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FULL PAPER

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A simple synthesis of symmetric phthalocyanines and their respective perfluoro and transition-metal complexes

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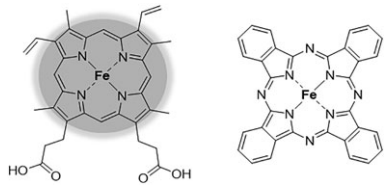
We report a simple synthesis protocol for making phthalocyanines (Pcs) starting from phthalonitriles. This method is general and requires no specialised equipment. The complexes are isolated and characterised using X-ray diffraction, NMR, FTIR and Raman spectroscopy and high-resolution mass spectrometry. First, we study and present a one-step synthesis route to a metal-free Pc (H_2PcH_{16}), as well as to the corresponding $MPcH_{16}$ complexes of Mn, Fe, Co, Ni, Cu and Zn. Then, we show that this route can also be used to make the fluorinated Pc analogues ($MPcF_{16}$). Finally, we present a new and useful procedure for inserting a metal ion into a metal-free H_2PcH_{16} ring, by direct metalation, yielding the corresponding $MPcH_{16}$ complex. This last method is especially useful if you want to make different $MPcH_{16}$ complexes.

KEYWORDS
macrocycles, metalation, NMR, one step synthesis, sustainable chemistry

1 | INTRODUCTION

Nature excels at evolving complex catalytic systems that can carry out "simple" chemical reactions cleanly and efficiently. The best (and to us chemists, most frustrating) examples are the enzymes nitrogenase[1] and methane monooxygenase,[2] which can fix nitrogen from the air and oxidise methane to methanol under ambient conditions, respectively. Another example is the activation of dioxygen, which is particularly challenging owing to its resonance stabilisation.[3] Here, one of nature's tools is the heme porphyrin molecule, which is embedded *in vivo* within the protective shell of the haemoglobin protein. This combined system shows many features of an ideal catalyst, operating efficiently at ambient temperature and pressure and using only a single iron atom per site. However, transferring this activity to *in vitro* and ultimately to industrial setups is far from trivial.

As part of our ongoing research into selective oxidation with molecular oxygen,[4–6] we tried building synthetic porphyrin analogues that could serve as good single-atom catalysts *in vitro*. For this, we turned to phthalocyanines (Pcs), which are highly stable two-dimensional macrocycles with a structure analogous to that of porphyrins (Scheme 1). Pcs are by no means new compounds. They were first characterized in 1934 by Linstead, after their discovery at Scottish Dyes Ltd., in Grangemouth.[7] Today, Pcs have a broad range of applications due to their strong colour and long-term stability. The copper phthalocyanine pigment is the single largest-volume colorant sold worldwide (mainly thanks to its availability and low price).[8,9] Pcs are applied as colour pigments for cars, due to their strong blue colour, insolubility in water, high dispersability and high heat stability.[10,11] They are also found in printing inks,[12]



SCHEME 1 left: Heme B, within the porphyrin highlighted in gray. Right: $FePcH_{16}$

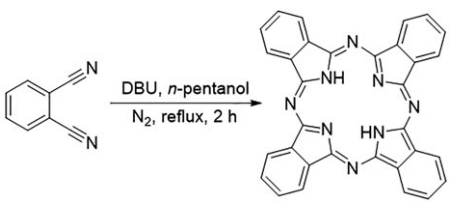
pen inks,[13,14] general dye applications, biomedical applications and in catalysis.[15–19]

Pcs can be made by the cyclisation of phthalonitriles in the presence of an organic base.[18,20–22] However, all these procedures include cumbersome and/or difficult synthesis or separation steps. The reactions require high temperature, typically above 180 °C,[23–25] leading to side products and lowering yields.[26] Other protocols require high pressure,[27] ionic liquids,[28] gaseous ammonia[26] or long reaction times (>150 hr).[29]

Notwithstanding the synthetic achievements of the above reports, one would prefer a simple, short and general synthesis protocol that requires no specialised equipment. In this paper, we present a one-step synthetic route to metal-free Pcs (hereafter noted as H_2PcH_{16}), their corresponding Mn, Fe, Co, Ni, Cu and Zn complexes ($MPcH_{16}$), and the perfluorinated analogues ($MPcF_{16}$). Furthermore, we present a new and facile procedure for making the same complexes by metalation of a metal-free H_2PcH_{16} ring.

2 | RESULTS AND DISCUSSION

First, we tried synthesising the metal-free H_2PcH_{16} ring following the procedures of Ogawa,[22] Wöhrle[30] and Kharisov.[21] These protocols give a good basis, advising the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base and alcohol solvents. They are based on the cyclisation of phthalonitrile (Scheme 2) but should be done under inert atmosphere, as moisture from the air can hydrolyse the nitrile groups, forming unwanted side products. The reaction proceeds best in an alcohol solvent, and is quite solvent-dependent.[22] We found that *n*-pentanol is the optimal choice because it also enables



SCHEME 2 Cyclisation of phthalonitrile gives the symmetric phthalocyanine

the solvation of various MPcs thanks to its higher boiling point. The reaction can be monitored visually, as dissolving the phthalonitrile in *n*-pentanol gives a milky liquid, which turns orange on addition of DBU. When this mixture is heated, it turns a dark blue-purple, indicating the formation of the Pc ring, which can then be washed and isolated (see experimental section for details).

We then turned to the metal-Pc complexes, or $MPcH_{16}$. In principle, these complexes can be made in two ways. One can either synthesise them in a single step from the metal precursor and phthalonitrile, or one can first synthesise H_2PcH_{16} ligand, and then complex it with the metal salt precursor. The first method is most commonly used, and here we present only a simplified variation. To the best of our knowledge, the second method is new.

The direct route to $MPcH_{16}$ is very similar to the synthesis of the H_2PcH_{16} ring. The reaction should be run under an inert atmosphere, not only to prevent the hydrolysis of the nitrile groups, but also to avoid unwanted oxidation of the metal cation (manganese, for example, will only form the complex as Mn^{2+}).[31] The choice of solvent is critical, because the reaction is run under reflux. Low-boiling point solvents such as pentane, cyclohexane, and even *n*-butanol gave only trace amounts of product. Control experiments showed that *n*-pentanol, which boils at 138 °C, gave the highest yields, with quantitative conversion of the phthalonitrile precursor after 2 hr.

We first optimised this protocol for $CuPcH_{16}$, and then applied it to the synthesis of the manganese, iron, cobalt, nickel and zinc analogues. All six complexes were characterised by IR, Raman, XRD and high-resolution MS (see experimental section and supporting information for details).

The FTIR spectra of H_2PcH_{16}, $CuPcH_{16}$ and $MnPcH_{16}$, Figure 1, show distinctive peaks. Small shifts between the Pcs are expected due to the different metals. The peak at

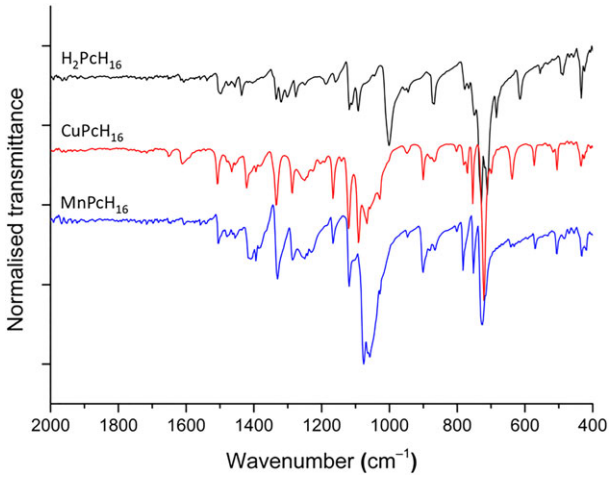


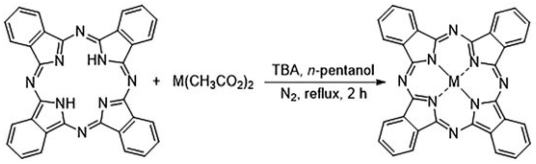
FIGURE 1 FTIR spectra of H_2PcH_{16} (black), $CuPcH_{16}$ (red) and $MnPcH_{16}$ (blue)

ca. 428 cm^{-1} shows the in-plane C–C–H bend, while that at ca. 717 cm^{-1} pertains to the out-of-plane C–C–H bend. Further, we observe the N–H bend at 752 cm^{-1}, the C–N stretch at 1118 cm^{-1}, the C–H bend (or possibly C–N stretch) at 1164 cm^{-1}, a strong C–C stretch peak at 1333 cm^{-1}, and the C=N stretch at 1508 cm^{-1}.[32–34]

The structure of $ZnPcH_{16}$ was also confirmed by ^{1}H-NMR, shown in Figure 2. The NMR clearly shows the formation of the highly symmetric complex, with only two types of chemically different hydrogen atoms, noted in the figure as α and β. The two double doublets at δ_H = 9.46–9.43 and at δ_H = 8.15–8.12 have coupling constants of 3.0 and 5.6 Hz, respectively, indicating *meta* and *ortho* coupling. This is in good agreement with what is expected for aromatic systems.[36]

The second route to $MPcH_{16}$ involves the insertion of a metal ion into a metal-free H_2PcH_{16} ring, giving the $MPcH_{16}$ product plus two equivalents of protons (Scheme 3). This is a new procedure, which we feel has merit, especially if you want to make several different $MPcH_{16}$ complexes. The main barrier to this reaction is the general insolubility of H_2PcH_{16} (it does dissolve in methylnaphthalene, even at room temperature, but unfortunately the metalation does not occur). However, we found that H_2PcH_{16} dissolves slightly under reflux in *n*-pentanol, giving an opportunity for the metal insertion to proceed. Once this starts, the reaction runs readily. Quantitative yield is reached after 2 h, and the product isolation is simple and straightforward (see experimental section for details). This reaction doesn't require inert atmosphere (control experiments showed that the metalation of $CuPcH_{16}$ proceeds readily under air).

This metalation requires an organic base to remove the acidic protons from the centre of the Pc ring. The reaction proceeds well with either tributylamine (TBA) or butyldimethylamine (BDMA), but no conversion was observed in the presence of DBU. We hypothesise that the 3D bulkiness of TBA and BDMA helps in unstacking the Pc rings, which are bound to each other by π–π



SCHEME 3 Complexation of the "empty" Pc with various metals; M = Mn, Fe, Co, Cu, Zn

interactions. At the end of the reaction, any excess base is easily removed by washing with dilute HCl.

The metalation was confirmed by powder X-Ray diffraction studies, which show a clear difference between the metal-free H_2PcH_{16} and the metalated $MPcH_{16}$. Figure 3 shows the diffraction patterns for three samples: an H_2PcH_{16} (black), a $CuPcH_{16}$ made using the direct route (red) and a $CuPcH_{16}$ made by the two-step method (blue). The H_2PcH_{16} sample shows four peaks in the region 2θ = 10–20°, namely at 13.6°, 14.95°, 15.95° and 16.8°. Conversely, both of the $CuPcH_{16}$ samples show peaks at 10.65°, 12.6°, 14.2°, 18.25° and 18.65°, which

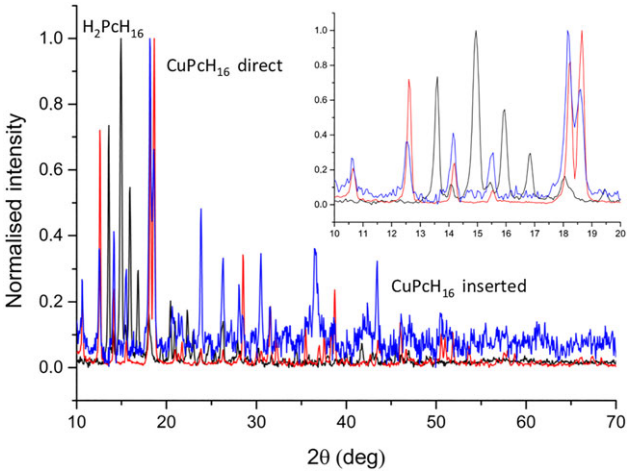


FIGURE 3 Powder x-ray diffraction spectrum of H_2PcH_{16} (black), $CuPcH_{16}$ (red) prepared via the direct route and $CuPcH_{16}$ (blue) made in the two-step method. The inset shows the zoomed-in spectra for the region 2θ = 10–20°

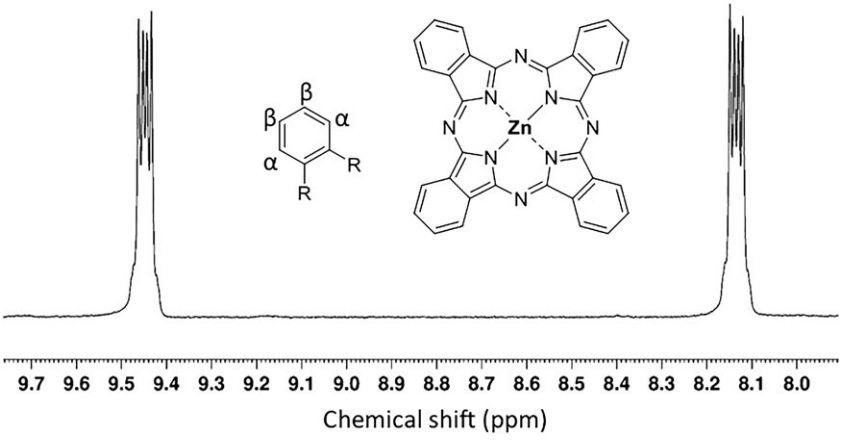
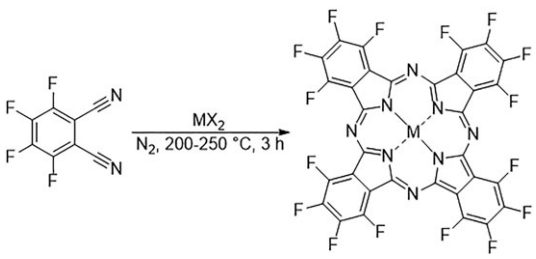


FIGURE 2 ^{1}H-NMR of $ZnPcH_{16}$ (300 MHz, $CDCl_3$). The α and β designations correspond to the two types of chemically different hydrogen atoms. Chemical shifts are reported relative to $CDCl_3$[35]

are distinct from those of H_2PcH_{16}. This also confirms that both metalation protocols result in the same $MPcH_{16}$ product.

The first route, starting from the phthalonitrile, can also be used for making the perfluorinated metal-Pc complexes $MPcF_{16}$ (Scheme 4). These are interesting because the perfluorinated ring creates a 'protective shell' around the complex that can prevent its oxidation and degradation. As an added bonus, the perfluorinated metal-Pc complexes are much more readily soluble in several organic solvents. Here we combined two different procedures, from van Lier et al.[37] and Morley and co-workers.[38]

Using 2,3,4,5-tetrafluorophthalonitrile as our starting material, we ran the reactions at higher temperatures, typically 200 °C for $CuPcF_{16}$ and 250 °C for $CoPcF_{16}$, $ZnPcF_{16}$, $FePcF_{16}$ and $MnPcF_{16}$, without any solvent (the reagent itself melts at ca. 85 °C, so in practice it serves as its own solvent). The synthesis is straightforward, giving the crude $MPcF_{16}$ complexes as dark blue/black solids. After crushing the hard black solids, any leftover metal salt is washed away with water. The product is then Soxhlet extracted using acetone and checked in NMR for starting material. Note that the type and the size of the reaction vessel is important here, because if you use a too-large round-bottomed flask the tetrafluorophthalonitrile will sublime on the top part of the flask, effectively separating your reagents from each other.



SCHEME 4 MX_2 = $Co(OAc)_2{\cdot}4H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, $Fe(OAc)_2$, $CuCl_2$, $Zn(OAc)_2{\cdot}2H_2O$

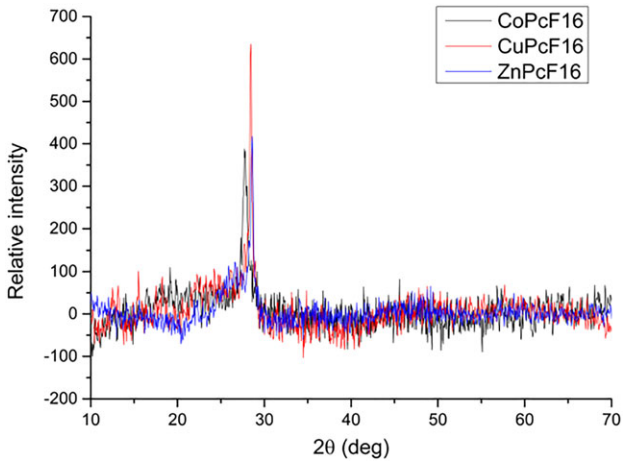


FIGURE 4 Powder x-ray diffraction of $MPcF_{16}$ complexes. The data for the iron and manganese complexes are omitted for clarity

Powder X-Ray diffraction studies of the different $MPcF_{16}$ compounds show one main single peak (Figure 4), which shifts slightly depending on the metal ion. In general, complexes of heavier metals show this peak at higher 2θ values: {$MnPcF_{16}$, 26.90°}; {$FePcF_{16}$, 27.65°}; {$CoPcF_{16}$, 27.70°}; {$CuPcF_{16}$, 28.45°}; and {$ZnPcF_{16}$, 28.6°}.

3 | CONCLUSIONS

We successfully developed the synthesis of H_2PcH_{16}, $MPcH_{16}$ and $MPcF_{16}$, for a variety of metals. Furthermore, we succeeded in inserting a metal into the H_2PcH_{16} structure. The synthetic protocols are easy, general and can be performed with standard lab equipment. We trust and hope that these simple and effective routes will help researchers who are interested in making phthalocyanines, increasing their variety of applications even further.

4 | EXPERIMENTAL SECTION

4.1 | Materials and instrumentation

All chemicals were purchased from either VWR chemicals, Fluorochem or Merck and were used without further purification, except for solvents, which were dried prior to reaction over 3 Å molecular sieves. All experiments were performed under nitrogen atmosphere, unless stated otherwise.

NMR spectra [^{1}H, ^{19}F] were measured on a Bruker AV 300 spectrometer. IR spectra (4000–400 cm^{-1}, resol. 0.5 cm^{-1}) were recorded on a Varian 660 FTIR spectrometer using ATR and the transmission technique. X-Ray diffraction (XRD) patterns were obtained with a MiniFlex II diffractometer using Ni-filtered CuKα radiation. The X-ray tube was operated at 30 kV and 15 mA, with a 0.01° step and 1 s dwell time. Raman spectra were recorded using a Renishaw InVia system (532 and 632.8 nm) and a Kaiser Optical Systems RXN-4 system (785 nm) coupled with fibre optics to an immersion probe with a short focal length.

Mass spectra were collected on two instruments: (A) AccuTOF LC, JMS-T100LP Mass spectrometer (JEOL, Akishima, Tokyo, Japan). ESI source, positive-ion mode; needle voltage 2500 V, orifice 1 voltage 120 V, orifice 2 voltage 9 V; ring Lens voltage 22 V; orifice 1 80 °C, desolvating chamber 250 °C. The samples were measured using flow injection with a flow rate of 0.01 ml/min, and the spectra were recorded with an average duration of 0.5 min. (B) AccuTOF GC v 4 g, JMS-T100GCV Mass

spectrometer (JEOL, Japan). FD emitter, Carbotec or Linden (Essen, Germany), FD 13 μm. Current rate 51.2 mA/min over 1.2 min.

4.2 | Procedure for synthesising the metal-free phthalocyanine (H_2PcH_{16})

Phthalonitrile (0.50 g, 3.9 mmol) was dissolved in *n*-pentanol (2 ml). Then 1,8-diazabicyclo(5.4.0)undec-7-ene (0.1 ml, 0.7 mmol, DBU) was added and the mixture was heated for 2 hr at 140 °C, forming a dark blue/purple solution (adding more DBU is unadvisable as this creates problems in the workup). The reaction was cooled down to ambient temperature, filtered and washed first with water (5 × 10 ml) and then with EtOH (5 × 10 ml) and dried in air at 20 °C. This yielded the product as dark blue/purple small needles, 0.33 gram (66 mol% based on phthalonitrile). HRMS (FD+) *m/z* calculated $C_{32}H_{18}N_8$, 514.165, found, 514.167. FTIR (cm^{-1}): 1110, 1095, 995, 717; Raman shift/cm^{-1}: 682, 723, 795, 1141, 1337, 1541. XRD (2θ°): 13.6, 14.95, 15.95, 16.8.

4.3 | General procedure for synthesising metal-containing phthalocyanines ($MPcH_{16}$) via the direct route

Phthalonitrile and the corresponding metal salt were dissolved in *n*-pentanol after which the DBU was added. The mixture was heated for 2 hr at 140 °C, forming a dark coloured solution. The reaction mixture was cooled down to ambient temperature, forming a solid. This was filtered under vacuum and washed with water (5 × 10 ml) and then with EtOH (5 × 10 ml). The residue was dried under air.

Example 1: $CuPcH_{16}$: Phthalonitrile (0.50 g, 3.9 mmol) and $Cu(OTf)_2$ (362 mg, 1.0 mmol) were dissolved in *n*-pentanol (2 ml). DBU (0.1 ml, 0.7 mmol) was added and the mixture was heated at 140 °C for 2 hr, forming a dark blue solution. The reaction was cooled down to ambient temperature, filtered under vacuum and washed with water (5 × 10 ml) and then with EtOH (5 × 10 ml). This gave the $CuPcH_{16}$ as a blue powder, 0.40 gram (70 mol% based on phthalonitrile). HRMS (FD+) *m/z* calculated $C_{32}H_{16}CuN_8$, 575.079, found, 575.107. FTIR (cm^{-1}): 1612, 1508, 1334, 1118, 1095, 717; Raman shift/cm^{-1}: 592, 680, 1142, 1340, 1449, 1523.

Example 2: $ZnPcH_{16}$: Phthalonitrile (0.50 g, 3.9 mmol) and $ZnCl_2$ (136 mg, 1.0 mmol) were dissolved in *n*-pentanol (2 ml). DBU (0.1 ml, 0.7 mmol) was added and the mixture was heated for 2 hr at 140 °C, forming a dark green solution. The reaction was cooled down to ambient temperature, filtered under vacuum and washed with water (5 x 10 ml) and then with EtOH (5 x 10 ml). This gave a green powder, weighing 263 mg (45 mol% based on phthalonitrile). HRMS (FD+) *m/z* calc. $C_{32}H_{16}N_8Zn$, 576.078, found 576.085. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.46–9.43 (8H, double doublet), 8.15–8.12 (8H, double doublet). FTIR (cm^{-1}):1594, 1482, 1328, 1112, 1083, 1058, 885, 746, 728; Raman shift/cm^{-1}: 160, 591, 674, 1330, 1495.

The syntheses of $FePcH_{16}$, $MnPcH_{16}$, $CoPcH_{16}$ and $NiPcH_{16}$ was similarly performed, using: $FeCl_2{\cdot}4H_2O$ (199 mg, 1 mmol, 16 mol% based on phthalonitrile), $MnCl_2{\cdot}2H_2O$, (162 mg, 1 mmol, 73 mol%), $CoCl_2{\cdot}6H_2O$ (238 mg, 1 mmol, 21 mol%), $Ni(OTf)_2$ (357 mg, 1 mmol, 66 mol%).

4.4 | Procedure for metalation of the H_2PcH_{16} (the two-step method)

The H_2PcH_{16} and the metal salt (1:2.5 equiv) were dissolved in *n*-pentanol. Tributylamine (TBA) was added and the mixture was heated for 2 hr at 160 °C and then cooled down to ambient temperature. The dark coloured mixture was filtered under ambient pressure, giving a dark-coloured cake. This was washed first with water (2 x 10 ml), then with 0.6 M HCl (1 x 10 ml), again with water (1 x 10 ml) and finally with EtOH (3 x 10 ml). The dark powder was dried in open air.

Example 1: $CuPcH_{16}$: The H_2PcH_{16} (20 mg, 0.04 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (20 mg, 0.1 mmol) were dissolved in *n*-pentanol (3.0 ml) together with the TBA (0.05 ml, 2 mmol). The mixture was heated for 2 hr at 160 °C, forming a dark blue solution. This was allowed to cool down to ambient temperature and then filtered, giving a dark-blue cake. The cake was washed first with water (2 x 10 ml), then with 0.6 M HCl (1 x 10 ml), again with water (1 x 10 ml) and finally with EtOH (3 x 10 ml). The resulting blue powder was dried in air, yielding 40 mg (100 mol% based on the H_2PcH_{16}). XRD (2θ°): 10.65, 12.6, 14.15, 18.25, 18.62, 23.8, 26.2.

Example 2: $MnPcH_{16}$: The H_2PcH_{16} (15 mg, 0.03 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (25 mg, 0.1 mmol) were dissolved in *n*-pentanol (3.0 ml) after which the TBA (0.05 ml, 2 mmol) was added. The reaction was heated at 160 °C for 2 hr, forming a green solution. The mixture was cooled down to ambient temperature and then filtered, giving a dark green cake. The cake was washed first with water (2 x 10 ml), then with 0.6 M HCl (1 x 10 ml), again with water (1 x 10 ml) and finally with EtOH (3 x 10 ml). While washing, the product lost its green colour, turning into a dark blue powder, which was air dried.

This gave 12 mg (70 mol% based on the H_2PcH_{16}). XRD (2θ°): 14.1, 15.5, 18.2, 23.75, 26.2.

The syntheses of $FePcH_{16}$, $ZnPcH_{16}$ and $CoPcH_{16}$ were performed similarly, starting from $Fe(OAc)_2$ (17 mg, 0.1 mmol, 100 mol% yield based on the H_2PcH_{16}), $Zn(OAc)_2{\cdot}2H_2O$ (26 mg, 0.12 mmol) and $Co(OAc)_2{\cdot}4H_2O$ (20 mg, 0.1 mmol, 57 mol% yield based on the H_2PcH_{16}).

4.5 | General procedure for the synthesis of metal-containing fluorophthalocyanine ($MPcF_{16}$)

Tetrafluorophthalonitrile and the corresponding metal salt were mixed and heated at 250 °C (200 °C in the case of copper) for 3 hr in a closed 10 ml round bottom flask. The reaction mixture was cooled down to ambient temperature, forming a black solid. This was crushed, filtered and washed with water (5 × 10 ml) and extracted by soxhlet using acetone. The acetone filtrate was collected and evaporated, yielding the product.

Example 1: $CuPcF_{16}$: Tetrafluorophthalonitrile (0.20 g, 1 mmol) and $CuCl_2$ (0.135 g, 1 mmol) were added and heated for 3 hr at 200 °C, forming a dark blue/green solid. After it was allowed to cool down to ambient temperature, it was vacuum filtrated and washed with water (5 × 10 ml), EtOH (5 × 10 ml) and acetone (10 × 10 ml), respectively. The acetone filtrate was evaporated and gave 95 mg, (45 mol% based on tetrafluorophthalonitrile). HRMS (FD+) *m/z* calc. $C_{32}CuF_{16}N_8$, 862.928, found, 862.974. FTIR (cm^{-1}): 1737, 1488, 1384, 1321, 1151, 962; Raman shift/cm^{-1}: 587, 734, 1360, 1480, 1525. XRD (2θ°): 28.45.

Example 2: $CoPcF_{16}$: Tetrafluorophthalonitrile (0.5 g, 2.5 mmol) and Co $(OAc)_2{\cdot}4H_2O$ (0.623 g, 2.5 mmol) were mixed and heated at 250 °C for 3 hr, forming a black solid. The solid was cooled down to ambient temperature, crushed, filtered and washed with water (5 x 10 ml). Soxhlet extraction using acetone gave a blue liquid. Filtration and evaporation of the acetone gave the product in 66 mg, (12 mol% based on tetrafluorophthalonitrile). HRMS (FD+) *m/z* calculated $C_{32}CoF_{16}N_8$, 858.932, found, 858.949. FTIR (cm^{-1}): 1471, 1261, 1097, 1027, 802; Raman shift/cm^{-1}: 587, 729, 1400, 1530, 1614. XRD (2θ°): 27.7.

The syntheses of $FePcF_{16}$, $ZnPcF_{16}$ and $MnPcF_{16}$ were performed similarly, starting from $Fe(OAc)_2$ (435 mg, 2.5 mmol, 15 mol% based on tetrafluorophthalonitrile), $Zn(OAc)_2{\cdot}2H_2O$ (550 mg, 2.5 mmol, 33 mol% yield) and $Mn(OAc)_2{\cdot}4H_2O$ (613 mg, 1 mmol, 16 mol% yield).

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