

# Synthesis of soluble halogenated aryloxy substituted indium phthalocyanines

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Received (in Cambridge, UK) 24th August 2001, Accepted 8th November 2001  
First published as an Advance Article on the web 3rd December 2001

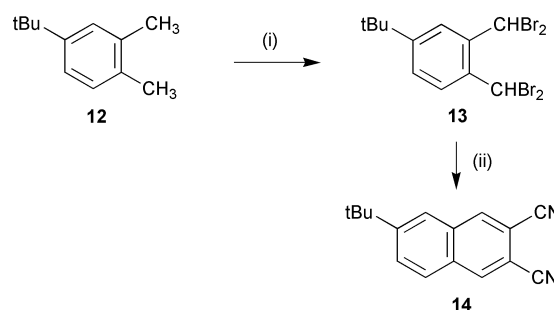
Phthalocyanines solubilised by either 8 or 16 aryloxy or haloaryloxy groups are described. A series of phthalocyanine derivatives were prepared containing indium. 1,2-Dinitriles and the corresponding diiminoisoindolines were used as precursors. A naphthalocyanine metallated with indium and solubilised with four *tert*-butyl groups is reported.

## Introduction

Optical limiters or reverse saturable absorbers are materials which display diminishing transmittance with increasing incident light intensity. This attenuation of the optical throughput can be used to protect various sensors against damage from pulsed laser sources.<sup>1–5</sup> Phthalocyanines are promising candidates for certain applications.<sup>6</sup> Peripheral substituents can fine-tune the ground state absorption to help create a good visible window by red shifting the long wavelength Q band absorption. A range of different metals can also be incorporated to help achieve desirable excited state characteristics. Population of triplet excited states from singlet states by intersystem crossing is desirable because more strongly absorbing triplet states can have a longer lifetime and enhance the limiter performance. Heavy metals, halogens and paramagnetic groups are known to promote intersystem crossing and so the synthesis of suitably functionalised phthalocyanines containing these features is of interest.<sup>6</sup> Phthalocyanines containing the metals Al, Si, V and In have been studied and shown to possess desirable properties.<sup>6</sup>

## Results and discussion

This paper reports the synthesis of unmetallated aryloxy substituted phthalocyanines **24–26**, metallated phthalocyanines **27–33** and **35–36** containing indium, a phenylthio substituted phthalocyanine **34** containing indium and a naphthalocyanine (a tetrabenzo[*b,k,t,c*]<sub>1</sub>phthalocyanine) **37** containing indium. Aryloxy groups substituted with fluoro, chloro, bromo or iodo groups were incorporated to allow the influence of remote halogens upon optical limiter performance to be investigated. The oxygen group itself causes a bathochromic shift of the long wavelength absorption maximum<sup>7–10</sup> which helps to widen the visible window. 4,5-Diaryloxy substituted dicyanobenzenes **3–9** were prepared by treatment of 4,5-dichloro-1,2-dicyanobenzene **1** with an appropriate phenol and K<sub>2</sub>CO<sub>3</sub> in DMSO. Compound **1** was prepared by a literature route from 4,5-dichlorobenzene-1,2-dicarboxylic acid.<sup>11</sup> Dinitrile **10** was prepared by treating **1** with thiophenol and base. Tetrakis(4-chlorophenoxy)-1,2-dicyanobenzene **11** was prepared by treating commercially available tetrafluorophthalonitrile **2** with 4-chlorophenol and K<sub>2</sub>CO<sub>3</sub> in DMSO. Related tetrakis(aryloxy)-1,2-dicyanobenzenes have been reported previously.<sup>12</sup> 6-*tert*-Butyl-2,3-dicyanonaphthalene **14** was prepared by the literature route shown in Scheme 1.<sup>13</sup> This involved free radical

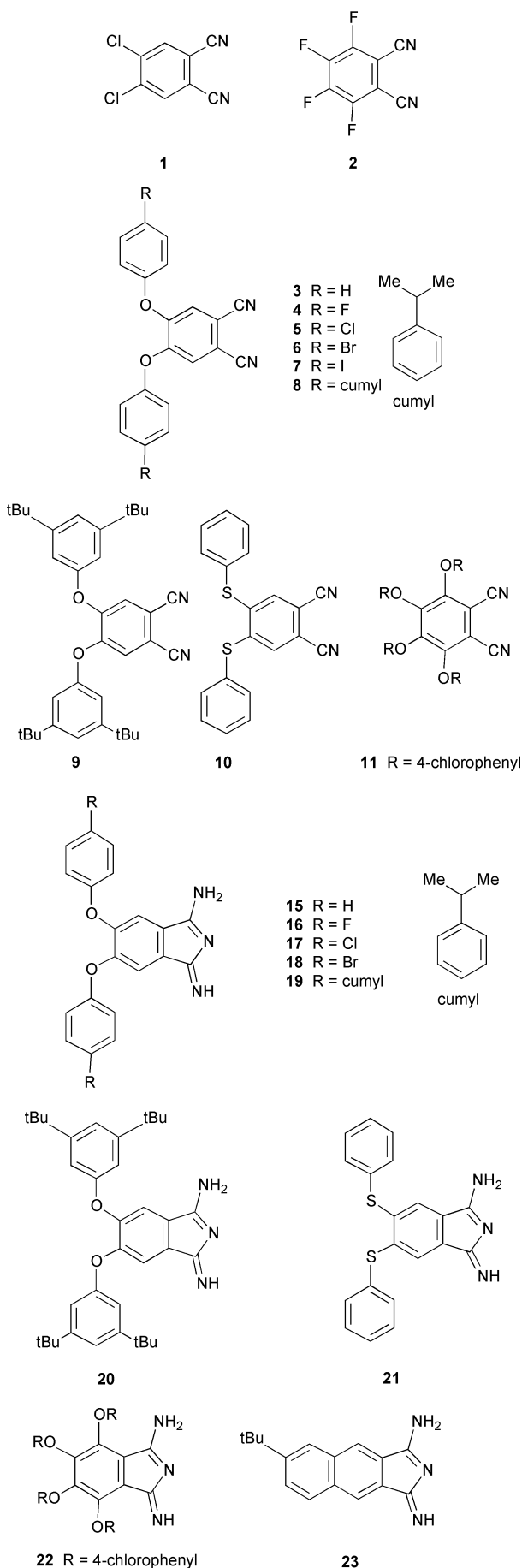


Scheme 1 Reagents and conditions (i) NBS–AIBN, 56%; (ii) NaI–fumaronitrile–DMF, 43%.

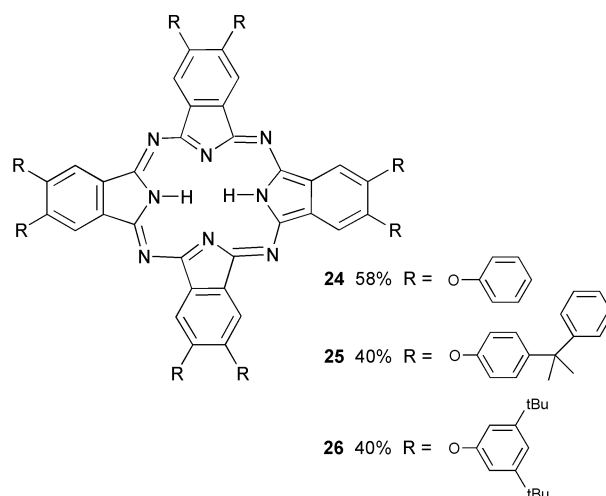
bromination of *o*-xylene **12** to give tetrabromoxylene **13**. Treatment with NaI in hot DMF eliminates bromine to give an intermediate diene which is intercepted by cycloaddition with fumaronitrile. Elimination of two more moles of HBr gives naphthalonitrile **14**. Treatment of the above dinitriles with ammonia gas in NaOMe–MeOH<sup>14–17</sup> gave the corresponding diiminoisoindolines **15–23**. The progress of the reaction can be monitored by IR observing the disappearance of the nitrile peak from 2230–2250 cm<sup>-1</sup>. A large broad peak in the range 3200–3500 cm<sup>-1</sup> corresponding to the NH stretch is observed. The diiminoisoindolines were used for the synthesis of InCl substituted phthalocyanines.

Non-metallated phthalocyanines **24–26** substituted with 8 aryloxy groups were prepared by cyclotetramerisation of dinitriles **3**, **8** and **9** respectively with the base DBU in hot pentanol.<sup>11,18–20</sup> On cooling the precipitated product was isolated by filtration. Metallated phthalocyanines **28–31** containing indium were prepared by cyclotetramerisation of the corresponding dinitriles by heating with InCl<sub>3</sub> in quinoline.<sup>21</sup> The other indium containing phthalocyanines were most satisfactorily prepared by heating the appropriate diiminoisoindoline with InCl<sub>3</sub> in quinoline. Treatment of phthalocyanine **29** with PhMgBr displaces the chlorine group with a phenyl group to give compound **36**. Similar methods have been used to prepare a range of indium containing phthalocyanines substituted with different axial groups.<sup>21</sup> Naphthalocyanine **37** was prepared as a mixture of isomers by cyclotetramerisation of dihydrodiimino-1*H*-benz[*J*]isoindole **23** by heating with InCl<sub>3</sub> in quinoline.

The UV spectrum of each phthalocyanine is important because a low absorption cross section in the visible region provides the optical window for an RSA device. The octasubsti-



tuted aryloxyphthalocyanines **24–26** have a long wavelength absorption at around 700 nm. Substitution with InCl produces little overall change in this absorption maximum. The octakis(arylthio)phthalocyanine **34** containing InCl has a long wave-



length maximum at 735 nm which is shifted bathochromically by about 50 nm compared to the value for the corresponding octakis(aryloxy)phthalocyanine **27**. Sulfur substituents produce a greater bathochromic shift than oxygen substituents. Phthalocyanine **35** substituted with 16 aryloxy groups shows a maximum at 738 nm which is shifted bathochromically compared to the octakis(aryloxy)phthalocyanine **27**. Naphthalocyanines are of particular interest for optical limiters because of the much wider visible window that they exhibit. Naphthalocyanine **37** has a main maximum at 793 nm. This peak is bathochromically shifted compared to the InCl containing phthalocyanines.

In summary a range of different phthalocyanines have been prepared which will allow a study of the influence of structural factors upon optical limiting performance to be evaluated.

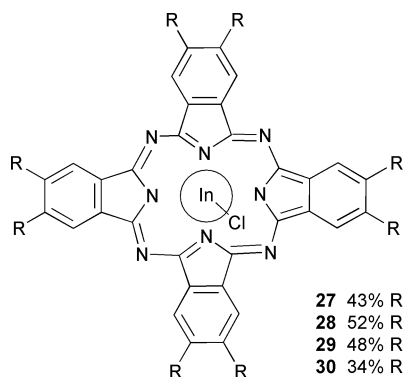
## Experimental

Ultraviolet spectra were recorded on a Perkin-Elmer Lambda 15 UV-VIS spectrometer using dichloromethane as the solvent. Infrared spectra were recorded on an ATI Mattson FTIR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained at 250 MHz and 62.9 MHz respectively on a Bruker AC 250 spectrometer and at 400 MHz and 100.5 MHz respectively on a Varian 400 spectrometer. Chemical shifts,  $\delta$ , are given in ppm relative to  $\text{SiMe}_4$ . Coupling constants,  $J$ , are given in Hz. Mass spectra were carried out at the University of Wales, Swansea using either the low resolution electron impact or fast atom bombardment methods. Butterworth Laboratories, using a PE 2400 CHN analyser, conducted elemental analyses. Melting points were carried out using a Kofler hot-stage microscope and are uncorrected.

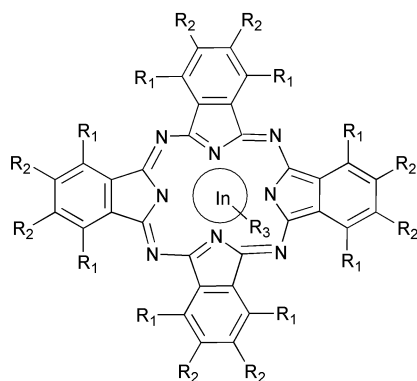
### 4,5-Disubstituted 1,2-dicyanobenzenes

**General procedure.** 4,5-Dichloro-1,2-dicyanobenzene **1** (1.97 g, 10 mmol) and 60 mmol of a phenol or thiophenol were heated at 90 °C in DMSO (20 ml) with stirring under  $\text{N}_2$ .  $\text{K}_2\text{CO}_3$  powder (2.76 g, 20 mmol) was added in portions ( $8 \times 20$  mmol) every 5 min. The mixture was heated for a further 30 min. After cooling the mixture was added to ice- $\text{H}_2\text{O}$  (200 ml), filtered and the product was recrystallised from MeOH.

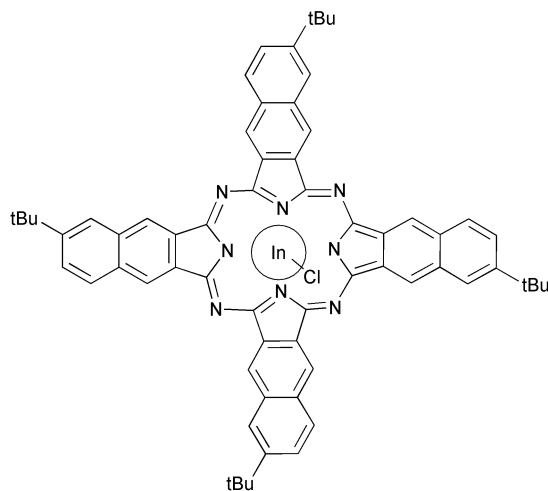
**4,5-Diphenoxy-1,2-dicyanobenzene 3.** Yield 70%, mp 148–149 °C (lit. 149 °C<sup>11</sup>) (Found: C, 76.8; H, 3.9; N, 9.1.  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$  requires C, 76.9; H, 3.85; N, 9.0%);  $\lambda_{\text{max}}$ (EtOH)/nm 296;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  688, 747, 818, 876, 906, 1074, 1162, 1210, 1246, 1304, 1397, 1457, 1501, 1561, 1591, 1609 and 2236;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 7.08 (4H, d,  $J$  7.6), 7.15 (2H, s), 7.30 (4H, t) and 7.45 (2H, t);  $\delta_{\text{C}}$  (62.9 MHz;  $\text{CDCl}_3$ ) 110.4, 115.0, 120.0, 122.0, 126.0, 130.6, 152.0 and 154.1;  $m/z$  (EI) 312 ( $\text{M}^+$ , 100%).



- 27** 43% R = phenoxy  
**28** 52% R = 4-fluorophenoxy  
**29** 48% R = 4-chlorophenoxy  
**30** 34% R = 4-bromophenoxy  
**31** 23% R = 4-iodophenoxy  
**32** 66% R = 4-cumylphenoxy  
**33** 46% R = 3,5-di-*tert*-butylphenoxy  
**34** 50% R = phenylthio



- 35** 38% R<sub>1</sub> = R<sub>2</sub> = 4-chlorophenoxy R<sub>3</sub> = Cl  
**36** 12% R<sub>1</sub> = H, R<sub>2</sub> = 4-chlorophenoxy R<sub>3</sub> = Ph



**37** 26%

**4,5-Bis(*p*-fluorophenoxy)-1,2-dicyanobenzene 4.** Yield 72%, mp 186–188 °C (Found: C, 68.7; H, 3.0; N, 7.8. C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub> requires C, 69.0; H, 2.9; N, 8.0%); λ<sub>max</sub>(EtOH)/nm 291; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 784, 854, 863, 1011, 1087, 1190, 1207, 1298, 1384, 1495, 1569, 1617 and 2229; δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>) 7.01 (4H, m), 7.10 (4H, m) and 7.12 (2H, s); δ<sub>C</sub> (100.5 MHz; CDCl<sub>3</sub>) 111.6, 115.9, 118.3, 118.5, 122.5, 122.6, 150.8, 150.9, 152.9, 160.0 and 162.5; *m/z* (EI) 348 (M<sup>+</sup>, 100%).

**4,5-Bis(*p*-chlorophenoxy)-1,2-dicyanobenzene 5.** Yield 70%, mp 188–190 °C (Found: C, 63.2; H, 2.5; N, 7.3. C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 63.0; H, 2.6; N, 7.35%); λ<sub>max</sub>(EtOH)/nm 293; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 772, 824, 1010, 1090, 1187, 1223, 1303, 1324, 1399, 1483, 1502, 1581, 1599 and 2226; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 7.0 (4H, d, *J*, 9.2), 7.2 (2H, s) and 7.4 (4H, d, *J*, 9.2); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 111.1, 114.7, 116.7, 121.0, 122.4, 130.7, 151.5 and 152.7; *m/z* (EI) 380/382/384 (M<sup>+</sup>, 100%).

**4,5-Bis(*p*-bromophenoxy)-1,2-dicyanobenzene 6.** Yield 78%, mp 212–214 °C (Found: C, 51.2; H, 1.9; N, 5.9. C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>Br<sub>2</sub> requires C, 51.1; H, 2.1; N, 6.0%); ν<sub>max</sub>(EtOH)/nm 292; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 773, 862, 1012, 1067, 1221, 1305, 1323, 1398, 1484, 1503, 1576, 1597 and 2225; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 7.0 (4H, d, *J*, 8.9), 7.2 (2H, s) and 7.5 (4H, d, *J*, 8.9); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 111.2, 114.7, 118.9, 121.4, 122.6, 133.7, 151.4 and 153.3; *m/z* (EI) 468/470/472 (M<sup>+</sup>, 100%).

**4,5-Bis(*p*-iodophenoxy)-1,2-dicyanobenzene 7.** Yield 76%, mp 214–217 °C (Found: C, 42.2; H, 1.6; N, 5.0. C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>I<sub>2</sub> requires C, 42.4; H, 1.8; N, 4.95%); λ<sub>max</sub>(EtOH)/nm 292; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 768, 830, 1009, 1220, 1305, 1324, 1395, 1481, 1502, 1564, 1598 and 2224; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 7.73 (4H, d, *J*, 8.85), 7.21 (2H, s) and 6.80 (4H, d, *J*, 8.85); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 89.6, 111.2, 114.7, 121.7, 122.7, 139.6, 151.3 and 154.1; *m/z* (EI) 564 (M<sup>+</sup>, 100%).

**4,5-Bis(cumylphenoxy)-1,2-dicyanobenzene 8.** Yield 82%, mp 166–168 °C (Found: C, 83.15; H, 5.8; N, 5.3. C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> requires C, 83.2; H, 5.8; N, 5.1%); λ<sub>max</sub>(EtOH)/nm 292; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 701, 798, 1015, 1215, 1319, 1385, 1499, 1561, 1590, 2236 and 2959; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 1.71 (12H, s), 6.96 (4H, m), 7.16 (2H, m) and 7.18–7.31 (14H, m); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 30.7, 42.7, 109.9, 115.2, 119.4, 121.7, 125.9, 126.8, 128.2, 129.0, 148.7, 150.0, 151.8 and 152.1; *m/z* (EI) 548 (M<sup>+</sup>, 100%).

**4,5-Bis(3,5-di-*tert*-butylphenoxy)-1,2-dicyanobenzene 9.** Yield 91%, mp 240–241 °C (Found: C, 80.4; H, 8.0; N, 5.4. C<sub>36</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub> requires C, 80.6; H, 8.2; N, 5.2%); λ<sub>max</sub>(EtOH)/nm 308; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 706, 898, 918, 952, 1077, 1220, 1291, 1418, 1435, 1505, 1576, 1605, 2230, 2867, 2903 and 2962; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 1.33 (36H, s), 6.90 (4H, s), 7.10 (2H, s) and 7.35 (2H, s); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 31.4, 35.0, 109.7, 114.7, 115.4, 120.5, 152.5, 153.4, 153.9, 155.0; *m/z* (EI) 536 (M<sup>+</sup>, 100%).

**4,5-Bis(phenylthio)-1,2-dicyanobenzene 10.** Yield 46%, mp 157–159 °C (lit. 159 °C<sup>7</sup>) (Found: C, 69.6; H, 3.4; N, 8.0; S, 18.5. C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub> requires C, 69.8; H, 3.5; N, 8.1; S, 18.6%); λ<sub>max</sub>(EtOH)/nm 293; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1210 and 2227; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 7.0 (2H, s) and 7.54 (10H, m); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 111.8, 115.4, 128.6, 130.0, 130.7, 135.2 and 144.2 (one resonance is missing); *m/z* (EI) 344 (M<sup>+</sup>, 100%).

**3,4,5,6-Tetrakis(*p*-chlorophenoxy)-1,2-dicyanobenzene 11.** 4-Chlorophenol (19.3 g, 150 mmol) and 3,4,5,6-tetrafluoro-1,2-dicyanobenzene (3.93 g, 19.63 mmol) in DMSO (50 ml) at 90 °C under N<sub>2</sub> were treated with 12 portions of K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20 mmol) at 5 min intervals. After heating for a further 1.5 h the mixture was allowed to cool, added to ice–H<sub>2</sub>O (400 ml) and filtered to give the product as a colourless solid which was recrystallised from MeOH. Yield 20%, mp 208–210 °C (Found: C, 60.6; H, 2.4; N, 4.4. C<sub>32</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>4</sub> requires C, 60.8; H, 2.5; N, 4.4%); ν<sub>max</sub>(EtOH)/nm 290; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 650, 824, 982, 1012, 1089, 1166, 1205, 1302, 1375, 1440, 1486, 1561, 1588 and 2231; δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 6.43 (4H, d, *J*, 8.85), 6.72 (4H, d, *J*, 8.85), 7.11 (4H, d, *J*, 9.2) and 7.22 (4H, d, *J*, 9.2); δ<sub>C</sub> (62.9 MHz; CDCl<sub>3</sub>) 108.4, 111.1, 116.8, 117.5, 129.5, 129.6, 129.8, 129.9, 146.5, 149.1, 153.9 and 154.8; *m/z* (EI) 632/634/636/638 (M<sup>+</sup>, 100%).

**1,2-Bis(dibromomethyl)-4-*tert*-butylbenzene 13.**<sup>13</sup> A mixture of 4-*tert*-butyl-*o*-xylene **12** (5.0 g, 31 mmol), *N*-bromosuccinimide (NBS) (21.9 g, 123 mmol) and a small quantity of AIBN in CCl<sub>4</sub> was heated under reflux for 10 h. The reaction mixture was filtered while hot and the solvent was removed *in vacuo* and the crude product used without further purification owing to the reactivity of the bis(dibromomethyl) groups. Yield 56%, δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 1.34 (9H, s), 7.11 (2H, s), 7.18 (1H, s), 7.39 (1H,

d, *J* 8.2) and 7.60 (1H, d, *J* 8.2);  $\delta_{\text{C}}$  (62.9 MHz;  $\text{CDCl}_3$ ) 31.1, 36.7, 125.8, 126.0, 127.1, 127.3, 127.8, 129.6, 130.9 and 153.8; *m/z* (FAB) 474/476/478/480/482 ( $\text{M}^+$ , 100%).

**6-*tert*-Butyl-2,3-dicyanonaphthalene 14.** A mixture of crude 1,2-bis(dibromomethyl)-4-*tert*-butylbenzene **13** (14.7 g, 31 mmol), fumaronitrile (2.4 g, 31 mmol) and sodium iodide (30 g, 0.2 mol) in DMF was heated at 75–80 °C for 7 h. The reaction mixture was cooled to room temperature and an aqueous solution of  $\text{Na}_2\text{SO}_4$  was added. The precipitate was filtered and washed with  $\text{CH}_2\text{Cl}_2$  to give the *title compound* (3.1 g, 43%) mp 193–194 °C (lit. 194–195 °C<sup>13</sup>);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  471, 840, 901, 926, 1262, 1384, 1624, 2229, 2871, 2904 and 2954;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.43 (9H, s), 7.90 (3H, m), 8.29 (1H, s) and 8.31 (1H, s);  $\delta_{\text{C}}$  (62.9 MHz;  $\text{CDCl}_3$ ) 30.9, 35.5, 109.3, 109.9, 116.2, 123.9, 128.4, 130.0, 131.5, 133.4, 135.4, 135.9 and 154.6 (one resonance is missing); *m/z* (FAB) 234 ( $\text{M}^+$ , 100%).

### 5,6-Disubstituted 1,3-diiminoisoindolines

**General procedure.**<sup>14–17</sup> The dicyanobenzene (7 mmol) derivative was gently refluxed in NaOMe–MeOH solution (200 ml, 0.7 g Na in 500 ml MeOH) for 5 h with  $\text{NH}_3$  bubbled through the solution. The end point was determined by observing the disappearance of the CN stretch on aliquots examined by IR. The reaction mixture was allowed to cool and concentrated under vacuum to give the crude product. They were used immediately in the preparation of the corresponding InCl phthalocyanines without further purification.

**5,6-Diphenoxy-1,3-diiminoisoindoline 15.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 284;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  565, 741, 871, 1030, 1069, 1211, 1270, 1385, 1458, 1490, 1597, 1637, 2853, 2925 and 3430;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 6.80 (3H, m, 3 × NH), 7.00 (4H, m), 7.11 (4H, m), 7.20 (2H, s) and 7.34 (2H, m);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 114.6, 116.5, 120.0, 121.3, 125.8, 131.1, 152.2 and 157.1; *m/z* 329 ( $\text{M}^+$ , 100%).

**5,6-Bis(*p*-fluorophenoxy)-1,3-diiminoisoindoline 16.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 293;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1201 and 3428;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 6.91 (3H, m), 7.11 (4H, m), 7.21 (2H, s) and 7.26 (4H, m);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 112.7, 118.2, 119.9, 120.1, 126.3, 126.4, 152.3, 152.4, 154.0, 160.2 and 162.9; *m/z* (EI) 365 ( $\text{M}^+$ , 100%).

**5,6-Bis(*p*-chlorophenoxy)-1,3-diiminoisoindoline 17.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 288;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  824, 1010, 1090, 1143, 1213, 1284, 1407, 1485, 1543, 1637, 2854, 2932, 2965 and 3417;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 6.87 (3H, m), 7.12 (4H, d), 7.24 (2H, s) and 7.49 (4H, d);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 112.3, 116.2, 118.4, 123.1, 124.6, 131.4, 154.3 and 154.6; *m/z* (EI) 397/399/401 ( $\text{M}^+$ , 100%).

**5,6-Bis(*p*-bromophenoxy)-1,3-diiminoisoindoline 18.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 289;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  822, 1009, 1070, 1164, 1211, 1297, 1411, 1482, 1580 and 3416;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 6.80 (3H, m), 7.02 (4H, d), 7.32 (2H, s) and 7.59 (4H, d);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 112.5, 116.3, 120.8, 122.4, 124.9, 136.3, 152.7 and 155.0; *m/z* (EI) 485/487/489 ( $\text{M}^+$ , 100%).

**5,6-Bis(cumylphenoxy)-1,3-diiminoisoindoline 19.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 286;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  701, 867, 961, 1080, 1202, 1298, 1363, 1421, 1479, 1594, 1655, 2867, 2904, 2964 and 3421;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.66 (12H, s), 6.87 (4H, d, *J* 8.85), 7.17 (4H, d, *J* 8.85) and 7.25 (15H, m);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 30.9, 42.6, 77.3, 112.3, 118.3, 125.8, 126.8, 128.1, 128.4, 146.7, 150.4, 151.2, 154.0 and 165.2; *m/z* (EI) 565 ( $\text{M}^+$ , 100%).

**5,6-Bis(3,5-di-*tert*-butylphenoxy)-1,3-diiminoisoindoline 20.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 291;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  457, 709, 860, 1015, 1030, 1047, 1118, 1204, 1308, 1364, 1425, 1454, 1556,

1596, 2830, 2868, 2968 and 3436;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.26 (36H, s), 6.88 (7H, m), 7.19 (2H, s) and 7.21 (2H, s);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 32.4, 36.1, 112.1, 114.7, 115.4, 119.6, 134.5, 152.7, 154.1 and 156.4; *m/z* (EI) 553 ( $\text{M}^+$ , 100%).

**5,6-Bis(phenylthio)-1,3-diiminoisoindoline 21.** Yield 97%,  $\lambda_{\text{max}}$ (EtOH)/nm 285;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  738, 855, 905, 1023, 1066, 1143, 1174, 1225, 1270, 1318, 1379, 1439, 1533, 1644, 2831, 2854, 2970 and 3427;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 6.76 (3H, m), 7.07 (2H, s) and 7.30–7.60 (10H, m);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 115.2, 117.6, 128.0, 131.0, 131.9, 135.5, 144.8 and 152.5; *m/z* 361 ( $\text{M}^+$ , 100%).

**4,5,6,7-Tetrakis(*p*-chlorophenoxy)-1,3-diiminoisoindoline 22.** Yield 97%,  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1200 and 3417;  $\lambda_{\text{max}}$ (EtOH)/nm 290 and 322; *m/z* (EI) 649/651/653 ( $\text{M}^+$ , 100%).

**6-*tert*-Butyl-2,3-dihydro-1,3-diimino-1*H*-benz[*f*]isoindole 23.** Yield 97%,  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  472, 578, 726, 815, 904, 1030, 1159, 1257, 1384, 1458, 1542, 1626, 2852, 2925, 2952 and 3422;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.04 (9H, s), 6.91 (3H, s, br), 7.16 (4H, s, br), 7.42 (1H, s, br);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 31.0, 34.6, 112.0, 120.2, 120.4, 124.1, 125.8, 128.7, 130.8, 131.4, 131.7, 133.8, 149.7 and 171.3; *m/z* (FAB) 251 ( $\text{M}^+$ , 100%).

### 2,3,9,10,16,17,23,24-Octasubstituted phthalocyanines

**General procedure.**<sup>18–20</sup> The appropriate dicyanobenzene (4 mmol) and DBU (0.6 g, 4 mmol) in pentanol (50 ml) were refluxed for 48 h. The dark green solution was filtered and the precipitated product Soxhlet extracted with MeOH, then dried under vacuum.

**2,3,9,10,16,17,23,24-Octaphenoxypthalocyanine 24.**<sup>11</sup> Yield 58%, mp >275 °C (Found: C, 76.6; H, 3.9; N, 9.0.  $\text{C}_{80}\text{H}_{50}\text{N}_8\text{O}_8$  requires C, 76.8; H, 4.0; N, 8.95%);  $\lambda_{\text{max}}$ (EtOH)/nm (log  $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) 344, 673 and 700 (5.2);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  702, 833, 1007, 1203, 1272, 1385, 1399, 1438, 1491, 1618, 1637 and 3416;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) –0.80 (2H, s), 7.16 (16H, d), 7.24 (16H, t), 7.37 (8H, t) and 8.82 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 112.7, 115.9, 121.3, 126.5, 128.2, 130.9, 153.1 and 156.7; *m/z* 1250 ( $\text{M}^+$ , 100%).

**2,3,9,10,16,17,23,24-Octakis(cumylphenoxy)phthalocyanine 25.** Yield 40%, mp 112–114 °C (Found: C, 82.8; H, 5.8; N, 5.1.  $\text{C}_{152}\text{H}_{130}\text{N}_8\text{O}_8$  requires C, 83.1; H, 6.0; N, 5.1%);  $\nu_{\text{max}}$ (EtOH)/nm (log  $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) 328, 606, 637, 667 and 701 (5.3);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  700, 763, 1014, 1215, 1278, 1351, 1429, 1501, 1599, 2869, 2928, 2966 and 3426;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) –0.78 (2H, s), 1.68 (48H, s), 7.11–7.27 (72H, m) and 8.75 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 31.9, 43.7, 118.7, 119.7, 120.1, 126.8, 126.9, 127.8, 129.0, 129.1, 129.2, 129.7, 151.7 and 156.4; *m/z* (FAB) 2194 ( $\text{M}^+$ , 100%).

**2,3,9,10,16,17,23,24-Octakis(3,5-di-*tert*-butylphenoxy)-phthalocyanine 26.** Yield 46%, mp >275 °C (Found: C, 80.6; H, 8.7; N, 5.5.  $\text{C}_{144}\text{H}_{178}\text{N}_8\text{O}_8$  requires C, 80.5; H, 8.4; N, 5.2%);  $\lambda_{\text{max}}$ (EtOH)/nm (log  $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) 348, 607, 640, 669 and 703 (5.3);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  706, 961, 1011, 1087, 1199, 1298, 1385, 1423, 1439, 1459, 1588, 2867, 2904, 2963 and 3430;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) –0.89 (2H, s), 1.61 (144H, s), 7.41 (16H, s), 7.53 (8H, s) and 9.33 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz;  $\text{CDCl}_3$ ) 31.7, 35.3, 113.0, 114.2, 117.7, 133.1, 151.4, 152.8 and 157.1 (one resonance is missing); *m/z* (FAB) 2146 ( $\text{M}^+$ , 100%).

### Metallated phthalocyanines

**General procedure.**<sup>21,13,15</sup> The appropriate dicyanobenzene (6.5 mmol, for compounds **28–31**) or diiminoisoindoline (6.5 mmol, for compounds **27** and **32–37**) and InCl<sub>3</sub> (2.2 mmol) in dry quinoline (15 ml) were refluxed for 2 h. After cooling

MeOH was added to precipitate the product. The product was washed thoroughly with MeOH (500 ml) and dried under vacuum.

**2,3,9,10,16,17,23,24-Octaphenoxypthalocyaninatoindium chloride 27.** Yield 43%, mp >275 °C (Found: C, 68.4; H, 3.2; N, 7.9. C<sub>80</sub>H<sub>48</sub>N<sub>8</sub>O<sub>8</sub>InCl requires C, 68.6; H, 3.5; N, 8.0%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 346, 612 and 683 (5.4);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  688, 743, 891, 1030, 1088, 1162, 1204, 1272, 1332, 1399, 1450, 1489 and 1589;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.00–7.41 (40H, m) and 8.80 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 126.8, 129.1, 130.7, 133.0, 133.2, 135.1, 136.7 and 153.4; *m/z* (FAB) 1398/1400 (M<sup>+</sup>, 100%), 1364 (M<sup>+</sup> – Cl).

**2,3,9,10,16,17,23,24-Octakis(*p*-fluorophenoxy)phthalocyaninatoindium chloride 28.** Yield 52%, mp >275 °C (Found: C, 62.0; H, 2.8; N, 7.2. C<sub>80</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>F<sub>8</sub>ClIn requires C, 62.25; H, 2.6; N, 7.3%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 366, 627 and 697 (5.15);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  831, 894, 1029, 1091, 1136, 1195, 1274, 1339, 1401, 1452, 1502 and 1608;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.20 (16H, m), 7.21 (16H, m) and 8.74 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 114.4, 117.4, 117.7, 117.9, 134.2, 152.4, 153.4, 159.3 and 161.7; *m/z* (FAB) 1542/1544 (M<sup>+</sup>, 100%), 1508 (M – Cl).

**2,3,9,10,16,17,23,24-Octakis(*p*-chlorophenoxy)phthalocyaninatoindium chloride 29.** Yield 0.6 g, 48%, mp >275 °C (Found: C, 57.5; H, 2.6; N, 6.5. C<sub>80</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Cl<sub>8</sub>In requires C, 57.3; H, 2.3; N, 6.7%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 364, 630, 669 and 690 (5.42);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1088, 1208, 1268, 1398, 1451, 1485 and 1585;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.13 (16H, d, *J* 8.9), 7.39 (16H, d, *J* 8.9) and 8.97 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 120.7, 121.1, 130.4, 130.9, 131.1, 134.6, 151.6 and 156.4; *m/z* (FAB) 1670/1672/1674/1676 (M<sup>+</sup>, 100%).

**2,3,9,10,16,17,23,24-Octakis(*p*-bromophenoxy)phthalocyaninatoindium chloride 30.** Yield 34%, mp 243–245 °C (Found: C, 47.1; H, 1.8; N, 5.4. C<sub>80</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Br<sub>8</sub>ClIn requires C, 47.3; H, 2.0; N, 5.5%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 364, 629, 667 and 698 (5.05);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1090, 1209, 1281, 1399, 1451, 1482, 1560, 1579 and 1618;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.06 (16H, d, *J* 8.9), 7.53 (16H, d, *J* 8.9) and 8.00 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 116.1, 117.8, 120.4, 121.1, 121.5, 134.1, 151.5 and 157.1; *m/z* (FAB) 2024/2026/2028/2030 (M<sup>+</sup>, 100%).

**2,3,9,10,16,17,23,24-Octakis(*p*-iodophenoxy)phthalocyaninatoindium chloride 31.** Yield 23%, mp 220–222 °C (Found: C, 39.9; H, 1.5; N, 4.8. C<sub>80</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>I<sub>8</sub>ClIn requires C, 39.9; H, 1.7; N, 4.7%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 363, 629, 671 and 699 (5.1);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  894, 1007, 1098, 1208, 1281, 1400, 1449, 1479, 1560 and 1618;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 6.96 (16H, d, *J* 8.9), 7.83 (16H, d, *J* 8.9), 8.98 (8H, d);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 96.1, 116.2, 121.4, 122.3, 140.0, 140.3, 153.8 and 156.5; *m/z* (FAB) 2406/2408 (M<sup>+</sup>, 100%).

**2,3,9,10,16,17,23,24-Octakis(cumylphenoxy)phthalocyaninatoindium chloride 32.** Yield 2.8 g, 66%, mp 139–141 °C (Found: C, 77.6; H, 5.3; N, 4.5. C<sub>152</sub>H<sub>128</sub>N<sub>8</sub>O<sub>8</sub>InCl requires C, 77.85; H, 5.5; N, 4.8%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 366, 629 and 699 (5.17);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  764, 893, 1029, 1084, 1172, 1211, 1270, 1385, 1399, 1476, 1637, 2868, 2924 and 2965;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.71 (48H, s), 7.08–7.28 (72H, m) and 9.02 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 32.1, 43.7, 118.9, 119.8, 126.8, 127.9, 129.2, 129.4, 134.9, 147.2, 151.7, 152.4, 153.7 and 156.4; *m/z* 2342/2344 (M<sup>+</sup>, 100%).

**2,3,9,10,16,17,23,24-Octakis(3,5-di-*tert*-butylphenoxy)phthalocyaninatoindium chloride 33.** Yield 1.83 g, 46%, mp >200–202 °C (Found: C, 74.9; H, 7.75; N, 4.7. C<sub>144</sub>H<sub>176</sub>N<sub>8</sub>O<sub>8</sub>InCl requires C, 75.3; H, 7.7; N, 4.9%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log

$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 356, 633 and 703 (5.3);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  712, 961, 1036, 1090, 1200, 1270, 1296, 1399, 1458, 1586, 1609, 2866, 2904 and 2964;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.33 (144H, s), 7.13 (16H, s), 7.25 (8H, s), 9.08 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 32.5, 36.2, 113.8, 115.4, 118.7, 134.5, 152.7, 153.8, 153.9 and 157.8; *m/z* (FAB) 2294/2296 (M<sup>+</sup>, 100%).

**2,3,9,10,16,17,23,24-Octakis(phenylthio)phthalocyaninatoindium chloride 34.** Yield 50%, mp 169–171 °C (Found: C, 62.7; H, 3.1; N, 7.5; S, 17.0. C<sub>80</sub>H<sub>48</sub>N<sub>8</sub>S<sub>8</sub>InCl requires C, 62.9; H, 3.2; N, 7.3; S, 16.8%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 357, 659 and 735 (5.16);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  688, 741, 838, 943, 1023, 1063, 1111, 1175, 1278, 1324, 1368, 1402, 1475, 1580, 1677 and 1719;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.12–7.35 (40H, m) and 8.72 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 126.8, 129.1, 130.8, 133.0, 135.1, 136.8, 142.2 and 153.8; *m/z* (FAB) 1526/1528 (M<sup>+</sup>, 15%), 1491 (M<sup>+</sup> – Cl, 100%).

**1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecakis(*p*-chlorophenoxy)phthalocyaninatoindium chloride 35.** Yield 38%, mp 188–190 °C (Found: C, 57.35; H, 2.2; N, 4.3. C<sub>128</sub>H<sub>64</sub>N<sub>8</sub>O<sub>16</sub>Cl<sub>17</sub>In requires C, 57.2; H, 2.4; N, 4.2%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 344, 659, 682 and 738 (5.29);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1206;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 6.41 (16H, d, *J* 8.9), 6.70 (16H, d, *J* 8.9), 6.90 (16H, d, *J* 8.9) and 7.04 (16H, d, *J* 8.9);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 117.6, 120.2, 128.0, 129.1, 129.8, 130.2, 130.3, 145.3, 145.4, 152.8, 156.0 and 157.4; *m/z* (FAB) 2680/2682/2684/2686 (M<sup>+</sup>, 100%).

**Phenyl[2,3,9,10,16,17,23,24-octakis(*p*-chlorophenoxy)phthalocyaninato]indium 36.** A freshly prepared solution of PhMgBr (3 M, 2 ml) was added dropwise to a stirred solution of phthalocyanine **29** (200 mg, 0.074 mmol) in dry THF (20 ml). After monitoring the reaction by TLC (silica gel/toluene), the reaction was stopped when all of the phthalocyanine complex had been consumed. The resulting deep green solution was then poured onto ice, extracted several times with Et<sub>2</sub>O, washed with water and dried over MgSO<sub>4</sub>. The solvent was evaporated *in vacuo* and the residue was subjected to column chromatography. Elution with dichloromethane gave the *title compound* as a green solid (24 mg, 12%) mp >275 °C (Found: C, 57.5; H, 2.6; N, 6.5. C<sub>86</sub>H<sub>45</sub>N<sub>8</sub>O<sub>8</sub>Cl<sub>9</sub>In requires C, 57.3; H, 2.4; N, 6.7%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 384, 627 and 697 (5.24);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  692, 735, 1020, 1088, 1161, 1209, 1268, 1283, 1398, 1453, 1488 and 1585;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 4.00 (2H, s, br), 5.93 (2H, s), 6.11 (1H, s), 7.15 (16H, d, *J* 8.9), 7.41 (16H, d, *J* 8.9) and 9.01 (8H, s);  $\delta_{\text{C}}$  (100.5 MHz; CDCl<sub>3</sub>) 121.5, 121.9, 123.0, 123.1, 126.6, 130.9, 131.3, 131.7, 131.9, 134.9, 152.3 and 156.7 (4 resonances are missing); *m/z* (FAB) 2722/2724/2726 (M<sup>+</sup>, 100%).

**Tetra-*tert*-butyltetra-*b,k,t,c*]phthalocyaninatoindium chloride (tetra-*tert*-butylphthalocyaninatoindium chloride) 37.** Yield 26%, mp >275 °C (Found: C, 70.3; H, 5.2; N, 9.9. C<sub>64</sub>H<sub>56</sub>N<sub>8</sub>InCl requires C, 70.6; H, 5.3; N, 10.3%);  $\nu_{\max}(\text{EtOH})/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 324, 706, 749 and 793 (5.39);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  472, 544, 569, 1022, 1084, 1102, 1259, 1355, 1459, 1560, 1626, 1637, 1655, 2905, 2930 and 2955;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.80 (36H, s) and 8.05–8.98 (20H, m); *m/z* (FAB) 1086/1088 (M<sup>+</sup>, 100%), 1051 (M<sup>+</sup> – 35(Cl)).

## Acknowledgements

We are grateful to the EPSRC national mass spectrometry service center for mass spectra.

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