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Synthesis of nitroxide-functionalized phthalocyanines

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Abstract—A nitroxide-functionalized phthalonitrile and a diimino-isoindoline were prepared via Pd(0)-catalyzed cyanation from the corresponding dibromide and subsequent addition of ammonia, without interference from the radical moieties. The structures of these radicals were confirmed by single-crystal X-ray structure determinations. Metal-templated macrocyclization of these species under standard Linstead conditions or in 2-(dimethylamino)ethanol at reflux gave the corresponding metallated and free-base phthalocyanines, which were characterized using UV–vis, FTIR and EPR spectroscopy as well as mass spectrometry.

1. Introduction

Over the past 25 years there have been a number of reports describing the synthesis and characterization of porphyrinic macrocycles containing nitroxide free-radical moieties. The majority of these accounts concerned porphyrins substituted at either the β-pyrrole or *meso*-position with flexible tether-linked nitroxide groups and focussed on the spin–spin interactions between the nitroxide and metals coordinated within the macrocycle core.[1–9] The results of this early work permitted the calculation of metal–nitroxide distances in spin-labelled macrocyclic systems using Electron Paramagnetic Resonance (EPR) spectroscopy.[10] Further studies concerning porphyrinic macrocycles coordinated to, or covalently linked to nitroxide entities have addressed the characterization of the excited multiplet states of these species[11,12] and the quenching of the macrocycle triplet state by the nitroxide moiety.[13,14] More recently, Kobayashi and co-workers have utilized transient absorption and time-resolved EPR spectroscopy to thoroughly analyze the excited multiplet states of porphyrins[15,16] and phthalocyanines[11,17,18] with axially coordinated, or covalently linked, nitroxide ligands and proposed the use of nitroxide substituents for the control of singlet oxygen yields[19] and magnetic properties.[20] Herein, we describe the synthesis, electronic absorption and preliminary EPR investigations of phthalocyanines featuring three or four nitroxide rings, fused directly to the macrocycle core. Rather than being attached by flexible tethers, the nitroxide groups are forced to adopt a fixed geometry with respect to the π-system of the macrocycle.

2. Results and discussion

2.1. Synthesis and characterization of nitrile and diimino-isoindoline nitroxides

The synthesis of the target nitroxide phthalocyanines first required the preparation of the dinitrile **3** and diimino-isoindoline **4** precursors. Rosemund–von Braun reaction of dibromo-nitroxide **1**[21–23] (30 mM in DMF) with copper(I) cyanide gave dinitrile **3** in 29% yield. Additionally, small amounts of the mono-nitrile **2** were also isolated. Alternatively, reaction of dibromide **1** with zinc cyanide in the presence of $Pd(PPh_3)_4$ in *N*,*N*-dimethylformamide (DMF) at 85 °C[24] gave dinitrile **3** in superior yield (95%) (Scheme 1). There is precedent for palladium(0) catalyzed coupling of nitroxide-containing substrates with no apparent interference from the radical moiety.[25,26] To facilitate the macrocyclization reactions, dinitrile **3** was quantitatively converted to the more reactive diimino-isoindoline **4** by treatment with methanolic ammonia catalyzed by sodium methoxide. The solid state structures of nitroxides **2** and **3** were confirmed

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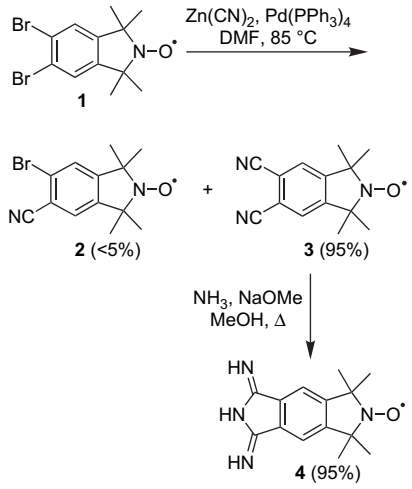
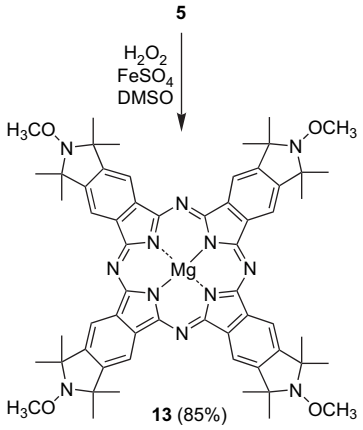
using single-crystal X-ray structure determinations (see Supplementary data).[27]



Scheme 1. Synthesis of phthalocyanine precursors **3** and **4**.

2.2. Synthesis and characterization of phthalocyanine nitroxides

Linstead macrocyclization of dinitrile **3** using magnesium butoxide in *n*-butanol at reflux[28] gave two turquoise macrocyclic products, which were readily isolated by chromatography (Scheme 2). Characterization of these compounds was non-trivial, primarily due to the paramagnetic nature of the nitroxide moiety. The ^{1}H NMR spectra of the products exhibited the paramagnetic broadening that is typical of isoindoline nitroxides, with only a single broad methyl signal evident. Mass spectrometry of nitroxides is also complicated by the radical moiety, often resulting in very poor sensitivity due to the propensity of the nitroxide group to undergo redox chemistry with both the matrix and solvent when ionized.[29] Here, positive ion FAB mass spectrometry of the products was inconclusive, exhibiting poor signal to noise, with no high-mass species apparent. In positive ion ESI mode however, it was possible to obtain high resolution mass spectra, which enabled identification of the less polar product (40%) as the magnesium phthalocyanine **5**. This compound was converted by reaction with methyl radicals, generated from a Fenton system in DMSO, into the phthalocyanine **13** (85%), further confirming the structure of the precursor nitroxide **5** (Scheme 3). In contrast to nitroxide phthalocyanine **5**, phthalocyanine **13** was found to strongly fluoresce (red) under long-wavelength UV irradiation. Intramolecular quenching of the first excited singlet state of the phthalocyanine core by the nitroxide moieties in **5** suppressed fluorescence, while in the methyl-adduct **13**, this did not occur and the macrocycle was free to fluoresce (Fig. 1).



Scheme 3. Conversion of nitroxide **5** into phthalocyanine **13**.

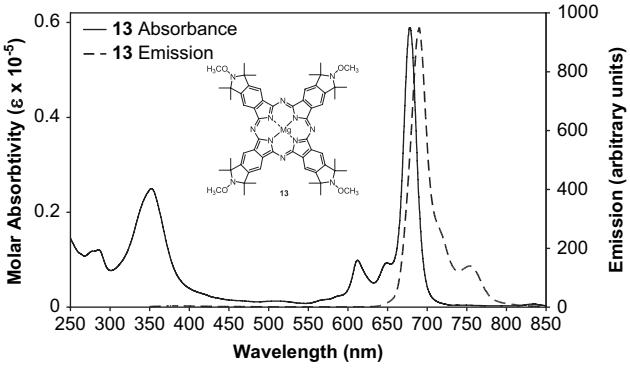
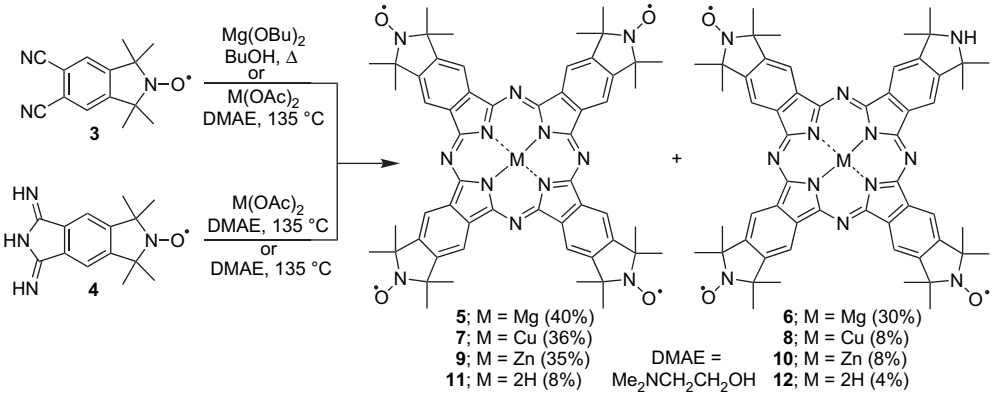


Figure 1. UV–vis absorbance and emission spectra of phthalocyanine **13** in CH_2Cl_2 (λ_{ex}=343 nm).



Scheme 2. Synthesis of phthalocyanines **5**–**12**.

The more polar turquoise solid isolated (30%) from the Linstead macrocyclization was identified as the 3:1 nitroxide-amine phthalocyanine **6**, primarily on the basis of the high resolution ESI MS data. As the secondary amine analogue of **3** was absent from the starting material used in these reactions, the formation of this compound must represent the in situ reduction of a nitroxide moiety in either dinitrile **3**, phthalocyanine **5** or one of the relevant intermediates. This is an unusual process, not normally observed in the chemistry of isoindoline nitroxides. Single electron reduction of nitroxides can be facile and generates hydroxylamine species, but the formation of a secondary amine usually requires more rigorous conditions, such as palladium-catalyzed hydrogenation at elevated pressures. When the Linstead macrocyclization was repeated using diimino-isoindoline **4**, phthalocyanine **5** was obtained as the only major macrocyclic product (10%).

Additionally, we investigated macrocyclization reactions of diimino-isoindoline **4** using copper(II) and zinc(II) acetates in 2-(dimethylamino)ethanol (DMAE) at 135 °C, which gave the corresponding phthalocyanine metal complexes **7** and **9** (~35%). Macrocyclization of diimino-isoindoline **4** in the same solvent alone gave the free-base phthalocyanine **11**, although in modest yield (8%) due to the lack of a metal template. In each case, a minor turquoise dye was also isolated and these were tentatively identified as the mixed 3:1 nitroxide-amine phthalocyanines **8** (8%), **10** (8%) and **12** (4%), on the basis of their high resolution mass spectra. In the positive ion ESI mass spectrometry of the phthalocyanines, the tetra-nitroxides **5**, **7** and **9** were detected as Na^+ adducts of the expected molecular ion while the tri-nitroxides **6**, **8** and **10** were detected as the H^+ adducts of the expected molecular ion, probably due to the ease of protonation of the secondary amine group.

2.3. Electronic absorption of the phthalocyanine nitroxides

The nitroxide phthalocyanines were turquoise coloured in both solution and the solid states. Accordingly, the UV–vis profiles of the metallated macrocycles were very similar (Figs. 2 and 3) with the compounds exhibiting B- and Q-band absorptions typical of phthalocyanine species at approximately 345 nm and 675 nm, respectively. The nature of the coordinated metal had relatively little effect on the absorbance profile of the phthalocyanines. In contrast, the free-bases **11** and **12** exhibited split Q-bands, in accordance with their reduced symmetry. The nitroxide moieties had little apparent effect on the absorption spectra of the macrocycles, as is evident from the comparison of methyl-adduct **13** with its nitroxide precursor **5**, indicating the absence of strong electronic interactions between the nitroxide groups and the macrocycle core. The substitution of one nitroxide for an amine moiety in the 3:1 nitroxide-amine phthalocyanines resulted only in slight broadening of the Q-band compared with the analogous tetra-nitroxide compounds and this may be due to increased capacity for hydrogen-bonding and hence aggregation, due to the secondary amine group.

2.4. EPR investigations

Considering the relative proximity of the radical and metal centres in the phthalocyanines, EPR investigations were undertaken to assess intramolecular nitroxide–nitroxide and nitroxide–metal interactions. Molecular modelling indicated that the distance between the nitroxide nitrogen and coordinated metal is approximately 8.9 Å, while the inter-nitroxide distances (measured from nitroxide nitrogen to nitroxide nitrogen) are approximately 17.8 Å across the macrocycle and 12.6 Å along the side of the macrocycle. The EPR spectra of the metallated tetra- and tri-nitroxides were acquired at X-band in solution at 298 K. The samples were prepared in chloroform at a concentration of ~10 μM, to minimize intermolecular interactions, and deoxygenated by bubbling with argon.

The room temperature EPR spectra of the tetra-nitroxide phthalocyanines **5**, **7** and **9** exhibit a number of interesting features (Fig. 4). Evidence of exchange coupling in the spectra of **5** and **9** is apparent as additional features between, and outside of, the normal nitrogen manifolds. In contrast, Cu(II) phthalocyanine **7** (Fig. 4) does not exhibit exchange coupling of the same order of magnitude but rather the three-line profile typical of isolated nitroxide moieties in addition to a broad, low-intensity absorbance at lower field, attributed to the centrally coordinated Cu(II). Additional Cu(II) hyperfine resonances are apparent in the expanded spectrum, although these are partially obscured by the nitroxide resonances.

The room temperature EPR spectra of 3:1 nitroxide-amine phthalocyanines **6**, **8** and **10** are also obviously dependant upon the coordinated metal ion (Fig. 5). The spectrum of Mg(II) complex **6** is similar to that observed for the Mg(II)

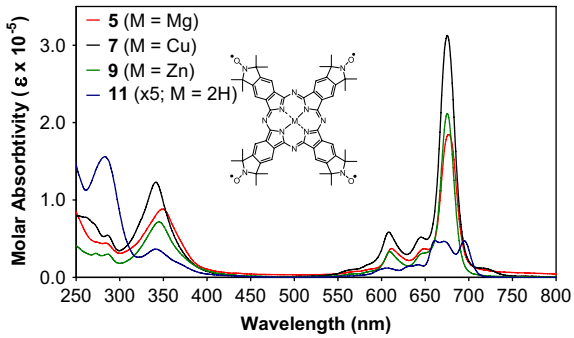


Figure 2. UV–vis spectra of tetra-nitroxide phthalocyanines **5**, **7**, **9** and **11** in CH_2Cl_2.

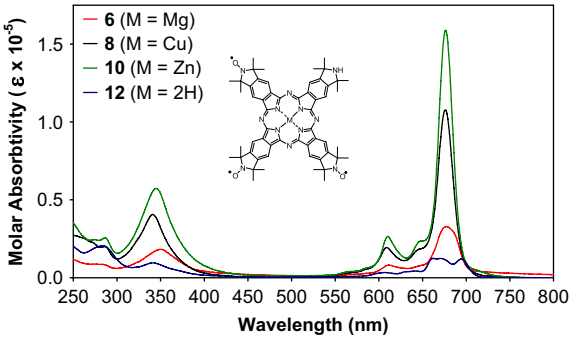


Figure 3. UV–vis spectra of 3:1 nitroxide-amine phthalocyanines **6**, **8**, **10** and **12** in CH_2Cl_2.

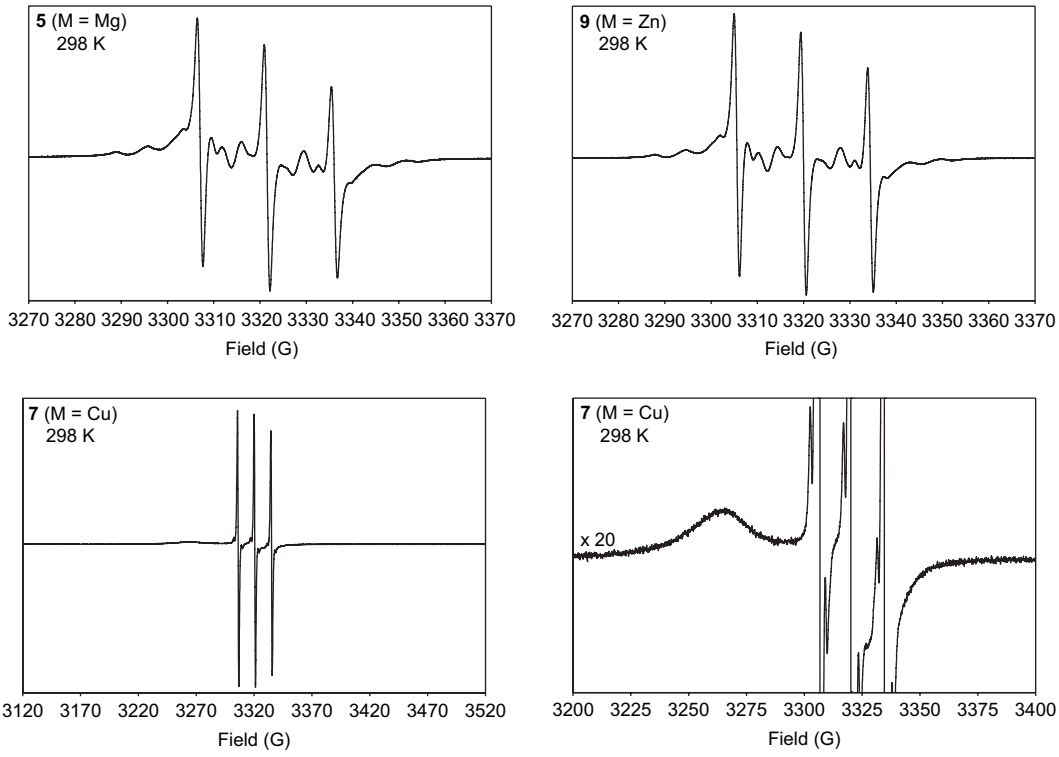


Figure 4. X-band EPR spectra of tetra-nitroxide phthalocyanines **5** (ν=9.32617 GHz), **7** (ν=9.32381 GHz) and **9** (ν=9.32174 GHz) in $CHCl_3$ at 298 K. The spectrum of **7** has been expanded (×20) to show the Cu(II) signal.

tetra-nitroxide **5**, with evidence of exchange coupling in the form of extra features between and outside the nitrogen manifolds. In contrast, the signals due to exchange coupling in Zn(II) complex **10** are very weak, with the spectrum resembling that of an isolated nitroxide group. It is only upon expansion (×75) that the components due to exchange coupling become apparent. Cu(II) phthalocyanine **8** also displays a spectrum (Fig. 5) consistent with isolated nitroxide groups, but with the addition of a broad, low-intensity signal at low field, which may be attributed to the paramagnetic Cu(II) metal ion. Again, it appears that additional Cu(II) resonances are present among the nitroxide resonances.

These results indicate that the centrally coordinated metal ion influences the magnitude of the exchange coupling between the nitroxide moieties, even when the metal ion is diamagnetic. This phenomenon suggests the possibility of controlling magnetic interactions in these and similar systems, according to the integration of different diamagnetic metal ions. Further studies are currently being conducted in this area to investigate the origin of the exchange pathways when diamagnetic or paramagnetic metal ions are present.

3. Conclusions

A range of phthalocyanines, each containing either three or four fused nitroxide-containing rings, have been prepared from dinitrile and diimino-isoindoline nitroxide precursors. These phthalocyanines contain a variety of centrally coordinated metal ions possibly allowing for their use as building-blocks for the development of molecule-based magnetic materials. EPR spectroscopy suggests that the centrally coordinated metal ion may be utilized to control intramolecular exchange interactions between nitroxide groups, even when the metal is diamagnetic. Notably, the nitroxide moieties of the reported phthalocyanines exist in a fixed geometry with respect to the macrocycle core, which may simplify the study of interactions between the free-radical moieties and coordinated metal ions.

4. Experimental

4.1. General

All reactions were conducted in oven- or flame-dried glassware. Hexanes refer to the alkane fraction with bp 40–60 °C. Solvents for reactions were distilled prior to use: MeOH (from Mg); 2-(dimethylamino)ethanol (distilled under reduced pressure, stored over 3 Å molecular sieves); CH_2Cl_2 (from CaH_2); *n*-butanol (from Mg). All other reagents were used as commercially supplied. TLC was carried out on pre-coated silica gel 60 F_{254} plates. Chromatography refers to flash chromatography on silica gel 60, 230–400 mesh (eluants are given in parentheses). 5,6-Dibromo-1,1,3,3-tetramethylisoindolin-2-yloxyl (**1**) was prepared according to previously published procedures[22] from 2-benzyl-1,1,3,3-tetramethylisoindoline[30] via 5,6-dibromo-1,1,3,3-tetramethylisoindoline.

EPR spectra were recorded on a Bruker Elexsys E500 EPR spectrometer (X-band, ~9.2 GHz) using an EIP 548B microwave frequency counter and a Bruker 035 M gaussmeter for microwave frequency and magnetic field calibration.

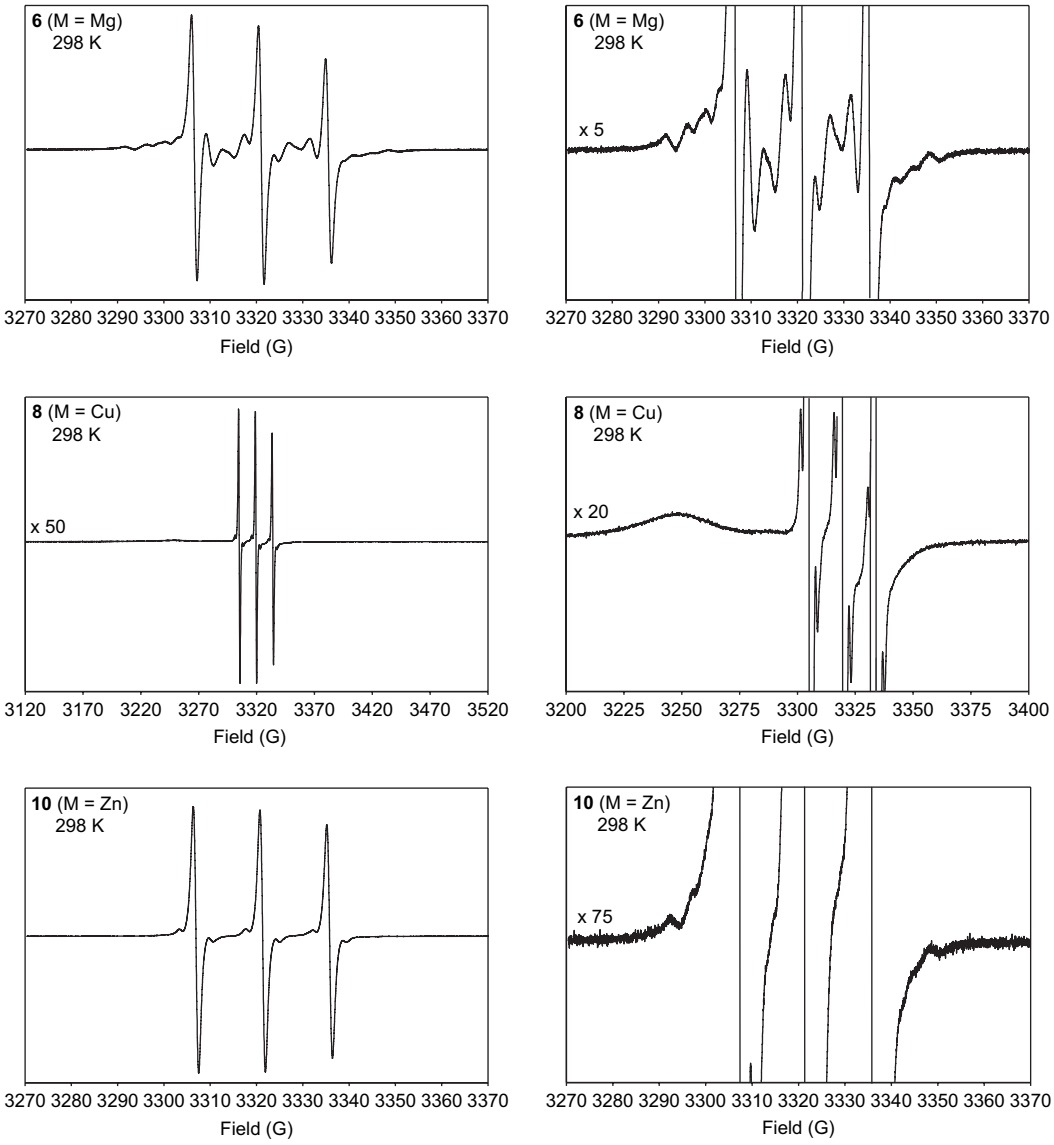


Figure 5. X-band EPR spectra of 3:1 nitroxide-amine phthalocyanines **6** (ν=9.32478 GHz), **8** (ν=9.32030 GHz) and **10** (ν=9.32548 GHz) in $CHCl_3$ at 298 K. Expansions are shown on the right to clearly illustrate low-intensity components of the spectra.

4.2. 5,6-Dicyano-1,1,3,3-tetramethylisoindolin-2-yloxyl (3)

(a) Dry, deoxygenated DMF (200 μL) was added to dibromide **1** (50 mg, 144 μmol), $Zn(CN)_2$ (40.4 mg, 346 μmol, 2.4 equiv) and $Pd(PPh_3)_4$ (83 mg; 72 μmol, 0.5 equiv) under Ar. The mixture was heated with stirring at 85 °C for 5 h, cooled to room temperature, diluted with 8% aqueous NH_3 (20 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic phase was washed with 8% aqueous NH_3 (10 mL) and brine (10 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (EtOAc/hexane 3:7) gave dinitrile **3** (33 mg, 95%) as yellow prismatic needles: mp 243–248 °C (dec sublim. at 150 °C); R_f 0.24 (EtOAc/hexane 3:7); IR (thin film) 2231, 1731, 1667, 1463, 1162, 923 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 246 (4.40) nm; MS (EI) *m/z* 240, 225, 210, 195, 167; HRMS (EI) calcd for $C_{14}H_{14}N_3O$: ($M^{+\bullet}$), 240.1137; found ($M^{+\bullet}$), 240.1128. Anal. calcd for $C_{14}H_{14}N_3O$: C, 69.98; H, 5.87; N, 17.49. Found: C, 70.08; H, 5.79; N, 17.55. In addition to dinitrile **3**, small amounts of Ph_3P, dibromide **1** and nitrile **2** were isolated. Nitrile **2**: mp 213–225 °C (sublim.); R_f 0.34 (EtOAc/hexane 3:7); IR (thin film) 2229, 1667, 1611, 1388, 1361, 1164 cm^{-1}; MS (EI) *m/z* 295/293 ($M^{+\bullet}$), 278/280, 263/265, 248/250, 249, 204, 169, 154; HRMS (EI) calcd for $C_{13}H_{14}BrN_2O$: ($M^{+\bullet}$), 293.0289; found: ($M^{+\bullet}$), 293.0287. Anal. calcd for $C_{13}H_{14}BrN_2O$: C, 53.08; H, 4.80; N, 9.52. Found: C, 52.91; H, 4.74; N, 9.44. (b) Dibromide **1** (50 mg, 144 μmol) in DMF (3 mL) was added with stirring to CuCN (77 mg, 860 μmol, 6 equiv) in DMF (2 mL) and the mixture was heated to reflux under Ar for 24 h. The yellow-brown reaction mixture was poured into 12% aqueous NH_3 (60 mL) and stirred for 15 min, giving a blue solution. This was extracted with CH_2Cl_2 (3×20 mL) and the combined organic extracts were washed repeatedly with 6% aqueous NH_3 (20 mL) until the washings were no longer blue. The organic phase was washed with brine (20 mL), dried (Na_2SO_4), rotary evaporated and the resultant green

oil was dried further under vacuum and chromatographed (EtOAc/hexane 1:9) to give dinitrile **3** (10 mg, 29%) and traces of nitroxide **2**.

4.3. 5,5,7,7-Tetramethylpyrrolo[3,4-*f*]isoindole-1,3-diylidenediamin-6-yloxyl (4)

Na (1.4 mg, 61 μmol) was added to dinitrile **3** (105 mg, 438 μmol) in dry MeOH (16 mL) at room temperature under Ar. NH_3 was bubbled through the solution, which was heated to 60 °C. After 2 h, rotary evaporation gave crude diimino-isoindoline **4** as yellow powder, which was used directly without further purification: R_f 0.05 (EtOH/EtOAc 1:4); IR (thin film) 3262, 1632, 1547, 1427, 1161 cm^{-1}; MS (EI) *m/z* 257, 243, 227, 211; HRMS (EI) calcd for $C_{14}H_{17}N_4O$: ($M^{+\bullet}$), 257.1402; found: ($M^{+\bullet}$), 257.1398.

4.4. Linstead macrocyclization of dinitrile 3

(a) Mg turnings (22 mg, 905 μmol, 22 equiv) and *n*-butanol (2.0 mL) were heated to reflux with stirring under argon for 24 h. The mixture was allowed to cool to room temperature, dinitrile **3** (10 mg, 41.7 μmol) added and the mixture was heated to reflux under Ar for a further 30 h, developing a strong turquoise colour. Rotary evaporation and chromatography (EtOAc/hexane 1:9 to 1:4) gave phthalocyanine **5** (4 mg, 40%) as a turquoise blue solid: R_f 0.63 (EtOAc), R_f 0.77 (EtOH/EtOAc 1:4), R_f 0.31 (MeOH/$CHCl_3$ 1:19); IR (thin film) 1731, 1469, 1292, 1161, 1067, 981, 714 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (log ε) 284 (4.34), 349 (4.81), 611 (4.42), 649 (4.40), 677 (5.20) nm; ^1H NMR (270 MHz, $CDCl_3$) δ 1.24 (br s); HRMS (ESI^+) calcd for $C_{56}H_{56}MgN_{12}NaO_4$: ([M+Na]$^{+\bullet}$), 1007.4295; found: ([M+Na]$^{+\bullet}$), 1007.4281. Further elution gave a minor dye identified as the phthalocyanine **6** (3 mg, 30%) as a turquoise solid: R_f 0.27 (EtOH/EtOAc 1:4); UV–vis (CH_2Cl_2) λ_{max} (log ε) 282 (3.88), 350 (4.26), 611 (3.90), 649 sh, 677 (4.51) nm; IR (thin film) 1730, 1464, 1292, 1261, 1066, 799 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.25 (br s); HRMS (ESI^+) calcd for $C_{56}H_{58}MgN_{12}O_3$: ([M+H]$^{+\bullet}$), 970.4605; found: ([M+H]$^{+\bullet}$), 970.4606. (b) Linstead macrocyclization of diimino-isoindoline **4** under comparable conditions gave phthalocyanine **5** (10%).

4.5. Macrocyclization of dinitrile 3 and diimino-isoindoline 4 in 2-(dimethylamino)ethanol

(a) $Cu(OAc)_2$ (10.3 mg, 57 μmol, 0.26 equiv) and diimino-isoindoline **4** (56 mg, 218 μmol) in 2-(dimethylamino)ethanol (4 mL) were heated to 135 °C under Ar, with the mixture immediately developing a deep blue colour. After 5 h, the mixture was cooled, diluted with H_2O (20 mL) and brine (40 mL) and extracted with $CHCl_3$ (4×20 mL). The organic phase was washed with H_2O (3×20 mL) and then once with brine (20 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (MeOH/$CHCl_3$ 1:49 to 1:19) gave phthalocyanine **7** (20 mg, 36%) as a turquoise solid: R_f 0.72 (EtOAc); R_f 0.80 (EtOH/EtOAc 1:4); R_f 0.58 (MeOH/$CHCl_3$ 1:19); UV–vis (CH_2Cl_2) λ_{max} (log ε) 285 (4.58), 341 (4.94), 608 (4.61), 645 (4.60), 675 (5.37) nm; IR (thin film) ν_{max} 1730, 1463, 1293, 1074 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.29 (br s); MS (FAB^+) *m/z* 1026, 1010, 994, 980, 964, 947, 933; HRMS (ESI^+) calcd for $C_{56}CuH_{56}N_{12}NaO_4$: ([M+Na]$^{+\bullet}$), 1046.3741; found: ([M+Na]$^{+\bullet}$), 1046.3743. Further elution gave phthalocyanine **8** (7 mg, 8%): R_f 0.05 (EtOAc); R_f 0.26 (MeOH/$CHCl_3$ 1:19); UV–vis (CH_2Cl_2) λ_{max} (log ε) 285 (4.30), 341 (2.61), 608 (4.29), 610 sh, 678 (5.03) nm; IR (thin film) ν_{max} 1730, 1668, 1464, 1294, 1161, 1075 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.29 (br s); MS (FAB^+) *m/z* 1009, 994, 979, 964, 948, 932, 917; HRMS (ESI^+) calcd for $C_{56}CuH_{58}N_{12}O_3$: ([M+H]$^{+\bullet}$), 1009.4050; found: ([M+H]$^{+\bullet}$), 1009.4041. (b) Macrocyclization using $Zn(OAc)_2$, (2.2 mg, 12 μmol, 0.26 equiv), diimino-isoindoline **4** (12 mg, 47 μmol) and 2-(dimethylamino)ethanol (1 mL) gave phthalocyanine **9** (4.2 mg, 35%) as a turquoise solid; R_f 0.68 (EtOAc); R_f 0.78 (EtOH/EtOAc 1: 4); R_f 0.43 (MeOH/$CHCl_3$ 1:19); UV–vis (CH_2Cl_2) λ_{max} (log ε) 286 (4.38), 344 (4.75), 609 (4.42), 647 (4.40), 675 (5.24) nm; IR (thin film) ν_{max} 1730, 1464, 1292, 1161, 1069, 981 cm^{-1}; MS (FAB^+) *m/z* 1026, 1011, 965; HRMS (ESI^+) calcd for $C_{56}H_{56}N_{12}NaO_4Zn$: ([M+Na]$^{+\bullet}$), 1047.3736; found: ([M+Na]$^{+\bullet}$), 1047.3728. Further elution gave phthalocyanine **10** (1 mg, 8%): R_f 0.10 (EtOAc); R_f 0.25 (EtOH/EtOAc 1:4); R_f 0.02 (MeOH/$CHCl_3$ 1:19); UV–vis (CH_2Cl_2) λ_{max} (log ε) 286 (4.31), 345 (4.65), 610 (4.31), 650 (4.30), 676 (5.11) nm; IR (thin film) ν_{max} 1731, 1669, 1464, 1293, 1161, 1071 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.25 (br s); MS (FAB^+) *m/z* 1011, 995, 980, 965, 948, 933; HRMS (ESI^+) calcd for $C_{56}H_{58}N_{12}O_3Zn$: ([M+H]$^{+\bullet}$), 1010.4046; found: ([M+H]$^{+\bullet}$), 1010.4040. (c) Macrocyclization using $Zn(OAc)_2$ (2.0 mg, 11 μmol, 0.5 equiv), dinitrile **3** (5 mg, 21 μmol) and 2-(dimethylamino)ethanol (0.5 mL) gave phthalocyanines **9** (1 mg, 20%) and **10** (<1 mg). (d) Heating diimino-isoindoline **4** (28 mg, 109 μmol) in 2-(dimethylamino)ethanol (2 mL) for 5 h at 135 °C under Ar gave phthalocyanine **11** (2 mg, 8%) as a turquoise solid: R_f 0.66 (EtOAc); R_f 0.73 (EtOH/EtOAc 1:4); R_f 0.66 (MeOH/$CHCl_3$ 1:19); UV–vis (CH_2Cl_2) λ_{max} (log ε) 340 (3.86), 605 (3.37), 642 (3.51), 661 (3.97), 671 (3.97), 694 (3.98) nm; IR (thin film) ν_{max} 2226, 1731, 1541, 1423, 1280, 1164 cm^{-1}. Further elution gave phthalocyanine **12** (1 mg, 4%) as a turquoise solid: R_f 0.08 (EtOAc); R_f 0.28 (EtOH/EtOAc 1:4); R_f 0.26 (MeOH/$CHCl_3$ 1:19); UV–vis (CH_2Cl_2) λ_{max} (log ε) 340 (3.98), 606 (3.51), 642 (3.63), 662 (4.09), 671 (4.09), 694 (4.08) nm; IR (thin film) ν_{max} 2226, 1732, 1541, 1465, 1423, 1291 cm^{-1}.

4.6. O-Methylation of phthalocyanine 5

$FeSO_4 \cdot 7H_2O$ (3.7 mg, 13.3 μmol, 6.6 equiv) was added with stirring to nitroxide **5** (2 mg, 2.03 μmol) and H_2O_2 (35%; 20 μl, 187 μmol, 92 equiv) in DMSO (1 mL). After 20 min, the mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organics were washed with H_2O (3×10 mL), once with brine (10 mL) and then dried (Na_2SO_4). Rotary evaporation and chromatography (EtOAc/hexane 1:1) gave phthalocyanine **13** (1.8 mg, 85%) as a turquoise solid: R_f 0.78 (EtOAc); UV–vis (CH_2Cl_2) λ_{max} (log ε) 285 (4.08), 352 (4.39), 612 (3.99), 649 (3.97), 678 (4.77) nm; IR (thin film) ν_{max} 1732, 1619, 1470, 1295, 1070, 1051 cm^{-1}; ^1H NMR (400 MHz, d_5-pyridine) δ 1.94 (br s, 48H), 4.02 (s, 12H), 9.87 (s, 8H); MS (FAB^+) *m/z* 1045; FAB^+ HRMS; calcd for $C_{60}H_{69}MgN_{12}O_4$: ([M+H]$^{+\bullet}$), 1045.5415; found: ([M+H]$^{+\bullet}$), 1045.5433; HRMS (ESI^+) calcd for $C_{60}H_{68}MgN_{12}NaO_4$: ([M+Na]$^{+\bullet}$), 1067.5234; found: ([M+Na]$^{+\bullet}$), 1067.5210.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.170.

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27. Crystallographic data (excluding structure factors) for the structures **2** and **3** in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 284485 and CCDC 284486, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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