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New *meso*-substituted *trans*-A_2B_2 di(4-pyridyl)-porphyrins as building blocks for metal-mediated self-assembling of 4 + 4 Re(I)–porphyrin metallacycles†

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The reaction between 5-(4-pyridyl)dipyrrylmethane and aromatic aldehydes affords *meso*-arylsubstituted *trans*-A_2B_2 di(4-pyridyl)porphyrins which are key building blocks in the metal-mediated self-assembling of supramolecular structures. A careful optimization of the reaction conditions allowed us to obtain 5,15-diphenyl-10,20-di(4-pyridyl)porphyrin (**P1**), and two analogues bearing on the *meso*-phenyl substituents two dipropyl- (**P4**) or dihexyl-alkyl chains (**P5**), with yields ranging from 53 to 63%. Porphyrin **P1** reacts with $Re(CO_5)Br$ to give the expected 4 + 4 Re(I)–porphyrin metallacycle which has been fully characterized by means of infrared, NMR and UV-Vis (absorption and emission) spectroscopies and by guest inclusion studies. Unexpectedly the addition of alkyl chains to the porphyrin fragment, which increase the solubility of the porphyrin in organic solvents, has the opposite effect on the adduct with Re(I). Indeed, the reaction between $Re(CO_5)Br$ and porphyrins **P4,5** gives very insoluble materials, hampering their complete characterization.

Introduction

Self-assembling of tailored building blocks is a widely used strategy for obtaining complex molecular architectures in solution and in the solid state. Among the different approaches that can be exploited to guide the self-assembling process, the metal-mediated directional-bonding has emerged over the years as a general, high yielding synthetic strategy that gives access to a variety of 2D (rhomboids, squares, rectangles, triangles, *etc*.) and 3D (trigonal pyramids and prisms, cubes, cuboctahedra, double squares, adamantanoids, dodecahedra, and a variety of other cages) supramolecular ensembles.[1] One of the most attractive characteristics of the metal-mediated self-assembling approach is the relatively high degree of control that can be achieved on the geometry and on the thermodynamic and kinetic stability of the supramolecular adducts. This is obtained by the appropriate selection of organic ligands with a topologically well-defined set of donor atoms which are combined with metal fragments with the desired properties such as the bite angle, number and geometry of the binding sites and stability of the metal–ligand interaction. In this context, porphyrin-based ligands and in particular *meso* substituted pyridyl-porphyrins have attracted increasing interest because of several appealing features: rigid and planar geometries, high chemical stability, inherent symmetry, intense electronic absorption bands in the visible region, a relatively long fluorescence decay time, and facile tunability of their optical and redox properties by metallation/functionalization.[2] Conjugation of these chromophoric ligands with several metal ions (Pd(II), Pt(II), Ru(II), Re(I))[3] has led to a variety of coordination adducts with interesting potential applications in the fields of optoelectronic, catalysis, molecular recognition, *etc*.

A particularly interesting class of metal-bridged arrays is that formed by porphyrin ligands with Re(I) complexes. Indeed, this metal ion, usually introduced using the $Re(CO)_5X$ (X = Cl or Br) precursor, ensures high thermodynamic stability of the supramolecular adducts at room temperature. At high temperatures, however, rhenium–N bonds are labile enough to allow for conversion of kinetic structures (such as open oligomers) to thermodynamic structures during the assembly process. The group of J. T. Hupp has shown that in weakly coordinating solvents such as a mixture of toluene and tetrahydrofuran, the 1 : 1 combination of $Re(CO)_5X$ and a rigid or semi-rigid dipyridyl ligand (L) generally produces molecular squares (Fig. 1) in high yield.[4] The strong *trans* labilizing effect of CO allows a pair of *cis* carbonyl ligands, and only those, to be replaced first with solvent molecules and then with the pyridyl donors, while maintaining a *fac* geometry of the residual ones. With ditopic ligands, the number of Re–N bonds is maximized by forming cyclic as opposed to open structures and strain is minimized by forming structures having square geometries (although triangular assemblies are known).[5]

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†Electronic supplementary information (ESI) available: Additional experimental information, including NMR, IR and UV-Vis spectra. See DOI: 10.1039/c3ob40452h

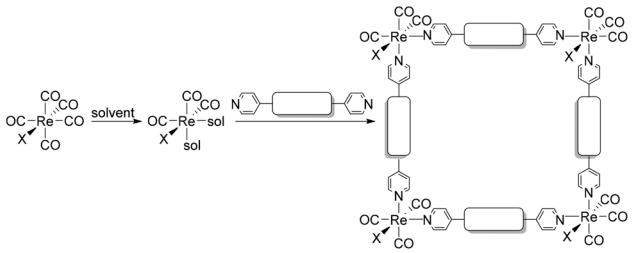


Fig. 1 Formation of a 4 + 4 Re(I)–L metallacycle.

The 4 + 4 Re(I)–L metallacycles thus obtained have a roughly cubical box structure with edges, in the case of L = *trans*-dipyridylporphyrin, about 2 nm long. The porphyrin ligands may rotate around the Re–pyridyl bond and computational studies suggest that in the lowest energy conformers the four tetrapyrrolic rings assume a tilted disposition thus reducing the inner volume of the molecular box.[6] However, Hupp and co-workers have demonstrated that Re(I)-metallacycles with zincated porphyrin are able to incorporate inside the cavity different N-donor ligands that bind axially to the Zn(II) ions.[7] The ability of the Re(I)-metallacycle to bind substrates, combined with its photo-luminescence properties, is at the basis of the development of epoxidation catalysts,[8] chemosensors[9] and of polymeric materials with interesting properties for chemical sensing and molecular sieving.[10]

We have recently reported that a 4 + 4 Re(I)–porphyrin metallacycle, in which the porphyrins are functionalized with peripheral carboxylic acid residues, is able to form a dimeric nanopore in a phospholipid bilayer showing tuneable ionophoric activity.[11] In this case the robustness of the metallacycle was essential to preserve its structural integrity in the complex and competitive membrane environment. Indeed, the attempt to use Pd(II), which gives kinetically labile complexes, and di(*meso*-3-pyridyl)porphyrins to assemble a cyclic structure directly into liposomes led to a complex mixture of linear and cyclic adducts.[12]

Stimulated by this finding and following our interest in synthetic ionophores[13] we decided to widen the library of available 4 + 4 Re(I)–porphyrin metallacycles. Indeed, despite their interesting properties, the number of such adducts described in the literature is extremely limited and this is probably a consequence of the non-trivial synthesis of the porphyrin precursors, of the scarce solubility of the Re(I) adducts, and of their difficult characterization. In this manuscript we report on the synthesis and characterization of new *trans*-dipyridylporphyrins designed to improve their solubility in organic solvents, and our subsequent efforts to prepare and characterize new 4 + 4 Re(I)–porphyrin metallacycles.

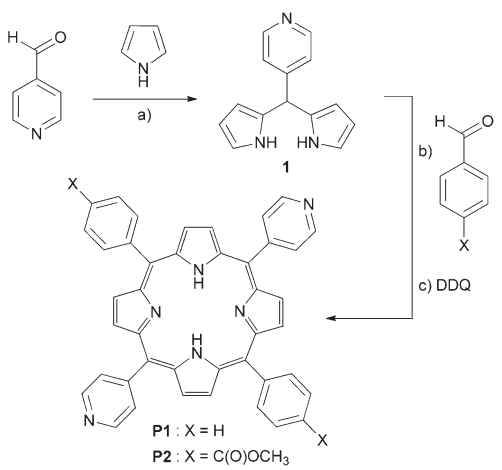
Results and discussion

Synthesis of *meso*-substituted *trans*-A_2B_2 di(4-pyridyl)-porphyrins

Despite the many literature reports, the synthesis of porphyrins is still facing problems of low yields and difficult purification. In particular, with *meso* substituted pyridylporphyrins the standard condensation procedures are often scarcely effective and a careful optimization of the experimental parameters is required to ensure a satisfactory yield of the desired product. We are interested in *meso*-substituted *trans*-A_2B_2 dipyridylporphyrins with two *trans meso* positions occupied by 4-pyridyl residues and the other two functionalized with conformationally rigid moieties, which may be further transformed into useful functional groups. We thus chose 5,15-diphenyl-10,20-di(4-pyridyl)porphyrin (*trans*-DPyDPhP, **P1**) as a lead compound for the optimization of the synthetic procedures.

trans-A_2B_2 dipyridylporphyrins may be prepared with the conventional Adler's synthesis by mixing the two aldehydes and pyrrole in acidic conditions.[14] This approach is still followed, particularly when also the isomers other than the *trans*-A_2B_2 are desired, but the yields are usually in the range 2–4% and the purification of the six regioisomers formed is quite time consuming.[15] A more convenient method for the direct synthesis of *meso*-substituted *trans*-A_2B_2 porphyrins is the reaction of a dipyrromethane with an aldehyde in acidic conditions proposed by Lindsey (Scheme 1).[16] With this approach the reported yields of *trans*-DPyDPhP,[17] and of other related porphyrins with differently substituted phenyl rings, are in the 6–16% range.[18] Moving from this standpoint, we investigated a set of reaction conditions in order to increase the synthetic efficiency. To ensure flexibility in the substitution pattern of the phenyl rings we started with 5-(4-pyridyl)dipyrrylmethane which is easily prepared in 65% yield from 4-pyridinecarboxyaldehyde and pyrrole.[19] The dipyrromethane was reacted with benzaldehyde in the presence of trifluoroacetic acid (TFA) under different reaction conditions, as summarized in Table 1.

All the reactions were carried out using equimolar concentrations of dipyrromethane and aldehyde (6.4×10^{-3} M) and varying the number of equivalents of TFA, the solvent, the temperature and the reaction time. The reaction is very sensitive to the different parameters and in several conditions we



Scheme 1 (a) Pyrrole as a solvent, 85 °C, 15 h, 65%; (b) TFA, DCM, 20 min., 0 °C; (c) r.t., 1 h, 53% from **1**.

Table 1 Optimization of the *trans*-DPyDPhP synthesis[a]

Entry	TFA	Temp.	Time	Solvent	Yield
1	0.22 eq.	rt	Overnight	DCM	Traces
2	0.22 eq.	rt	Overnight	MeOH	Traces
3	1 eq.	rt	Overnight	DCM	Traces
4	1 eq.	rt	Overnight	MeOH	Traces
5	1 eq.	Reflux	Overnight	MeOH	Traces
6	5 eq.	rt	Overnight	MeOH	Traces
7	10 eq.	0 °C	3 hours	DCM	12%
8	10 eq.	0 °C	20 minutes	DCM	23%
9	43 eq.	0 °C	20 minutes	DCM	53%

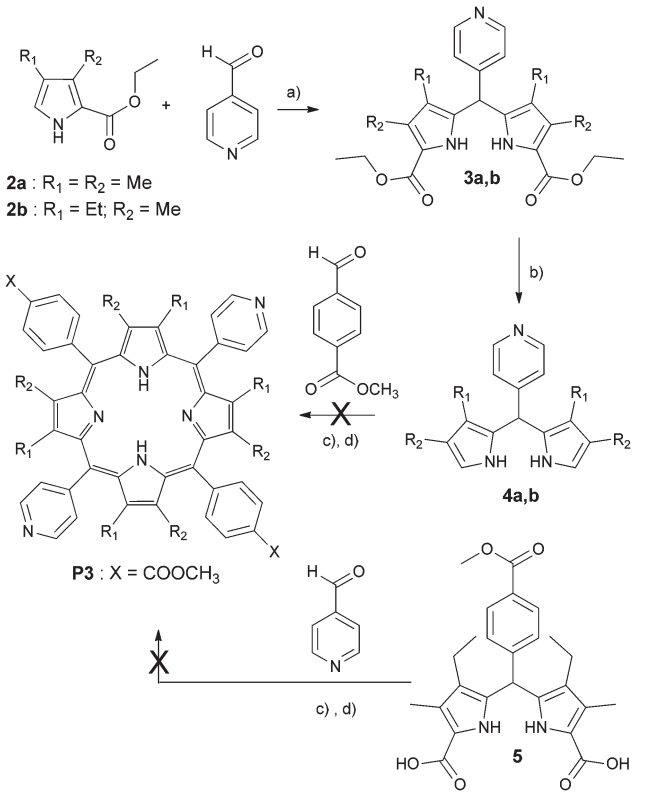
[a] All reactions were carried out using equimolar amounts of dipyrromethane and aldehyde (2.24 mmol) in 350 mL of solvent. The reaction was quenched by the addition of DDQ (4.48 mmol).

obtained only traces of the desired product. The best results were obtained for a high number of equivalents of the acid, a short reaction time and a low temperature (entry 9). In these conditions the yield in isolated product is 53%, which is pretty high for porphyrin synthesis. Using this optimized procedure we also obtained 39% yield in the synthesis of 5,15-di(4-carboxymethylphenyl)-10,20-di(4-pyridyl)porphyrin (**P2**).[11]

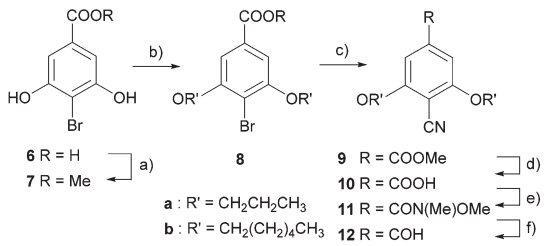
Porphyrins and porphyrins adducts, in particular their neutral Re(I) derivatives, are generally poorly soluble in organic solvents and an increased solubility is usually obtained by the insertion of alkyl chains in positions 3,4 of the β-pyrrolic ring. We therefore prepared the dipyrromethanes **4a,b** and **5**[20] by condensation of the substituted pyrrole, obtained *via* the Barton–Zard synthesis,[21] and the appropriate aldehyde (Scheme 2). Each dipyrromethane was then reacted with the complementary aldehyde in order to obtain porphyrins **P3a,b**. However, either under the optimized reaction conditions reported above, or by increasing the temperature, the reaction times and also testing different procedures,[22] the desired porphyrins were never obtained. Although there are several examples of *meso* tetra-aryl porphyrins per-alkyated on the β-pyrrolic rings, a search of the literature shows that the only known compound containing *meso*-pyridyl groups is the 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,10,15,20-tetra-(4-pyridyl)-porphyrin which was prepared by Adler's method.[23] Clearly, the high steric hindrance of the alkyl substituents together with the peculiar reactivity of the pyridyl moiety makes the preparation of this type of porphyrins quite difficult.

Due to the synthetic problems illustrated above, we decided to insert the alkyl chains on the *meso* aryl rings. We therefore prepared aldehydes **12a,b** bearing two propyloxy or hexyloxy chains in *meta* position and a cyano group in *para* (Scheme 3). This last one could be eventually easily transformed into some useful functional groups.

The synthesis started from commercially available 4-bromo-3,5-dihydroxybenzoic acid which was transformed into its methyl ester in 96% yield. The ester was then reacted with propyl- or hexylbromide by Williamson ether synthesis to give **8a**[24] and **8b** in 95% and 90% yield, respectively. Nucleophilic substitution of the bromoderivate **8** with CuCN gave the cyano compound **9**. The drastic reaction conditions required for this

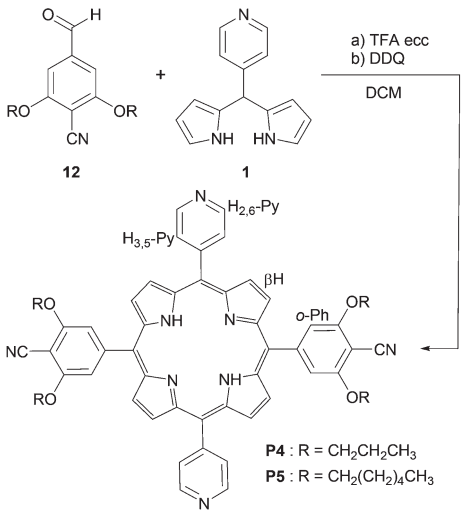


Scheme 2 (a) *p*-TSA, toluene, reflux, 48 h, **3a** = 81.6%, **3b** = 39.8%; (b) NaOH, ethylene glycol, reflux, 24 h, **4a** = 88.4%, **4b** = 53.4%; (c) TFA, DCM, 20 min., 0 °C; (d) r.t., 1 h, no product was isolated.



Scheme 3 (a) H_2SO_4, MeOH, reflux, 18 h, 96%; (b) 1-bromoalkane, K_2CO_3, TBABr, acetone, reflux, 18 h, **8a** = 95%, **8b** = 90%; (c) CuCN, DMF, reflux, 48 h; (d) LiOH, THF–MeOH, TBABr, r.t., 18 h, **10a** = 70%, **10b** = 81% from **8**; (e) hydroxylamine hydrochloride, 4-methylmorpholine, isobutyl chloroformate, DCM, r.t., 18 h, **11a** = 57%, **11b** = 67%; (f) $LiAlH_4$, THF, r.t., 4 h, **12a** = 79%, **12b** = 75%.

step (reflux at 150–160 °C in a strongly acidic medium) promoted the partial hydrolysis of the methyl ester. Therefore, the following hydrolysis step was conducted directly on the crude of the reaction affording the desired carboxylic acids **10a** and **10b** in 70% and 81% yield, respectively, calculated from **8**. The acids were transformed into the corresponding Weinreb amides **11a** and **11b** with 57% and 67% yield, respectively, by treatment with hydroxylamine hydrochloride in the presence of 4-methylmorpholine as a base and isobutyl chloroformate as a condensing agent. Final reduction with $LiAlH_4$ gave aldehydes **12a** and **12b** with 79% and 75% yield, respectively.



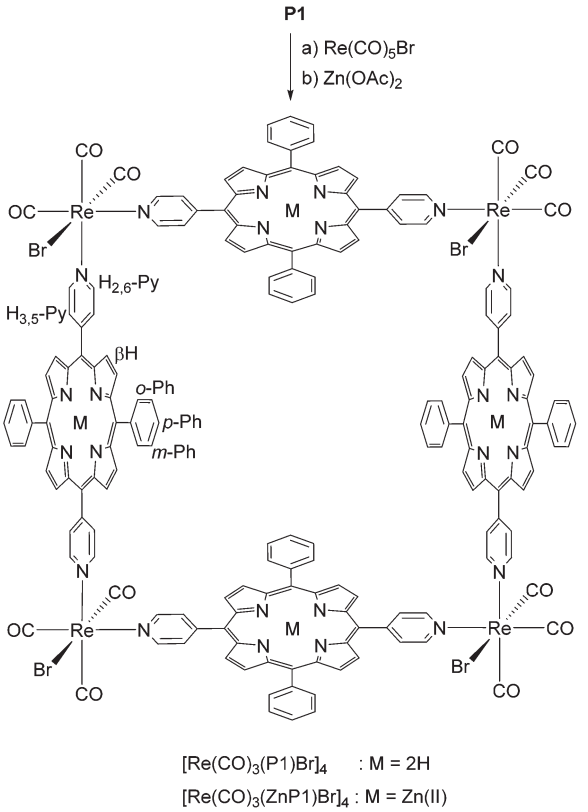
Scheme 4 (a) TFA, DCM, 20 min., 0 °C; (b) r.t., 1 h, **P4** = 61%, **P5** = 63%; from **12**.

Reaction of aldehydes **12a,b** with dipyrromethane **1** under optimized conditions (TFA 43 eq., DCM, 0 °C, 20 min, followed by oxidation with DDQ) gave porphyrins **P4** and **P5** in 61% and 63% yield, respectively (Scheme 4). The two porphyrins were fully characterized by ^{1}H-NMR, ^{13}C-NMR, IR and UV-Vis spectroscopies and ESI-MS spectrometry. As expected, porphyrins **P4** and **P5** are very well soluble in the common organic solvents.

Synthesis and characterization of 4 + 4 Re(I)–porphyrin metallacycles

The assembling of the 4 + 4 Re(I)–porphyrin metallacycles followed the procedure reported by Hupp and co-workers.[7a] Equimolar amounts of porphyrin **P1** and $Re(CO)_5Br$ (0.162 mmol) dissolved in 4 : 1 THF–toluene (80 mL) were heated at reflux for 48 hours (Scheme 5). Precipitation of the crude product and repeated washing cycles with diethyl ether afforded metallacycle $[Re(CO)_3(P1)Br]_4$ as a maroon microcrystalline powder in 87% yield. The zincated derivative $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ was obtained by treatment of a chloroform solution of $[Re(CO)_3(P1)Br]_4$ with a saturated solution of $Zn(OAc)_2$ in methanol. After stirring overnight the solvents were evaporated and the residue was washed thoroughly with methanol to eliminate the excess of $Zn(OAc)_2$. $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ was obtained as a purple solid in 72% yield. While the $[Re(CO)_3(P1)Br]_4$ is soluble in common solvents such as $CHCl_3$, DMSO, and THF, its zincated derivative is less soluble.

Following the original 1997 report by Hupp and co-workers,[7a] only about seven tetraporphyrin metallacycles with Re-$(CO)_3$X (X = Cl^- or Br^-) corners differing in the nature of the *trans*-di(pyridyl)porphyrin edges have been described.[4,7b,11] Moreover, full characterization of these metallacycles remains problematic and partially unachieved. Difficulties in gaining an unambiguous characterization derive from several inherent properties of these neutral tetraporphyrin assemblies, in particular their low solubility and high tendency to form



Scheme 5 (a) THF–toluene 4 : 1, 48 h, reflux, 87%; (b) $CHCl_3$, overnight, r.t., 72%.

aggregates in solution and the insufficient volatility, which strongly hampers the use of mass spectrometry experiments. In addition, rotational freedom of the porphyrin edges around the metal–pyridyl bond may lead to a population of conformers, which is further complicated by the presumably statistical distribution of the *syn*/*anti* isomers derived by the orientation of the halide ligand on each rhenium corner that can be up or down with respect to the square framework.[4] As a consequence, the structural data present in the literature are scarce and the determination of the size and nuclearity of such metallacycles (4 + 4 *vs.* 3 + 3 or else) is based on one gel permeation chromatography study,[25] on the determination of the diffusion coefficients using pulsed-field-gradient NMR,‡[26] and on one reported FAB mass spectrum.[7a] We have recently reported the characterization of one such metallacycle by means of infrared, NMR and UV-Vis (absorption and emission) spectroscopies which, combined with guest inclusion studies, gave support to the cyclic 4 + 4 structure.[11] We, therefore, applied the same methodological approach for the characterization of $[Re(CO)_3(P1)Br]_4$.

‡The reported NMR characterization of these species is very poor. Apart our previous communication (ref. 11), in which we reported some ^{1}H NMR data, this is the first paper, to our knowledge, in which a 4 + 4 Re(I)–dipyridylporphyrin metallacycle has been fully characterized by ^{1}H NMR. The only other two ^{1}H NMR spectra we found in the literature, refer to 4 + 4 Pt(II)–porphyrin metallacycles (ref. 3*d* and 3*f*).

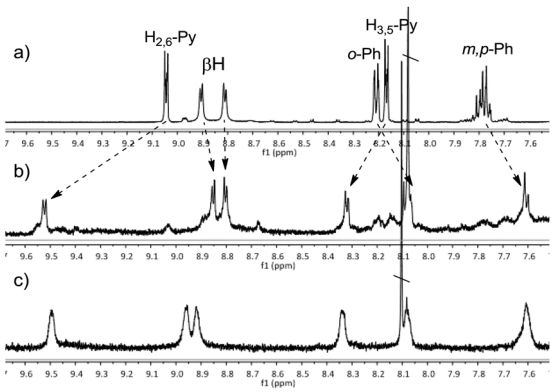


Fig. 2 Selected regions of the ^{1}H-NMR spectra (500 MHz, $CDCl_3$) of (a) porphyrin **P1**, (b) $[Re(CO)_3(P1)Br]_4$, and (c) $[Re(CO)_3(Zn{\cdot}P1)Br]_4$.

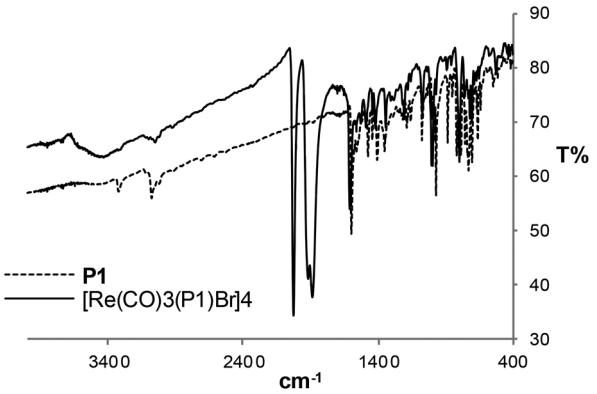


Fig. 3 IR spectra in KI of **P1** (dashed line) and $[Re(CO)_3(P1)Br]_4$ (solid line).

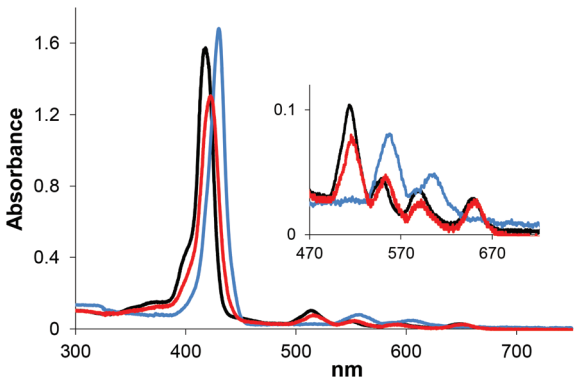


Fig. 4 UV-Vis spectra of **P1** (black), $[Re(CO)_3(P1)Br]_4$ (red), and $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ (blue) in chloroform at *ca.* 2×10^{-5} M concentration (calculated with respect to the porphyrin). The inset shows an enlargement of the Q bands region.

Fig. 2 shows the downfield region of the ^{1}H-NMR spectra (500 MHz, $CDCl_3$) of porphyrin **P1**, metallacycle $[Re(CO)_3(P1)Br]_4$ and its zincated analogue $[Re(CO)_3(Zn{\cdot}P1)Br]_4$. The number of resonances in the ^{1}H-NMR spectrum of $[Re(CO)_3(P1)Br]_4$ is consistent with the formation of a highly symmetric cyclic structure, with proton chemical shifts in good agreement with those reported for other related metallacycles (assignments were done with a 2D HH-COSY experiment, see ESI†). The spectrum indicates that all the available pyridyl fragments are bound to Re(I). The doublet of the $H_{2,6}$-Py protons is downfield shifted as compared to the parent porphyrin as a consequence of coordination of the pyridyl group to the Re(I) center ($\Delta\delta$ = 0.48 ppm), and the doublet of the $H_{3,5}$-Py protons is also downfield shifted but to a minor extent ($\Delta\delta$ = 0.15 ppm) due to the bigger distance from the coordination site. The spectrum shows relatively sharp peaks together with broader and less intense bands, which are probably partly due to the presence of conformers resulting from a slow rotation of the porphyrins edges around the metal-pyridyl bond and/or to a distribution of geometrical isomers, and partly to small amounts of impurities. As a matter of fact, the spectrum seems to average and clean upon metallation of the porphyrin cores (Fig. 2c). The ^{1}H NMR of $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ shows also a downfield shift of the resonances of the βH protons of the pyrrolic rings, which is consistent with the electron withdrawing effect of the central zinc(II) ion.

Infrared spectroscopy in the carbonyl stretching region is distinctive for the presence of *fac*-tricarbonyl rhenium(I) fragments: as shown in Fig. 3, three strong CO stretching bands appear at ν = 2027, 1922 and 1892 cm^{-1} in the IR spectrum of $[Re(CO)_3(P1)Br]_4$, which are absent in that of the parent porphyrin **P1**. Coordination of the pyridyl nitrogen to the Re(I) complex is also supported by the bathochromic shift of 4.8 nm (λ_{max} **P1** = 418 nm, λ_{max} $[Re(CO)_3(P1)Br]_4$ = 422.8 nm) in the Soret region of the UV-Vis spectrum (Fig. 4), in agreement with net removal of electron density from the porphyrin ring upon rhenium–pyridyl bond formation. Metallation of the porphyrins with Zn(II) induces a further bathochromic shift of the Soret band (λ_{max} $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ = 430.2 nm) and the expected collapse of the four Q-bands into two.

An indirect proof of the zinc(II) tetraporphyrin metallacycle structure can be obtained by guest inclusion studies. $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ can accommodate a cruciform ligand of appropriate dimension within its cavity, and it has a perfect complementarity with 5,10,15,20-tetra(4-pyridyl)porphyrin (H_2-TPyP, Fig. 5 top). Thus the metallacycle is expected to form a strong host–guest complex, *via* four contemporary zinc–pyridyl bonds with H_2-TPyP. The results of a fluorescence titration of $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ with H_2-TPyP are shown in Fig. 5 (bottom).

Addition of H_2-TPyP induced a progressive quenching of the emission intensity of the metallacycle. For concentrations of H_2-TPyP > $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ the spectra are influenced by the presence of free H_2-TPyP (maximum emission at 647 and 715 nm, dashed black line), which produces an increase in fluorescence. Fitting the fluorescence data at different wavelengths, with a 1 : 1 binding model that takes into account also the emission of the free porphyrin, gives a log K_{ass} = 7.06 (s.d. 0.12) in agreement with the reported data[7a,10] and this confirms the formation of a strong 1 : 1 complex between metallacycle $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ and H_2-TPyP (Fig. 6).

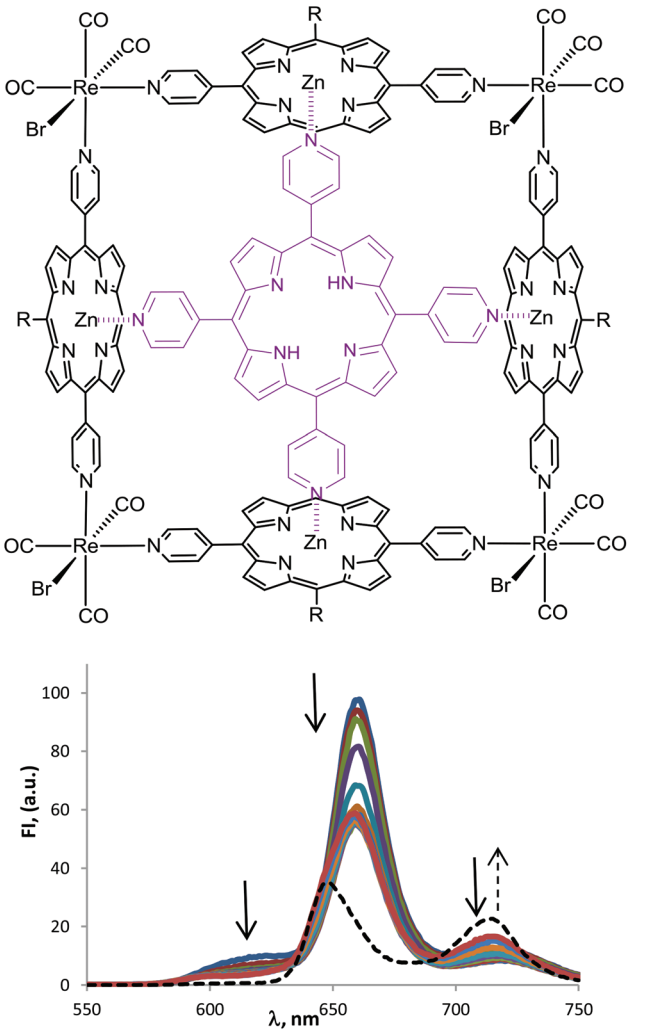


Fig. 5 Top: structure of the 1 : 1 complex of $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ with H_2-TPyP. Bottom: fluorimetric titration of $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ ($CHCl_3$, 1×10^{-6} M) with H_2-TPyP ($CHCl_3$, 0–3 × 10^{-6} M), λ_{exc} = 425 nm. The black dashed curve is the emission spectra of H_2-TPyP ($CHCl_3$, 1×10^{-6} M, λ_{exc} = 425 nm).

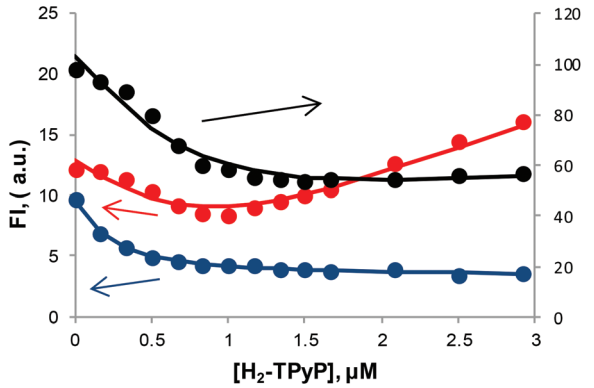


Fig. 6 Fluorescence emission of $[Re(CO)_3(Zn{\cdot}P1)Br]_4$ at 616 nm (blue), 661 nm (black), and 718 (red) with increasing concentration of H_2-TPyP (data from Fig. 5). The lines are the calculated titration curves on the basis of a 1 : 1 binding model and log K_{ass} = 7.06. The arrows indicate the ordinate axis of reference.

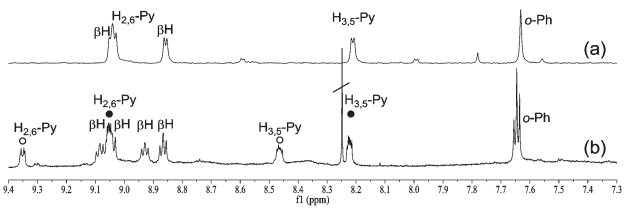


Fig. 7 Selected regions of the ^{1}H-NMR spectra (500 MHz, DMSO-d_6) of (a) porphyrin **P4**, (b) the product obtained from the reaction of **P4** and $Re(CO)_5Br$ at 65 °C. The empty and full circles indicate the resonances pairwise connected in the HH-COSY spectrum.

We then studied the assembling reaction between $Re(CO)_5Br$ and porphyrins **P4** or **P5** with the scope of obtaining a new class of 4 + 4 metallacycles with a broader range of solubility, thanks to the presence of the alkyl chains on the porphyrin fragments. However, the results were somewhat disappointing. Reaction of **P4** with the Re(I) complex in the conditions illustrated above, and also increasing the reaction time and/or changing the ratio of THF–toluene, gives a purple solid very poorly soluble in THF, $CHCl_3$ and DMSO, and insoluble in DCM, MeOH, acetone, CH_3CN and hexane. The UV-Vis and IR spectra are very similar to those reported above for $[Re(CO)_3(P1)Br]_4$, thus indicating that all the pyridines are coordinated to the Re(I) centre (see ESI†). However, the ^{1}H-NMR spectrum (DMSO-d_6) is more complex than expected, with relatively broad resonances (see ESI†). By increasing the temperature, the proton resonances become sharper but the high number of peaks in the aromatic region clearly indicates the presence of a structure with a lower symmetry with respect to that corresponding to a metallacycle with four equivalent porphyrins in free (and fast) rotation around the pyridyl–rhenium bond (Fig. 7). The spectrum recorded in DMSO-d_6 at 65 °C in fact shows the presence of two sets of resonances relative to the pyridyl protons: one at δ = 9.35 and 8.46 ppm and the other at δ = 9.06 and 8.22 ppm, which are pairwise connected in the HH-COSY spectrum (see ESI†), as indicated in Fig. 7 by empty and full circles, respectively. The individual signals of these two sets integrate for 2H. In between, and partially overlapping with these sets (δ = 9.2–8.8 ppm), there is a group of four multiplets, integrating for 2H each, for a total of 8H, assigned to the βH. These observations might be consistent with the formation of the species $[Re(CO)_3(P4)_2Br]$ bearing two porphyrins with only one metal-coordinated pyridyl fragment each and four non-equivalent βH protons, thus representing a "corner" of the desired metallacycle. Indeed, a comparison of the pyridyl protons chemical shifts of this species with those of the parent porphyrin **P4** (Fig. 7) shows that the upfield set of pyridyl resonances (δ = 9.06 and 8.22 ppm, full circles) may well correspond to those of unbound pyridyl fragments, present in a 1 : 1 ratio as compared with the resonances of rhenium-bound ones. However, a closer inspection of the ^{1}H NMR signals multiplicities is in disagreement with such a conclusion. In fact, each pyridyl proton signal consists of closely overlapping doublets (typically arising from the presence of a *syn*/*anti* isomer distribution

derived by the different possible orientations of the halide ligand in Re(I)–dipyridyl metallacycles),[4] each βH protons signal consists of two partially overlapping doublets, and the resonances of the *ortho* phenyl protons appear as three partially overlapping singlets.§ Taken together, these observations are indicative of the presence of the expected 4 + 4 porphyrin metallacycle, with the porphyrin edges in a rigid somewhat tilted conformation (present as a statistical distribution of geometrical *syn*/*anti* isomers) with very distinct proton magnetic environments deriving from the orientation of the protons which point inside (toward the shielding cone of the other porphyrin rings) or outside the metallacycle. This possibility has been already suggested to explain the crowded aromatic region of the ^{1}H NMR spectra of two 4 + 4 Pt(II) porphyrin metallacycles.[3d,f]‡ Careful TLC analysis of the isolated product indicates the presence of a single spot with high mobility (R_f = 0.86, SiO_2, $CHCl_3$–EtOH, 98/2), typical of a discrete porphyrin metallacycle, and very similar to those found for $[Re(CO)_3(P1)Br]_4$ described above, and $[Re(CO)_3(P2)Br]_4$.[11] Additional NMR experiments (2D ROESY, and DOSY) did not give any further element to unambiguously assign the nature and 3D structure of this species.

The results with **P5** were more disappointing. The purple solid obtained from the reaction with $Re(CO)_5Br$ is practically insoluble in all organic solvents. Therefore, the characterization was limited to the acquisition of the UV-Vis and IR spectra which show coordination of the pyridyl nitrogen to Re(I) (see ESI†) and to TLC analysis, which indicates the absence of unreacted porphyrin and the presence of a single spot.

Conclusions

Despite the body of work on porphyrin synthesis present in the literature there is still a large margin for improvement, in particular given the strong sensitivity of the acid catalyzed condensation reaction to the substitution pattern of the target porphyrin. We have shown that a careful control of the reaction conditions led to high yield in the preparation of *meso* substituted *trans*-A_2B_2 dipyridylporphyrins bearing two variably substituted aromatic groups in the *meso* positions. These types of porphyrins are of particular importance being the key building blocks in the design and self-assembling of metal-mediated discrete structures, and may as well extend the pool of functional building units for infinite 2D and/or 3D hollow structures. Presently, we have exploited this feature in the preparation of a new 4 + 4 Re(I)–porphyrin metallacycle which has been fully characterized by means of infrared, NMR and UV-Vis (absorption and emission) spectroscopies and by guest inclusion studies. Quite unexpectedly the addition of alkyl chains to the porphyrin fragment, which is a common approach employed to increase the solubility of porphyrins in organic solvents, resulted counterproductive in the final targeted 4 + 4 Re(I)–porphyrin metallacycles. Indeed, using porphyrins bearing alkyl chains on the two *meso* phenyl substituents, we were unable to provide an unambiguous characterization of the isolated species, although several data suggest the formation of the metallacycle. In any case, the solubility of the product obtained decreases on increasing the length of the alkyl chains. We are now investigating this effect and screening alternative substituents of the porphyrin fragments and the chemical modification of the cyano substituents on the phenyl rings of the metallacycles to obtain more soluble systems and therefore widening their application in the realization of supramolecular functional architectures.

§ Moreover, ML_2 "corners" gives usually well resolved ^{1}H-NMR spectra with a characteristic upfield shifts of the proton resonances of the *meso* phenyl substituents, which is not observed in this case (see ref. 3*i*).

Experimental

Materials and general methods

All commercially available reagents were purchased from Aldrich, Fluka and Strem Chemicals and used without purification unless otherwise mentioned. Solvents were purchased from Aldrich, VWR, Fluka and Riedel, and deuterated solvents from Cambridge Isotope Laboratories and Aldrich. Reactions were monitored by TLC on Merck silica gel plates (0.25 mm) or on Fluka aluminium oxide plates and visualized by UV light, I_2, or by $KMnO_4$–H_2SO_4. Chromatography was performed on Merck silica gel 60F-254 (230–400 mesh) or Merck aluminium oxide 90 standardized and the solvents employed were of analytical grade. Size exclusion chromatography was carried out using Sephadex™ LH-20 (Amersham Biosciences). NMR spectra were recorded on a Varian 500 spectrometer (operating at 500 MHz for proton and at 125 MHz for carbon) or on a Jeol 400 or 270 spectrometer (operating at 400 or 270 MHz for proton and at 100 MHz or 67.8 for carbon, respectively). Chemical shifts (δ) are reported in ppm using the solvent residual signal as an internal reference and the multiplicity of each signal is designated by the conventional abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets. Coupling constants (J) are quoted in Hz. Electrospray ionization (ESI) measurements were performed on a Perkin Elmer APII at 5600 eV by Dr Fabio Hollan, Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy. Melting points (m.p.) were measured with a Büchi SHP-20 apparatus and are not corrected. Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR/Raman 2000 instrument in the transmission mode; samples were prepared as KI pellets. UV-Visible Spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer.

5-(4-Pyridyl)dipyrromethane (**1**),[19] 3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid ethyl ester (**2a**),[21b] 4-ethyl-3-methyl-1*H*-pyrrole-2-carboxylic acid ethyl ester (**2b**),[21a] 5-(4-carbomethoxyphenyl)-2,8-dimethyl-3,7-diethyl-1,9-dicarboxydipyrromethane (**5**),[20] methyl-4-bromo-3,5-dihydroxy benzoate (**7**)[24] and methyl-4-bromo-3,5-dipropoxy benzoate (**8a**)[24] have been prepared with improved and/or modified literature procedures.

5,10,15,20-Tetra(4-pyridyl)porphyrin (H_2-TPyP) was purchased from Aldrich. [ReBr(CO)$_5$] was prepared as reported in the literature.[27]

5,15-Diphenyl-10,20-di-(4-pyridyl)porphyrin (P1 – optimized conditions). 5-(4-Pyridyl)dipyrromethane (0.500 g, MW = 223.27, 2.24 mmol) and freshly distilled benzaldehyde (238 mg, MW = 106.12, 2.24 mmol) were dissolved in 350 mL of anhydrous DCM under Ar. The mixture was cooled at 0 °C with an ice bath and TFA (7.15 mL, MW = 114.02, d = 1.535, 96.3 mmol) was added drop-wise. The reaction mixture was stirred at 0 °C for 20 minutes and DDQ (1.015 g, MW = 227.00, 4.48 mmol) was then added. The mixture was stirred at room temperature for 1 hour. The organic phase was washed with saturated $NaHCO_3$ and water, dried over anhydrous Na_2SO_4 and the solvent removed. Purification by column chromatography (silica, $CHCl_3$–EtOH from 100/0 to 98/2) afforded a purple solid. Recrystallization ($CHCl_3$–hexane) afforded 370 mg of product. Yield 53%.

^{1}H-NMR (500 MHz, δ-$CDCl_3$): −2.84 (s, 2H, NH), 7.76–783 (m, 6H, H3,4,5-Ph), 8.17 (d, J = 5.6 Hz, 4H, H3,5-Py), 8.21 (d, J = 6.7 Hz, 4H, H2,6-Ph), 8.81 (d, J = 4.5 Hz, 4H, βH), 8.91 (d, J = 4.5 Hz, 4H, βH), 9.04 (d, J = 5.5 Hz, 4H, H2,6-Py). UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 418 (100), 513.2 (6.6), 548.2 (2.9), 587.8 (2.3), 647.2 (1.8). ESI-MS (m/z): 617.4 [M + H$^+$], 639.4 [M + Na$^+$]. IR (KI pellets): $\tilde{\nu}$ = 1597, 1475, 1407 (m, $\tilde{\nu}_{C-C,\ Ar}$), 728, 735 (m, $\tilde{\nu}_{C-H,\ Ar}$). M.p. >300 °C.

Synthesis of 5-(4-pyridyl)-2,3,7,8-tetraalkyl-dipyrromethane (4a,b)

A solution of 3,4-dialkyl-1*H*-pyrrole-2-carboxylic acid ethyl ester (**2**, 5.98 mmol) in 20 mL of toluene anhydrous was heated at reflux under Ar. A catalytic amount of *p*-TSA (about 50 mg) was added followed by 4-pyridinecarboxaldehyde (0.28 mL, d = 1.137, MW = 107.11, 2.99 mmol). The reaction mixture was refluxed for 48 hours and then cooled to room temperature, washed with a saturated aqueous solution of $NaHCO_3$ (3 × 10 mL), with water (1 × 10 mL), dried over anhydrous Na_2SO_4, filtrated and concentrated. Purification by column chromatography (silica gel, DCM–AcOEt from 100/0 to 20/80) afforded the pure product **3**.

1,9-Ethoxycarbonyl-5-(4-pyridyl)-2,3,7,8-tetramethyl dipyrromethane, 3a. Yield = 81.6%, R_f: 0.15 (SiO_2, DCM–AcOEt, 6/4). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.24 (t, J = 7.1 Hz, 6H, $COOCH_2CH_3$), 1.82 (s, 6H, 3,7-CH_3), 2.26 (s, 6H, 2,8-CH_3), 4.10 (q, J = 7.1 Hz, 4H, $COOCH_2CH_3$), 5.53 (s, 1H, 5-H), 7.02 (d, J = 5.7 Hz, 2H, H3,5-Py), 8.46 (d, J = 5.7 Hz, 2H, H2,6-Py), 9.28 (br, 2H, NH). ^{13}C-NMR (125 MHz, $CDCl_3$): 8.81 (3,7-CH_3), 10.49 (2,8-CH_3), 14.19 ($COOCH_2CH_3$), 39.82 (5-C), 59.86 ($COOCH_2CH_3$), 118.37 (1,9-C), 118.64 (3,7-C), 121.83 (C2,6-Py), 127.53 (2,8-C), 130.36 (4,6-C), 149.11 (C1-Py), 150.23 (C3,5-Py), 162.11 ($COOCH_2CH_3$). ESI-MS (m/z): 424.3 [M + H$^+$], 446.2 [M + Na$^+$], 462.1 [M + K$^+$].

1,9-Diethoxycarbonyl-5-(4-pyridyl)-2,8-dimethyl-3,7-diethyl dipyrromethane, 3b. Yield = 39.8%, R_f: 0.32 (SiO_2, DCM–AcOEt, 6/4). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (t, J = 7.5 Hz, 6H, 3,7-CH_2CH_3), 1.31 (t, J = 7.1 Hz, 6H, $COOCH_2CH_3$), 2.28 (s, 6H, 2,8-CH_3), 2.31 (q, J = 7.5 Hz, 4H, 3,7-CH_2CH_3), 4.24 (q, J = 7.1 Hz, 4H, $COOCH_2CH_3$), 5.54 (s, 1H, 5-H), 7.02 (d, J = 5.2 Hz, 2H, H3,5-Py), 8.46 (br, 2H, NH), 8.55 (d, J = 5.2 Hz, 2H, H2,6-Py). ^{13}C-NMR (125 MHz, $CDCl_3$): 10.47 (2,8-CH_3), 14.47 ($COOCH_2CH_3$), 14.95 (3,7-CH_2CH_3), 17.29 (3,7-CH_2CH_3), 39.59 (5-C), 60.01 ($COOCH_2CH_3$), 118.86 (1,9-C), 123.28 (C2,6-Py), 124.94 (3,7-C), 127.11 (2,8-C), 129.44 (4,6-C), 149.02 (C1-Py), 150.40 (C3,5-Py), 161.70 ($COOCH_2CH_3$). ESI-MS (m/z): 452.4 [M + H$^+$], 474.4 [M + Na$^+$], 490.3 [M + K$^+$].

A mixture of the above product **3** (0.774 mmol) and NaOH 4 N (20 mL) was heated at reflux in ethylene glycol (40 mL) for 24 hours under Ar. After cooling, the reaction mixture was diluted with water (150 mL) and extracted with toluene (4 × 70 mL). The organic solvent was washed with water (2 × 70 mL), dried over anhydrous Na_2SO_4, filtrated and concentrated affording the desired product **4**.

5-(4-Pyridyl)-2,3,7,8-tetramethyl dipyrromethane, 4a. Brown solid, yield 88.4%. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.82 (s, 6H, 3,7-CH_3), 2.03 (s, 6H, 2,8-CH_3), 5.47 (s, 1H, 5-H), 6.42 (s, 2H, 1,9-H), 7.02 (d, J = 5.6 Hz, 2H, H3,5-Py), 7.81 (br, 2H, NH), 8.35 (d, J = 5.6 Hz, 2H, H2,6-Py). ^{13}C-NMR (100 MHz, $CDCl_3$): 9.11 (3,7-CH_3), 10.50 (2,8-CH_3), 40.50 (5-C), 114.27 (1,9-C), 115.07 (C2,6-Py), 119.02 (3,7-C), 123.70 (2,8-C), 125.95 (4,6-C), 149.87 (C1-Py), 151.55 (C3,5-Py). ESI-MS (m/z): 280.3 [M + H$^+$], 302.3 [M + Na$^+$], 318.0 [M + K$^+$].

5-(4-Pyridyl)-2,8-dimethyl-3,7-diethyl dipyrromethane, 4b. Brown solid, yield 53.4%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.92 (t, J = 7.5 Hz, 6H, 3,7-CH_2CH_3), 2.03 (s, 6H, 2,8-CH_3), 2.30 (q, J = 7.5 Hz, 4H, 3,7-CH_2CH_3), 5.49 (s, 1H, 5-H), 6.39 (s, 2H, 1,9-H), 7.04 (d, J = 5.4 Hz, 2H, H3,5-Py), 7.54 (br, 2H, NH), 8.40 (d, J = 5.4 Hz, 2H, H2,6-Py). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.42 (2,8-CH_3), 15.25 (3,7-CH_2CH_3), 17.60 (3,7-CH_2CH_3), 40.01 (5-C), 114.56 (1,9-C), 118.48 (C2,6-Py), 121.68 (3,7-C), 123.70 (2,8-C), 125.71 (4,6-C), 149.88 (C1-Py), 152.18 (C3,5-Py). ESI-MS (m/z): 308.3 [M + H$^+$], 320.3 [M + Na$^+$], 346.3 [M + K$^+$].

Attempts to prepare porphyrin P3a,b

In the attempts to prepare porphyrin **P3a,b** we reacted dypyrromethane **4a,b** with methyl 4-formylbenzoate or compound **5** with 4-pyridinecarboxaldehyde in a 1 : 1 ratio testing varying combinations of: solvent (DCM or MeOH), acid catalyst and its concentration (TFA from 1 to 43 eq.; $BF_3{\cdot}Et_2O$ catalytic), temperature (from 0 °C to reflux), reaction time (from 20 min to overnight). For the other general conditions and for the procedure of oxidation with DDQ see the synthesis of **P1**. In any case we did not obtain the desired porphyrin.

Synthesis of 4-cyano-3,5-dialkyloxy benzaldehyde (12a,b)

4-Bromo-3,5-dihydroxy benzoic acid (**6**, 530 mg, MW = 233.02, 2.27 mmol) was dissolved in 30 mL of methanol. H_2SO_4 (0.50 mL, MW = 98.078, d = 1.835, 9.35 mmol) was added and the mixture was heated at reflux for 18 hours. The solvent was evaporated and the residue was re-dissolved in 50 mL of water and 30 mL of AcOEt. The aqueous layer was extracted with AcOEt (3 × 30 mL) and the combined organic layers were

washed with water (2 × 50 mL), dried on anhydrous Na_2SO_4, filtrated and the solvent was removed under reduced pressure affording 541 mg of methyl-4-bromo-3,5-dipropoxy benzoate (**7**) as a colourless oil. Yield 96%.

^{1}H-NMR (500 MHz, CD_3OD): 3.85 (s, 3H, $COOCH_3$), 7.04 (s, 2H, Ar), 9.8 (br, 1H, COOH). ^{13}C-NMR (100 MHz, CD_3OD): 51.33 ($COOCH_3$), 103.75 (C4-Ar), 107.27 (C2-Ar), 129.69 (C1-Ar), 155.32 (C3-Ar), 166.74 ($COOCH_3$). IR (KI disks): $\tilde{\nu}$ = 1704 (s, $\tilde{\nu}_{C=O}$), 860 (m, $\tilde{\nu}_{Ar}$).

The ester **7** (206 mg, MW = 247.04, 0.834 mmol), the appropriate 1-bromoalkane (2.5 mmol) and tetrabutylammonium bromide (54 mg, MW = 322.38, 0.17 mmol) were dissolved in 5 mL of acetone. After addition of anhydrous K_2CO_3 (300 mg, MW = 138.21, 2.17 mmol) the reaction mixture was refluxed for 18 hours. The solvent was then removed and the residue taken up in as much diethyl ether and water as needed to obtain two homogeneous phases. The aqueous phase was extracted with diethyl ether. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and the ether evaporated to obtain the alkylated product.

Methyl-4-bromo-3,5-dipropoxy benzoate (8a). Brown oil, yield 95%. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.04 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_3$), 1.82 (m, 4H, $OCH_2CH_2CH_3$), 3.87 (s, 3H, $COOCH_3$), 4.05 (t, J = 6.4 Hz, 4H, $OCH_2CH_2CH_3$) 7.12 (s, 2H, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.61 ($OCH_2CH_2CH_3$), 22.55 ($OCH_2CH_2CH_3$), 52.39 ($COOCH_3$), 70.99 ($OCH_2CH_2CH_3$), 106.34 (C2-Ar), 107.73 (C4-Ar), 129.89 (C1-Ar), 156.58 (C3-Ar), 166.60 ($COOCH_3$).

Methyl-4-bromo-3,5-dihexyloxy benzoate (8b). Yellow oil, yield 90%. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.94 (t, J = 6.7 Hz, 6H, $O(CH_2)_5CH_3$), 1.32 (m, 8H, $O(CH_2)_3(CH_2)_2CH_3$), 1.48 (m, 4H, $O(CH_2)_2CH_2(CH_2)_2CH_3$), 1.81 (m, 4H, $OCH_2CH_2(CH_2)_3CH_3$), 3.88 (s, 3H, $COOCH_3$), 4.02 (t, J = 6.9 Hz, 4H, $OCH_2(CH_2)_4CH_3$) 7.17 (s, 2H, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.95 ($O(CH_2)_5CH_3$), 22.45 ($O(CH_2)_4CH_2CH_3$), 22.62 ($O(CH_2)_3CH_2CH_2CH_3$), 28.99 ($O(CH_2)_2CH_2(CH_2)_2CH_3$), 31.46 ($OCH_2CH_2(CH_2)_3CH_3$) 52.19 ($COOCH_3$), 69.42 ($OCH_2(CH_2)_4CH_3$), 106.22 (C2-Ar), 107.73 (C4-Ar), 129.79 (C1-Ar), 156.53 (C2-Ar), 166.40 ($COOCH_3$).

The alkyl derivative **8** (12.4 mmol) was added to a solution of CuCN (8.00 g, MW = 89.56, 89.0 mmol) in 200 mL of DMF and the reaction mixture was heated to reflux (150–160 °C) for 48 hours. After cooling to room temperature a solution of $FeCl_3$ (29 g in 80 mL of water and 20 mL of HCl conc.) was added. The mixture was heated at 70–80 °C for 2 hours and then extracted with $CHCl_3$. The combined extracts were washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4 and the solvent was removed *in vacuo* to afford a brown oil which is a mixture of ester **9** and acid **10**. The product was taken up in a mixture of THF–MeOH 1/1 (120 mL), 1.2 g of $LiOH{\cdot}H_2O$ were added and the reaction mixture was stirred for 18 hours. The mixture was concentrated and taken up with water and acidified with HCl 6 N to pH = 2. The product was extracted with AcOEt (3 × 30 mL), washed with water (2 × 20 mL) and brine (1 × 20 mL), dried over anhydrous sodium sulphate, filtered, and the solvent evaporated to afford the desired acid **10**.

4-Cyano-3,5-dipropoxy benzoic acid (10a). White solid, yield 70% from **8a**. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.05 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_3$), 1.91 (m, 4H, $OCH_2CH_2CH_3$), 4.10 (t, J = 6.5 Hz, 4H, $OCH_2CH_2CH_3$) 7.24 (s, 2H, Ar), 11.18 (br, 1H, COOH). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.40 ($OCH_2CH_2CH_3$), 22.27 ($OCH_2CH_2CH_3$), 71.60 ($OCH_2CH_2CH_3$), 96.65 (C4-Ar), 105.48 (C2-Ar), 112.96 (CN), 134.43 (C1-Ar), 162.07 (C3-Ar), 170.70 (COOH). IR (KI pellets): $\tilde{\nu}$ = 3200 (s, $\tilde{\nu}_{COOH}$), 2963–2890 (m, $\tilde{\nu}_{CH}$), 2228.9 (s, $\tilde{\nu}_{CN}$), 1724 (s, $\tilde{\nu}_{C=O}$), 763 (s, $\tilde{\nu}_{Ar}$).

4-Cyano-3,5-dihexyloxy benzoic acid (10b). White solid, yield 81% from **8b**. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.94 (t, J = 6.7 Hz, 6H, $O(CH_2)_5CH_3$), 1.33 (m, 8H, $O(CH_2)_3(CH_2)_2CH_3$), 1.46 (m, 4H, $O(CH_2)_2CH_2(CH_2)_2CH_3$), 1.83 (m, 4H, $OCH_2CH_2(CH_2)_3CH_3$), 4.01 (t, J = 6.5 Hz, 4H, $OCH_2(CH_2)_4CH_3$) 7.23 (s, 2H, Ar), 10.5 (br, 1H, COOH) ^{13}C-NMR (67.8 MHz, $CDCl_3$): 13.84 ($O(CH_2)_5CH_3$), 22.40 ($O(CH_2)_4CH_2CH_3$), 25.35 ($O(CH_2)_3CH_2CH_2CH_3$), 28.6 ($O(CH_2)_2CH_2(CH_2)_2CH_3$), 31.29 ($OCH_2CH_2(CH_2)_3CH_3$), 69.47 ($OCH_2(CH_2)_4CH_3$), 96.10 (C4-Ar), 105.22 (C2-Ar), 112.86 (CN), 134.72 (C1-Ar), 162.13 (C3-Ar), 169.81 (COOH).

To a solution of acid **10** (8.67 mmol) in 60 mL of DCM cooled to 0 °C, 4-methylmorpholine (1.90 mL, MW = 101.15, d = 0.92, 17.3 mmol) and isobutyl chloroformate (1.12 mL, MW = 136.58, d = 1.053, 8.67 mmol) were added. The resulting mixture was stirred for 20 minutes at 0 °C, and then hydroxylamine hydrochloride (930 mg, MW = 97.55, 9.54 mmol) was added. The reaction mixture was stirred for 1 hour at 0 °C, and for 18 hours at room temperature. The mixture was diluted with water and the organic phase was washed with water, citric acid 5% and brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, $CHCl_3$–MeOH from 100/0 to 90/10) gave the Weinreb amide **11**.

4-Cyano-*N*-methoxy-*N*-methyl-3,5-dipropoxybenzamide (11a). Yellow oil, yield 57%. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.05 (t, J = 6.4 Hz, 6H, $OCH_2CH_2CH_3$), 1.91 (m, J = 7.0 Hz, 4H, $OCH_2CH_2CH_3$), 3.32 (s, 3H, NCH_3), 3.53 (s, 3H, OCH_3), 4.01 (t, J = 7.4 Hz, 4H, $OCH_2CH_2CH_3$), 6.75 (s, 2H, Ar). ^{13}C-NMR (67.8 MHz, $CDCl_3$): 10.14 ($OCH_2CH_2CH_3$), 22.04 ($OCH_2CH_2CH_3$), 33.23 (NCH_3), 61.32 (OCH_3), 70.73 ($OCH_2CH_2CH_3$), 93.34 (C4-Ar), 103.76 (C2-Ar), 113.31 (CN), 140.15 (C1-Ar), 161.77 (C3-Ar), 168.38 (CO). IR (KI pellets): $\tilde{\nu}$ = 2227.94 (s, $\tilde{\nu}_{CN}$), 1644.62 (s, $\tilde{\nu}_{C=O}$), 914 (m, $\tilde{\nu}_{Ar}$).

4-Cyano-*N*-methoxy-*N*-methyl-3,5-dihexyloxybenzamide (11b). Yellow oil, yield 67%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (t, J = 7.0 Hz, 6H, $O(CH_2)_5CH_3$), 1.30 (m, 8H, $O(CH_2)_3(CH_2)_2CH_3$), 1.46 (m, 4H, $O(CH_2)_2CH_2(CH_2)_2CH_3$), 1.80 (m, 4H, $OCH_2CH_2(CH_2)_3CH_3$), 3.32 (s, 3H, NCH_3), 3.66 (s, 3H, OCH_3), 4.03 (t, J = 6.5 Hz, 4H, $OCH_2(CH_2)_4CH_3$), 6.74 (s, 2H, Ar). ^{13}C-NMR (67.8 MHz, $CDCl_3$): 14.07 ($O(CH_2)_5CH_3$), 22.59 ($O(CH_2)_4CH_2CH_3$), 22.55 ($O(CH_2)_3CH_2CH_2CH_3$), 28.01 ($O(CH_2)_2CH_2(CH_2)_2CH_3$), 28.86 ($OCH_2CH_2(CH_2)_3CH_3$), 31.49 ($NCH_3$), 61.32 ($OCH_3$), 69.51 ($OCH_2(CH_2)_4CH_3$), 93.49 (C4-Ar), 103.84 (C2-Ar), 113.36 (CN), 140.12 (C1-Ar), 161.80 (C3-Ar), 168.40 (CO).

A mixture of Weinreb amide **11** (1.67 mmol) in 40 mL of THF anhydrous was stirred and cooled to 0 °C under Ar. Then

3.3 mL of a 2 M $LiAlH_4$ solution in THF anhydrous (6.67 mmol) was added drop-wise. The mixture was stirred at room temperature for 4 hours; then, after cooling to 0 °C, a saturated solution of NH_4Cl and water was slowly added. The product was extracted with AcOEt (3 × 100 mL), washed with water (2 × 100 mL) and brine (1 × 100 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure to give the desired aldehyde **12**.

4-Cyano-3,5-dipropoxybenzaldehyde (12a). Yellow solid, yield 79%. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.06 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_3$), 1.85 (m, 4H, $OCH_2CH_2CH_3$), 4.08 (t, J = 6.5 Hz, 4H, $OCH_2CH_2CH_3$), 6.99 (s, 2H, Ar), 9.93 (bs, 1H, CHO). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.18 ($OCH_2CH_2CH_3$), 22.06 ($OCH_2CH_2CH_3$), 71.03 ($OCH_2CH_2CH_3$), 96.87 (C4-Ar), 104.64 (C2-Ar), 112.98 (CN), 140.63 (C1-Ar), 162.70 (C3-Ar), 191.08 (CHO).

4-Cyano-3,5-dihexyloxybenzaldehyde (12b). Yellow solid, yield 75%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (t, J = 6.5 Hz, 6H, $O(CH_2)_5CH_3$), 1.30 (m, 8H, $O(CH_2)_3(CH_2)_2CH_3$), 1.44 (m, 4H, $O(CH_2)_2CH_2(CH_2)_2CH_3$), 1.83 (m, 4H, $OCH_2CH_2(CH_2)_3CH_3$), 4.09 (t, J = 6.5 Hz, 4H, $OCH_2(CH_2)_4CH_3$), 6.97 (s, 2H, Ar), 9.92 (bs, 1H, COOH). ^{13}C-NMR (67.8 MHz, $CDCl_3$): 14.07 ($O(CH_2)_5CH_3$), 22.60 ($O(CH_2)_4CH_2CH_3$), 25.54 ($O(CH_2)_3CH_2CH_2CH_3$), 28.93 ($O(CH_2)_2CH_2(CH_2)_2CH_3$), 31.48 ($OCH_2CH_2(CH_2)_3CH_3$), 69.77 ($OCH_2(CH_2)_4CH_3$), 93.09 (C4-Ar), 104.68 (C2-Ar), 113.15 (CN), 140.64 (C1-Ar), 162.66 (C3-Ar), 191.02 (CHO).

Synthesis of porphyrins P4,5

5-(4-Pyridyl)dipyrrylmethane (0.213 g, MW = 223.27, 0.95 mmol) and 4-cyano-3,5-dialkyloxybenzaldehyde (0.95 mmol) were dissolved in 200 mL of anhydrous DCM under Ar. The mixture was cooled at 0 °C with an ice bath and TFA (3.0 mL, MW = 114.02, d = 1.535, 40.8 mmol) was added drop-wise. The reaction mixture was stirred at 0 °C for 20 minutes and DDQ (433 mg, MW = 227.00, 1.9 mmol) was then added. The mixture was stirred at room temperature for 1 hour. The organic phase was washed with saturated $NaHCO_3$ and water, dried over anhydrous Na_2SO_4 and the solvent was removed. Purification by column chromatography (silica, $CHCl_3$–EtOH from 100/0 to 98/2) afforded a purple solid. Recrystallization ($CHCl_3$–hexane) afforded the pure porphyrin.

5,15-Di[4-cyano-3,5-dipropoxyphenyl]-10,20-di[pyridyl]-porphyrin (P4). M.p. >300 °C, yield 61%. ^{1}H-NMR (500 MHz, δ-$CDCl_3$): −2.87 (s, 2H, NH); 1.10 (t, J = 7.4 Hz, 12H, O $CH_2CH_2CH_3$), 1.98 (m, 8H, $OCH_2CH_2CH_3$), 4.15 (t, J = 6.4 Hz, 8H, $OCH_2CH_2CH_3$), 7.44 (s, 4H, *o*-Ph), 8.20 (d, J = 5.5 Hz, 4H, H3,5-Py); 8.90 (d, J = 4.4 Hz, 4H, βH), 9.00 (d, J = 4.4 Hz, 4H, βH), 9.10 (d, J = 5.4 Hz, 4H, H2,6-Py). ^{13}C-NMR (125 MHz, δ-$CDCl_3$): 10.48 ($OCH_2CH_2CH_3$), 22.42 ($OCH_2CH_2CH_3$), 71.05 ($OCH_2CH_2CH_3$), 91.95 (C4-Ar), 111.71 (C2-Ar), 113.98 (CN), 117.74 and 119.41 (C*meso*), 129.27 (C3,5-Py), 148.17 (C1-Ar), 148.48 (C3,5-Py), 149.76 (C1-Py), 160.25 (C3-Ar). UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 419.5 (100), 507 (6.8), 544.5 (3.1), 587.5 (3.1), 649.0 (2.1). ESI-MS (m/z): 900.1 [M + H$^+$]. HRMALDI-MS m/z 899.4003 [M + H$^+$] (calcd for $C_{56}H_{51}N_8O_4$ 899.4033). IR (KI pellets): $\tilde{\nu}$ = 2990–2855 (m, $\tilde{\nu}_{C-H}$), 2249 (s, $\tilde{\nu}_{CN}$), 1615 (s, $\tilde{\nu}_{N-H}$), 1565 (s, $\tilde{\nu}_{C-C\ Ar}$), 1475 (s, $\tilde{\nu}_{CN}$), 1237 (s, $\tilde{\nu}_{C-O-C}$), 805, 783 (s, $\tilde{\nu}_{C-H\ Ar}$).

5,15-Di[4-cyano-3,5-dihexyloxy phenyl]-10,20-di[pyridyl]-porphyrin (P5). M.p. >300 °C, yield 63%. ^{1}H-NMR (500 MHz, δ-$CDCl_3$): −2.93 (s, 2H, NH), 0.87 (m, 12H, $O(CH_2)_5CH_3$), 1.32 (m, 16H, $O(CH_2)_3(CH_2)_2CH_3$), 1.50 (m, 8H, $O(CH_2)_2CH_2(CH_2)_2CH_3$), 1.90 (m, 8H, $OCH_2CH_2(CH_2)_3CH_3$), 4.15 (t, J = 6.4 Hz, 8H, $OCH_2(CH_2)_4CH_3$), 7.51 (s, 4H, *o*-Ph) 8.14 (d, J = 5.5 Hz, 4H, H3,5-Py), 8.86 (d, J = 4.4 Hz, 4H, βH), 8.96 (d, J = 4.4 Hz, 4H, βH), 9.07 (d, J = 5.5 Hz, 4H, H2,6-Py). ^{13}C-NMR (125 MHz, δ-$CDCl_3$): 13.82 ($O(CH_2)_5CH_3$), 22.37 ($O(CH_2)_4CH_2CH_3$), 25.41 ($O(CH_2)_3CH_2CH_2CH_3$), 28.80 ($O(CH_2)_2CH_2(CH_2)_2CH_3$), 31.32 ($OCH_2CH_2(CH_2)_3CH_3$), 69.59 ($OCH_2(CH_2)_4CH_3$), 91.89 (C4-Ar), 111.70 (C2-Ar), 113.70 (CN), 117.75 and 119.47 (C*meso*), 129.34 (C3,5-Py), 148.23 (C1-Ar); 148.59 (C3,5-Py); 149.88 (C1-Py); 160.39 (C3-Ar). UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 419.0 (100), 513 (5.3), 545.0 (1.9), 582.5 (2.2), 642.5 (1.9). ESI-MS (m/z): 1068.4 [M + H$^+$]. HRESI-MS m/z 1067, 6180 [M + H$^+$] (calcd for $C_{68}H_{75}N_8O_4$ 1067.5911). IR (KI pellets): $\tilde{\nu}$ = 2959–2955–2872 (m, $\tilde{\nu}_{C-H}$), 2229 (s, $\tilde{\nu}_{CN}$), 1623 (s, $\tilde{\nu}_{N-H}$), 1602 (s, $\tilde{\nu}_{C-C\ Ar}$), 1429 (s, $\tilde{\nu}_{CN}$), 1130 (s, $\tilde{\nu}_{C-O-C}$), 806, 783 (s, $\tilde{\nu}_{C-H\ Ar}$).

Synthesis of 4 + 4 Re(I)–porphyrin metallacycles

[Re(CO)$_3$(P1)Br]$_4$. 5,15-Diphenyl-10,20-di(4-pyridyl)porphyrin (**P1**, 100 mg, MW = 616.71, 0.162 mmol) and $Re(CO)_5Br$ (66 mg, MW = 406.163, 0.162 mmol) were dissolved in 80 mL of a mixture of freshly distilled 4 : 1 THF–toluene and heated at reflux for 48 h under Ar. After cooling, 50 mL of hexane was added to promote product precipitation. The purple product was centrifuged and then re-precipitated using chloroform and ethyl ether to give 136 mg of solid which was washed several times with diethyl ether. R_f: 0.83 (SiO_2, $CHCl_3$–EtOH, 98/2). Yield 87%. ^{1}H-NMR (500 MHz, δ-$CDCl_3$): −2.89 (s, NH) 7.61 (m, *m*,*p*-Ph), 8.05 (m, *o*-Ph), 8.32 (d, J = 5.6 Hz, H3,5-Py); 8.80–8.85 (d + d, J = 4.6 Hz, βH), 9.52 (d, J = 6.1 Hz, 16H, H2,6-Py). UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 422.8 (100), 515.4 (6.1), 553.2 (3.7), 590.6 (2.1), 650 (2.1). IR (KI pellets): $\tilde{\nu}$ = 2027–1922–1892 (m, $\tilde{\nu}_{CO\ fac}$) 1597–1475–1407 (m, $\tilde{\nu}_{C-C,\ Ar}$), 728–735 (m, $\tilde{\nu}_{C-H\ Ar}$).

[Re(CO)$_3$(Zn·P1)Br]$_4$. The above product (72 mg, MW = 3867.41, 1.9 × 10^{-5} mol) was dissolved in chloroform (70 mL) and a solution of zinc acetate dihydrate (19 mg, MW = 219.5, 8.7 × 10^{-5} mol) in methanol (less than 2 mL) was added. The mixture was stirred in the dark overnight. The solvents were removed under reduced pressure and the purple solid was washed with methanol and filtrated to give 56 mg of purple product. R_f: 0.72 (SiO_2, $CHCl_3$–EtOH, 98/2). Yield 72%. ^{1}H-NMR (500 MHz, δ-$CDCl_3$): 7.61 (m, 24H, *m*,*p*-Ph), 8.08 (m, 16H, *o*-Ph), 8.34 (m, 16H, H5,6-Py), 8.92 (m, 16H, βH), 8.96 (m, 16H, βH), 9.49 (m, 16H, H2,6-Py). UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 430.2 (100), 557.6 (3.1), 607.8 (1.0). IR (KI pellets): $\tilde{\nu}$ = 2027.5–1922–1890 (s, $\tilde{\nu}_{C=O\ fac}$), 1611 (s, $\tilde{\nu}_{C-C,\ C-N}$), 796.5 (s, $\tilde{\nu}_{C-H\ Ar}$).

$[Re(CO)_3(P4)Br]_4$. 5,15-Di[4-cyano-3,5-dipropoxyphenyl]-10,20-di(4-pyridyl)porphyrin (**P4**, 260 mg, MW = 899.05, 0.289 mmol) and $Re(CO)_5Br$ (117 mg, MW = 406.163, 0.289 mmol) were dissolved in 220 mL of freshly distilled 4 : 1 THF–toluene and heated at reflux for 48 h under Ar. After cooling, 200 mL of hexane was added to promote product precipitation. The product was centrifuged and then re-precipitated using chloroform and ethyl ether. Purification by size exclusion chromatography (SEC) (stationary phase: Sephadex™ LH-20, mobile phase: freshly distilled THF) afforded 345 mg of purple solid. R_f: 0.86 (SiO_2, CH_3Cl–EtOH, 98/2). Quantitative yield.

^{1}H-NMR (500 MHz, δ-DMSO-d_6): −2.94 (s, 8H, NH), 1.02 (m, $OCH_2CH_2CH_3$), 1.83 (m, $OCH_2CH_2CH_3$), 4.22 (m, OCH_2-CH_2CH_3), 7.67 (m, 16H, *o*-Ph), 8.22 (m, 8H, H3,5-Py), 8.46 (m, 8H, H3,5-Py), 8.88 (m, 8H, βH), 8.93 (m, 8H, βH), 9.06–9.10 (m, 24H, βH + H2,6-Py), 9.35 (m, 8H, H2,6-Py). UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 422.5 (100), 514.5 (7.4), 550.0 (3.7), 586.5 (3.7), 643.5 (1.8). IR (KI pellets): $\tilde{\nu}$ = 2990–2855 (m, $\tilde{\nu}_{C-H}$), 2029–1930–1916 (s, $\tilde{\nu}_{C=O\ fac}$), 2249 (s, $\tilde{\nu}_{CN}$), 1615 (s, $\tilde{\nu}_{N-H}$), 1565 (s, $\tilde{\nu}_{C-C\ Ar}$), 1475 (s, $\tilde{\nu}_{CN}$), 1237 (s, $\tilde{\nu}_{C-O-C}$), 805, 783 (s, $\tilde{\nu}_{C-H\ Ar}$).

$[Re(CO)_3(P5)Br]_4$. 5,15-Di[4-cyano-3,5-dihexyloxyphenyl]-10,20-di(4-pyridyl)porphyrin (**P5**, 200 mg, MW = 1067.37, 0.187 mmol) and $Re(CO)_5Br$ (76 mg, MW = 406.163, 0.187 mmol) were dissolved in 200 mL of freshly distilled 4 : 1 THF–toluene and heated at reflux for 48 h under Ar. After cooling, 200 mL of hexane was added to promote product precipitation. The product was centrifuged and then re-precipitated using chloroform and ethyl ether. Purification by size exclusion chromatography (SEC) (stationary phase: Sephadex™ LH-20, mobile phase: freshly distilled THF) afforded 670 mg of a purple solid. R_f: 0.88 (SiO_2, $CHCl_3$–EtOH, 98/2). Yield: 75%.

UV-Vis spectrum (λ_{max} (nm), relative intensity (%)) in CH_2Cl_2: 424 (100), 511 (5.3), 552.5 (4.7), 591.0 (2.0), 646.0 (1.0). IR (KI pellets): $\tilde{\nu}$ = 2959–2955–2872 (m, $\tilde{\nu}_{C-H}$), 2029–1929–1908 (s, $\tilde{\nu}_{C=O\ fac}$), 2229 (s, $\tilde{\nu}_{CN}$), 1623 (s, $\tilde{\nu}_{N-H}$), 1602 (s, $\tilde{\nu}_{C-C\ Ar}$), 1429 (s, $\tilde{\nu}_{CN}$), 1130 (s, $\tilde{\nu}_{C-O-C}$), 806, 783 (s, $\tilde{\nu}_{C-H\ Ar}$).

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