scheme 1. There have been several reports of the synthesis of deuterated porphyrin derivatives,[19–25] but no general methods have been developed for the direct perdeuteration of porphyrins. On the other hand, pyrrole is readily deuterated under acidic conditions.[26,27] We decided to explore whether similar deuteration conditions could be applied to dipyrromethane **2**. This might appear to be a risky strategy, because dipyrromethane **2** readily undergoes decomposition and oligomerisation in acid, but we discovered that deuteration could be accomplished using a two-phase system, by stirring **2** with trifluoroacetic acid-*d* in a mixture of deuterium oxide and dichloromethane. These reaction conditions result in no detectable decomposition or oligomerisation, *d*-**2** was isolated in 73% yield and ^{1}H NMR analysis shows that the pyrrolic positions are deuterated to a level of >97%. No deuteration occurs at the central CH_2. Condensation of *d*-**2** with 3,5-di-*tert*-butylbenzaldehyde in the presence of trifluoroacetic acid-*d* gave porphyrin *d*-H_2-**3**. Deuterium enrichment of *d*-H_2-**3** was slightly reduced to 91% on the pyrrolic positions, while enrichment to a



Scheme 1 Preparation of deuterated dimer *d*-**1a**. Ar = 3,5-di-*tert*-butylphenyl. (a) *d*-TFA, D_2O, CH_2Cl_2, 73%; (b) i. 3,5-di-*tert*-butylbenzaldehyde, TFA, CH_2Cl_2, ii. DDQ, 27%; (c) $Ni(OAc)_2$, DMF, reflux, 94%; (d) i. 3,5-di-*tert*-butylphenyllithium, THF, 0 °C to rt, ii. D_2O, iii. DDQ, 65%; (e) i. D_2SO_4, CH_2Cl_2, ii. $Zn(OAc)_2 \cdot 2H_2O$, MeOH, CH_2Cl_2, 77%; (f) $Sc(OTf)_3$, DDQ, PhMe, 32%.

degree of 33% was observed for the *meso*-hydrogens, suggesting scrambling of the hydrogens between these positions under the condensation conditions. Some overall reduction in the level of deuteration may have resulted from protic impurities in the dichloromethane reaction solvent, but the level of deuteration of the pyrrolic positions was sufficient for our purposes.

Metallation of *d*-H_2-**3** with nickel(II) acetate yielded the nickel(II) porphyrin *d*-Ni-**3**. Treatment of *d*-Ni-**3** with an excess of 3,5-di-*tert*-butylphenyllithium, using Senge's method,[28] followed by deuterium oxide work-up and oxidation gave nickel triarylporphyrin *d*-Ni-**4**. It is possible to perform the Senge arylation on the free base porphyrin *d*-H_2-**3** instead of *d*-Ni-**3**, but in our hands arylation of the nickel complex was more reproducible. Demetallation was accomplished with sulfuric acid-d_2 and, without isolation of the free-base porphyrin, metallation to the zinc complex was achieved by neutralisation and stirring with zinc(II) acetate. Analysis of the zinc porphyrin *d*-Zn-**4** by ^{1}H NMR indicated that further deuteration had occurred during treatment of *d*-Ni-**4** with D_2SO_4. The unsubstituted porphyrinic *meso*-position was 96% deuterated, and deuteration was also evident on the 3,5-di-*tert*-butylphenyl substituents (Fig. 2). The deuteration of the aryl groups is highest *para* to the porphyrin ring and occurs without any loss or migration of the *tert*-butyl groups. Sulfuric acid-d_2 mediated deuterium exchange has been reported for aryl-substituents on porphyrins.[25] Oxidative dimerisation of *d*-Zn-**4** was performed under the conditions described by Osuka,[5] and after recrystallisation, dimer *d*-**1a** was isolated in 32% yield. The un-deuterated dimer **1a**, previously reported by Osuka,[2,5] was also prepared. The ^{1}H NMR spectra of dimers **1a** and *d*-**1a**, compared in Fig. 3, allow the level of deuteration in dimer *d*-**1a** to be quantified (Fig. 2). The β-pyrrolic positions on dimer *d*-**1a** were approximately 91% deuterium-enriched and the phenyl substituents were also partially deuterated. The level of deuteration for dimer *d*-**1**, as deduced from NMR analysis, is consistent with analysis of the isotopic cluster for the molecular ion in the MALDI-TOF mass spectrum, shown in Fig 4.

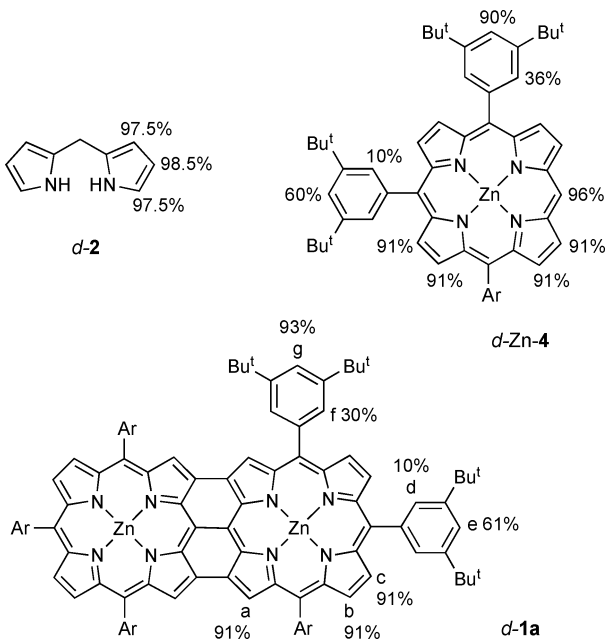


Fig. 2 Structures of *d*-**2**, *d*-Zn-**4** and *d*-**1a** showing the levels of deuteration at selected positions, as determined by comparison of the ^{1}H NMR spectra with those of the un-deuterated analogues.

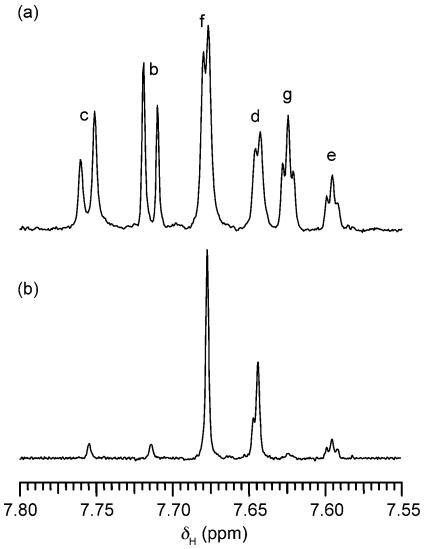


Fig. 3 ^{1}H NMR spectra for (a) dimer **1a** and (b) dimer *d*-**1a** (500 MHz in $CDCl_3$ containing a trace of d_5-pyridine). Assignment is included for the spectrum of **1a** (see Fig 2).

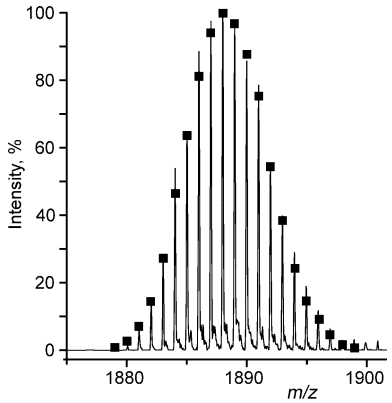


Fig. 4 MADLI-TOF mass spectrum for deuterated dimer *d*-**1a**. The simulated spectrum is represented by the black squares, and was calculated allowing for deuteration of 93% at the β-pyrrole positions and 33% at the aryl substituents.

The absorption spectra for dimers **1a** and *d*-**1a** (Fig. 5) are completely superimposable, showing that, as expected, the electronic structure of the dimer is not affected by deuteration. The room temperature fluorescence spectra of dimers **1a** and *d*-**1a**, with excitation at 440 nm, are also shown in Fig. 5. These spectra were recorded in deuterated solvent (CD_2Cl_2) so as to exclude any effects due to solvent C–H vibrations. The emission spectra were recorded for isoabsorbing solutions of the dimers and are not normalised, so they directly show that deuteration has no effect on the fluorescence quantum yield: $\Phi_{fD}/\Phi_{fH} = 1.00 \pm 0.05$.

If the ultrafast S_1 decay in this system were simply a consequence of the energy gap law [eqn (2)] then one would expect the Frank–Condon factor to be dominated by C–H vibrations.[15–17] Thus it seems likely that the ultrafast internal conversion in **1a** results from the availability of a specific deactivation pathway, such as

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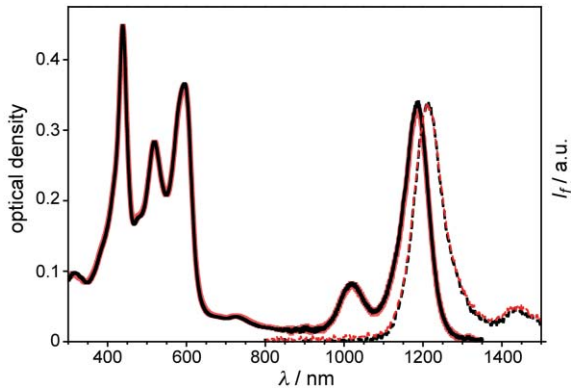

Fig. 5 UV-visible-nearIR absorption (solid lines) and luminescence spectra (dashed lines, isoabsorbing solutions, $\lambda_{ex} = 440$ nm) for **1a** (red) and *d*-**1a** (black) in CD_2Cl_2 at 298 K. The lowest energy absorption and highest energy emission peaks occur at 1185 nm and 1210 nm respectively.

an accessible intersection of the S_1 and S_0 surfaces, *via* a reaction coordinate involving the lower energy vibration of the C–C and C–N double bonds within the molecular framework (Fig. 1b).

Our conclusion that S_1 deactivation in **1a** is faster than can be accounted for by the energy gap law is supported by comparison with other related NIR chromophores. For example Therien and coworkers[29] have reported an alkyne-linked conjugated porphyrin pentamer exhibiting S_1–S_0 emission at 883 nm ($\Delta E = 135$ kJ mol^{-1}) with a fluorescence quantum yield of $\Phi_f = 0.14$ and a natural radiative lifetime of $\tau_0 = 3.56$ ns, so an upper limit to the rate of non-radiative deactivation in this chromophore (assuming $k_{isc} = 0$) is $k_{nr} = (1/\Phi_f - 1)/\tau_0 = 1.7 \times 10^9$ s^{-1}. According to eqn (2), with $f_0 = 10^{13}$ s^{-1}, this implies that $\alpha = 0.064$ kJ^{-1} mol. Dimer **1a** exhibits S_1–S_0 emission at 1100 nm ($\Delta E = 109$ kJ mol^{-1}) so the energy gap law predicts that it should have a non-radiative rate constant $k_{nr} \approx k_{ic} = 9.3 \times 10^9$ s^{-1}, which is about 20 times less than the experimental value of $k_{nr} \approx 2.2 \times 10^{11}$ s^{-1} (calculated from the singlet lifetime of 4.5 ps with $k_r \ll k_{nr}$ and thus negligible).

While dimers **1a–d** exhibit exceptionally short S_1 lifetimes, their T_1 lifetimes seem to be fairly normal. Although the T_1–S_0 energy gaps must be very small (less than the S_1–S_0 gaps) this does not result in exceptionally rapid T_1–S_0 intersystem crossing. Previously we reported that **1b** and **1c** have triplet lifetimes of 280 ns and 52 ns respectively (in oxygen-free benzene containing 1% pyridine).[14] The very low triplet yields of **1a** and **1d** make it difficult to measure their triplet lifetimes, but in the case of **1d** we were able to measure a triplet lifetime of 177 ± 25 μs (in O_2-free benzene with 1% pyridine). We also measured the triplet lifetime of **1d** by generating the triplet by energy transfer from the triplet state of tetraphenylporphyrin, giving a lifetime of 6.8 μs for the T_1 state of **1d** (in aerated dichloromethane with 1% pyridine). The heavy atoms reduce the triplet lifetime in **1b** and **1c**, and the triplet lifetime of **1d** is sensitive to the presence of oxygen, as expected, but in general the T_1 lifetime of these systems are normal, despite the small T_1–S_0 gap, providing another indication that the ultrafast S_1–S_0 decay is not simply a result of the small S_1–S_0 energy gap.

Conclusions

We have prepared a deuterated fused porphyrin dimer *d*-**1a** *via* deuteration of the dipyrromethane **2**. Its fluorescence quantum yield is completely unaffected by the deuteration ($\Phi_{fD}/\Phi_{fH} = 1.00 \pm 0.05$), demonstrating that C–H vibrations do not contribute to radiationless deactivation (*i.e.* internal conversion). This result suggests that a specific deactivation pathway is active *via* an accessible intersection of the S_1 and S_0 surfaces. The initial motivation for this study was to synthesise a fused porphyrin dimer with retarded internal conversion, and consequently improved triplet yield, for RSA applications.[12] Although we have not achieved this objective, our results indicate that it should be possible to create near-IR dyes with similar S_1–S_0 energy gaps to the *β*,*meso*,*β*-fused porphyrin oligomers but with slower rates of S_1–S_0 internal conversion, for instance by making an even more rigid molecular framework.

Experimental

NMR spectra were recorded on Bruker DPX250 or DPX400 instruments or AV500 with cryprobe. MALDI-TOF mass spectra were acquired by the EPSRC Mass Spectrometry Service, Swansea, UK from a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) matrix. Vis-NIR absorption spectra were recorded on a Perkin-Elmer Lambda 20 or Lambda 9 spectrometer. NIR fluorescence spectra of dimers **1** and *d*-**1** were recorded on an Edinburgh FLS920 spectrometer equipped with a Hamamatsu R5509-72 supercooled PMT (193 K) described earlier.[30] Bis(1*H*-pyrrol-2-yl)methane **2** and 3,5-di-*tert*-butylbromobenzene were prepared by literature methods.[31,32]

Preparation of *d*-2

Nitrogen was bubbled through a mixture of bis(1*H*-pyrrol-2-yl)methane **2** (2.00 g, 13.7 mmol), deuterium oxide (20 mL) and dichloromethane (200 mL). Trifluoroacetic acid-*d* (200 μl) was added and the mixture stirred vigorously at room temperature for 18 h. Anhydrous sodium carbonate was added to neutralise the aqueous layer and the organic layer was separated, dried over anhydrous magnesium sulfate and evaporated. This entire process was repeated twice, and the resultant product purified by bulb-to-bulb distillation under vacuum to give *d*-**2** as a white solid. Yield (1.54 g, 73%), mp 72–73 °C (lit.[31] 75 °C for **2**) ^{1}H NMR (200 MHz, $CDCl_3$; Me_4Si): δ_H, ppm 3.97 (2 H, s, CH_2), 6.04 (2 H, s, 97.5% ^{2}H), 6.12 (2 H, s, 98.5% ^{2}H), 6.62 (2 H, s, 97.5% ^{2}H), 7.64 (2 H, s, 97.5% ^{2}H). ^{2}H NMR (38.4 MHz, $CHCl_3$; Me_4Si) 6.14 (2 ^{2}H, s), 6.26 (2 ^{2}H, s), 6.68 (2 ^{2}H, s), 6.67 (2 ^{2}H, s, N-^{2}H). ^{13}C NMR (62.9 MHz, $CDCl_3$; Me_4Si) 26.1, 106.1 (t), 107.7 (t), 116.8 (t), 128.7. MS (FI$^+$): *m*/*z* 154.1341 (calcd. for $[C_9H_2D_8N_2]^+$ 154.1346).

Preparation of *d*-H_2-3

Nitrogen gas was bubbled through a solution of *d*-**2** (1.25 g, 8.11 mmol) and 3,5-di-*tert*-butylbenzaldehyde (1.80 g, 8.11 mmol) in dichloromethane (1600 mL). Trifluoroacetic acid-*d* (0.19 mL, 2.4 mmol) was added and the solution stirred at room temperature for 3 h. DDQ (2.36 g, 10.4 mmol) was added and the mixture stirred for 10 min before being neutralised by the addition of sodium bicarbonate (3 g). The mixture was filtered through a plug of silica, eluting with dichloromethane, the solvent removed and the residue recrystallised from dichloromethane by layered addition of methanol to give *d*-H_2-**3** as purple needles. Yield 770 mg (27%), ^{1}H NMR (500 MHz, $CDCl_3$; Me_4Si): −2.95 (2 H, s, N-H), 1.64

(36 H, s, *t*-butyl), 7.91 (2 H, t, phenyl 4-H), 8.22 (4 H, d, phenyl 2,6-H), 9.20 (4 H, s, pyrrole-H, 91% ^{2}H), 9.45 (4 H, s, pyrrole-H, 91% ^{2}H), 10.36 (2 H, s, *meso*-H, 33% ^{2}H). MS (MALDI-TOF$^+$): *m/z* 694.4 (calcd. for $[C_{48}H_{46}D_8N_4]^+$ 694.5).

Preparation of *d*-Ni-3

A suspension of *d*-H_2-**3** (650 mg, 0.935 mol), nickel(II) acetate (2.33 g, 9.35 mmol) and *N*,*N*-dimethylformamide (60 mL) was heated to reflux for 2 h. The solvent was removed under vacuum and the residue passed through a plug of silica eluting with dichloromethane. Recrystallisation from dichloromethane by layered addition of methanol give *d*-Ni-**3** as burgundy needles. Yield 660 mg (94%), ^{1}H NMR (400 MHz, $CDCl_3$; Me_4Si): 1.55 (36 H, s, *t*-butyl), 7.82 (2 H, t, phenyl 4-H), 7.98 (4 H, d, phenyl 2,6-H), 9.07 (4 H, s, pyrrole-H, 91% ^{2}H), 9.23 (4 H, s, pyrrole-H, 91% ^{2}H), 9.93 (2 H, s, *meso*-H, 33% ^{2}H). MS (ESI$^+$): *m/z* 751.4 (calcd. for $[C_{48}H_{44}D_8NiN_4 + H]^+$ 751.4).

Preparation of *d*-Ni-4

A solution of 1-bromo-3,5-di-*tert*-butylbenzene (1.18 g, 4.39 mmol) in THF (15 mL) was cooled to −78 °C and *n*-butyllithium (1.6 M in hexanes, 2.50 mL, 4.0 mmol) was added. The solution was stirred at −78° for 1 h, then transferred *via* syringe into a solution of *d*-Ni-**3** (300 mg, 0.399 mmol) in THF (15 mL) at 0 °C and the solution allowed to warm to room temperature with stirring for 1 h, to give a green solution. A mixture of D_2O and THF (1 mL : 4 mL) was added and the mixture poured into a rapidly stirred solution of DDQ (362 mg, 1.60 mmol) in dichloromethane (200 mL). The mixture was filtered through a plug of silica, eluting with dichloromethane. The solvent was removed and the residue purified by column chromatography over silica, using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 20) as eluent. Recrystallisation from dichloromethane by layered addition of methanol gave *d*-Ni-**4** as purple needles. Yield 242 mg (65%), ^{1}H NMR (400 MHz, $CDCl_3$; Me_4Si): 1.49 (18 H, s, *t*-butyl), 1.51 (36 H, s, *t*-butyl), 7.73 (1 H, t, phenyl 4-H), 7.76 (2 H, t, phenyl 4-H), 7.90 (2 H, d, phenyl 2,6-H), 7.93 (4 H, d, phenyl 2,6-H), 8.86 (2 H, s, pyrrole-H, 91% ^{2}H), 8.87 (2 H, s, pyrrole-H, 91% ^{2}H), 8.96 (2 H, s, pyrrole-H, 91% ^{2}H), 9.15 (2 H, s, pyrrole-H, 90% ^{2}H), 9.85 (2 H, s, *meso*-H, 42% ^{2}H). MS (ESI$^+$): *m/z* 938.6 (calcd. for $[C_{62}H_{64}D_8N_4Ni]^+$ 938.6).

Preparation of *d*-Zn-4

Sulfuric acid-d_2 (0.5 mL) was added to a solution of *d*-Ni-**4** (200 mg, 0.213 mmol) in dichloromethane (25 mL) and the mixture stirred at room temperature for 5 min to give a green solution. The solution was washed with water (25 mL) and aqueous sodium hydroxide (2 M, 25 mL). A solution of zinc acetate dihydrate (195 mg, 1.06 mmol) in methanol (2 mL) was added and the mixture heated to reflux for 5 min, then filtered through a short plug of silica, eluting with dichloromethane. Recrystallisation form dichloromethane by layered addition of methanol gave *d*-Zn-**4** as purple needles. Yield 156 mg (77%), ^{1}H NMR (400 MHz, $CDCl_3$; Me_4Si): 1.52 (18 H, s, *t*-butyl), 1.56 (36 H, s, *t*-butyl), 7.77 (1 H, t, phenyl 4-H, 60% ^{2}H), 7.79 (2 H, t, phenyl 4-H, 90% ^{2}H), 8.07 (2 H, d, phenyl 2,6-H, 10% ^{2}H), 8.10 (4 H, d, phenyl 2,6-H, 36% ^{2}H), 8.96 (2 H, s, pyrrole-H, 91% ^{2}H), 8.98 (2 H, s, pyrrole-H, 91% ^{2}H), 9.07 (2 H, s, pyrrole-H, 91% ^{2}H), 9.33 (2 H, s, pyrrole-H, 91% ^{2}H), 10.13 (2 H, s, *meso*-H, 96% ^{2}H). MS (ESI$^+$): *m/z* 949.6 (calcd. for $[C_{62}H_{59}D_{13}N_4Zn]^+$ 949.6).

Preparation of dimer *d*-1a

A mixture of *d*-Zn-**4** (50 mg, 53 μmol), scandium(III) triflate (130 mg, 264 mmol), DDQ (60.0 mg, 264 mmol) and toluene (50 mL) was stirred at 50 °C for 1 h. The colour darkened to dark purple. Once cool, the solution was washed with water (50 mL) and the organic layer separated and filtered through a plug of silica, eluting with dichloromethane–pyridine (1 : 0 to 100 : 1) and the solvent removed. The residue was purified by column chromatography over silica, eluting with light-petroleum (bp 40–60)–ethyl acetate–pyridine (10 : 1 : 1). Recrystallisation from a toluene–ethanol mixture gave dimer *d*-**1a** as a black solid. Yield 16 mg (32%) ^{1}H NMR (500 MHz, $CDCl_3$; Me_4Si): 1.42 (36 H, s, *t*-butyl), 1.46 (72 H, s, *t*-butyl), 7.36 (4 H, s, pyrrole-H, 91% ^{2}H), 7.60 (2 H, t, phenyl 4-H, 61% ^{2}H), 7.63 (4 H, t, phenyl 4-H, 93% ^{2}H), 7.64 (4 H, s, phenyl 2,6-H, 10% ^{2}H), 7.68 (8 H, s, phenyl 2,6-H, 30% ^{2}H), 7.71 (4 H, s, pyrrole-H, 91% ^{2}H), 7.76 (4 H, s, pyrrole-H, 91% ^{2}H). MS (MALDI-TOF$^+$): *m/z* 1888.2 (calcd. for $[C_{124}H_{121}D_{17}N_8Zn_2]^+$ 1888.1).

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