Synthesis and characterization of *trans*-di-(4-pyridyl)porphyrin dimers

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ABSTRACT: Preparation and characterization of a small library of symmetric *trans*-di(4-pyridyl)porphyrin dimers, obtained by either Glaser-Hay or Sonogashira coupling reactions from appropriately prepared *trans*-di-4-pyridylporphyrin precursors, is presented. The porphyrin dimers are differentiated by a phenyl-alkynyl bridge of increasing length at one *meso* position, while for all the derivatives the two remaining opposite *meso* positions are tailored with a phenyl moiety bearing a short polyether chain. Coordination of the four pyridyl groups towards appropriate metal fragments may be exploited to construct tubular hollow structures, with varied internal sizes, depending on the choice of the porphyrin dimer component.

KEYWORDS: *trans*-di-(4-pyridyl)porphyrin, porphyrin dimers, synthesis, metal-mediated self-assembling.

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INTRODUCTION

Pyridylporphyrins are essential elements in the modern molecular tool-box of the supramolecular chemist. They combine the peculiar structural, optical and redox properties of porphyrins with the ability to act as rigid, flat multitopic donors in the formation of metal-organic complexes [1]. Within the field of the metal-mediated directional bonding approach [2], these features along with the properties of several transition metal ions (e.g. Pd(II), Pt(II), Ru(II), Rh(II), Re(I)) has led to a variety of coordination adducts. These species can have many different topologies (such as rhomboids, squares, rectangles, triangles) and interesting potential applications in the fields of optoelectronic, catalysis, molecular recognition, etc [3].

In this context, we have recently started to investigate the interaction of pyridylporphyrin based metallacycles with phospholipid membranes and, in particular, their ability to modify the membrane permeability forming large self-assembled channels [4]. Following the approach developed in the group of J. T. Hupp [5], we prepared 4+4 Re(I)-porphyrin metallacycles starting from $Re(CO)_5Br$ and *trans*-A_2B_2 di-4-pyridylporphyrins bearing, in the two *meso* positions, different types of aromatic substituents [6].When peripheral carboxylic acid functionalized porphyrins were used, the resulting metallacycle showed a very interesting ionophoric activity that was attributed to its ability to assemble dimeric structures long enough to span the entire phospholipid bilayer, thus forming a trans-membrane nanopore [7]. These results encouraged us to further develop our porphyrin ligands, and the new molecules were designed to be able to form unimolecular tubular structures long enough to span a double-layer of a phospholipid membrane. Our target was to synthesize dimeric *trans*-di-4-pyridylporphyrins (Figure 1), which would ideally bind to 90° metal fragments in a 1:2 ratio thus forming 4+8 parallelepiped-shaped hollow structures with two hydrophilic ends (see also Figure 7). While dimeric porphyrins molecules are well known [8], examples of dimeric *trans*-di-4-pyridylporphyrins are very few as well as are the studies on their metal-mediated self-assembling behavior [9]. In this paper we report the synthesis of dimers **1a-1c**, their characterization and some preliminary experiments on their coordination abilities towards Re(I) and Pd(II) 90° metal fragments.

RESULTS AND DISCUSSION

Synthesis of the *trans*-di-4-pyridylporphyrin dimers

The structures of the target *trans*-di-4-pyridylporphyrin dimers are shown in Figure 1. They are symmetric dimers in which two *trans*-di-4-pyridylporphyrins are connected at the *meso* position with a phenyl-alkynyl bridge of increasing length. This kind of linking bridge has been chosen in order to ensure rigidity and linearity to the whole molecule, thus avoiding bent conformations. It also granted rather simple synthetic pathways through standard Glaser-Hay or Sonogashira coupling reactions. Moreover, for a better solubility in polar solvents and membrane compatibility, the dimers have been functionalized on the two opposite *meso* positions with phenyl rings bearing a short polyether chain. In the linear conformation, the overall length of dimers **1a-c**, estimated from molecular modelling and excluding the polyether chains, is about 36, 38, and 43 Å, respectively, sufficient in each case to span a phospholipid bilayer, which is about 40 Å thick.

The key intermediates in the synthesis of the tetra-pyridylporphyrin dimers are 5,15-bis-(4-pyridyl)-10-(4-ethynylphenyl)-20-(4-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl)porphyrin (**2a**), and 5,15-bis-(4-pyridyl)-10-(4-iodophenyl)-20-(4-[2-[2-(2-methoxyethoxy)ethoxy] ethoxy]phenyl)porphyrin (**3a**) (Figure 2).

Porphyrins **2a** and **3a** are A_2BC *trans meso*-substituted derivatives, which can be conveniently obtained by a modification of the Lindsey's approach [10], in which the 5-(4-pyridyl)dipyrromethane is reacted with half an equivalent of two different aldehydes (Scheme 1). This is a statistical approach, leading to the A_2BC porphyrin together with the two symmetric trans products (A_2B_2 and A_2C_2). Notably, if the two aldehydes have comparable reactivity the desired A_2BC isomers are obtained, in predominant yield. In the case of the synthesis of **2a** 5-(4-pyridyl)dipyrromethane was reacted with 4-[(trimethylsilyl)ethynyl]benzaldehyde and 4-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzaldehyde (Scheme 1) in a molar ratio 1:0.5:0.5. The latter aldehyde, commercially available but exceedingly expensive, was in turn obtained by a standard Mitsunobu reaction between 4-hydroxybenzaldehyde and triethylenglycolmonomethylether. The macrocyclization reaction was performed in CH_2Cl_2 at 0 °C and under Ar atmosphere using TFA as the acidic catalyst. After oxidation with DDQ in air, the crude product was neutralized and treated with tetrabutylammonium fluoride (TBAF) to remove the silyl protecting groups. Repeated purification steps by silica chromatography and crystallization from $CHCl_3$/MeOH afforded the three porphyrins in 12 % (**2a**), 7% (**2b**) and 3% (**2c**) yield. Starting from 4-iodobenzaldehyde, and following a similar scheme of reactions, porphyrins **3a**,**b** and **2c** were obtained in 17%, 8%, and 5% yield, respectively. All the porphyrins were fully characterized by ^{1}H- and ^{13}C-NMR, ESI-MS, IR, UV-Vis and emission spectroscopies (see also Fig. S1-S10 and Fig. S25-S26 of the Supplemental Material).

Porphyrins **2a** and **3a** were then used for the preparation of dimers **1**. Dimer **1b** was obtained in good yield *via* Glaser-Hay homocoupling of **2a** (Scheme 2). The reaction proceeds smoothly at room temperature in the presence of CuCl, tetramethylethylenediamine (TMEDA) and under a positive pressure of oxygen giving, after column chromatography purification, the desired product in good yield.

Dimers **1a** and **1c** were likewise obtained by Sonogashira coupling between **2a** and **3a** and between **3a** and 1,4-diethynylbenzene, respectively (Scheme 3). The copper-free variation of the Sonogashira coupling reaction was used in order to avoid possible undesired porphyrin-metallation side products. The coupling proceeds in the presence of $Pd(PPh_3)_4$ and a large excess of TEA in a THF/DMF mixture, under Ar atmosphere and under microwave irradiation for 1 hour, at 120 °C. After purification, dimers **1a** and **1c** were obtained in 24% and 62% yield, respectively.

Characterization of the *trans*-di-4-pyridylporphyrin dimers

All the porphyrin dimers were fully characterized by ESI-MS, ^{1}H- and ^{13}C-NMR, IR, UV-Vis and emission spectroscopies, with the mass spectra unambiguously identifying the nature of each product. The ^{1}H-NMR spectra (assigned by 2D H-H and H-C NMR experiments, see also Supplemental Material) of the three porphyrin dimers closely resemble that of the reference monomer porphyrin **2a**, reflecting the symmetry of the molecules. In particular, the upfield and the midfield regions of the reference porphyrin and the dimers, comprising the resonances of the NH core protons and of polyether chains, respectively, are practically superimposable (see Fig. S17 in the Supplemental Material). Small but significant differences are however observed in the downfield region of the spectra (Figure 3).

With respect to **2a**, the pattern of the β-pyrrolic protons (β-H, Figure 3) in the dimers is, in general, more resolved and the proton resonances of the phenyl ring bearing the ethynyl substituents (H_3- and H_4-Ph, Figure 3) are downfield shifted, to different extents depending on the dimer. As expected, due to the long distance from the linkers, the peaks corresponding to the pyridyl protons (H_α- and H_β- Py) and to the phenyl rings bearing the polyether chain (H_1- and H_2-Ph) are, on the contrary, essentially unchanged. A spectroscopic signature of dimer **1c** is the singlet at *ca.* 7.75 ppm. which can be ascribed to the protons of the central phenyl ring of the linker (H_5-Ph, Figure 3), lying on the center of symmetry of the molecule. Similarly to the ^{1}H-NMR analysis, the ^{13}C-NMR spectra of the various dimers are also very similar to that of porphyrin **2a**, except for the number and position of the ethynyl carbon signals, together with the

presence, for dimer **1c**, of two peaks around 135 ppm, assigned to the phenyl carbons of the linker (see Fig. S18 of the Supplemental Material).

To better characterize the dimers, their diffusion coefficients were determined using ^{1}H-DOSY NMR experiments. Figure 4 shows the ^{1}H-DOSY spectra for dimer **1a** and, for comparison, porphyrin **2c**. Similar 2D-maps were also obtained for dimers **1b** and **1c** and are reported in the Supplemental Material.

Inspection of the 2D-map of Figure 4 shows that all the signals of the two molecules, except the solvent and water residues, are aligned along one single value of diffusion coefficient indicating the presence in solution of a single species with a well-defined dimension. Moreover, the porphyrin monomer has a higher diffusion coefficient than the dimer, in agreement with the latter species having a bigger size. The diffusion coefficients for all these species together with their hydrodynamic diameters obtained from the Stokes-Einstein equation, while not being meaningful in terms of absolute values, are consistent with the expected increased dimension going from monomer **2a** to dimers **1** (see Table 1 in the Supplemental Material).

Finally, the absorption and emission spectroscopic features of the three dimers were investigated. Figure 5 reports the UV-vis spectra of the dimers (1 μm in DCM) in comparison with porphyrin **2a** (2 μM in DCM). The Soret band for the dimers is only slightly red-shifted (2-3 nm) with respect to the one of **2a**, while the position of the Q-bands is almost unaffected. The intensity of the absorption bands changes substantially among the series. Dimer **1b**, which is the exact double of the porphyrin monomer, has practically the same molar absorptivity of **2a**, while the intensity of the Soret and of the Q-bands decreases on going from **1a** to **1c**. Clearly the substitution with two phenyl ring in **1a** and the presence of the central phenyl in **1c** has a negative effect on the conjugation between the ethynyl group and the porphyrin aromatic macrocycle, resulting in a lower molar absorptivity.

Figure 6 reports the emission spectra of the dimers **1** (1 μM) and of porphyrin **2a** (2 μM) recorded in DCM with the excitation wavelength fixed at 420 nm. All the spectra are almost superimposable, both in terms of intensity and position of the emission bands, as might be expected.

Preliminary studies for the preparation of 4+8 *trans*-di-4-pyridylporphyrin metallacyclic assemblies

Preliminary investigations towards the preparation of 4+8 *trans*-di-4-pyridylporphyrin metallacyclic assemblies with a parallelepiped shape were performed using dimer **1b** in combination with two different 90° metal fragments. Despite the rotational freedom of the two macrocycles around the phenyl-alkynyl linker, we envisaged the possibility of a thermodynamic self-sorting process, leading to the successful obtainment of metallacyclic assemblies as unique products (Figure 7).

We first investigated the use of the [Pd(dppp)(OTf)$_2$] metal complex (dppp = 1,3-bis(diphenylphosphino)propane, OTf = trifluorosulphonate), which is known to readily form soluble 4+4 metallacycles with *trans*-di-4-pyridylporphyrins [11]. The solubility in both polar and apolar organic solvents is normally ascribed both to the positive charge of the metal complex, due to the loss of the two triflate anions upon coordination of two pyridyl groups, and to the out-of-plane phenyl substituents of the dppp ancillary ligand disfavoring possible aggregation of the resulting assemblies. Also, the two phosphorus atoms of the ancillary dppp ligand are a useful tag for ^{31}P-NMR investigations. However, simply mixing dimer **1b** with two equivalents of [Pd(dppp)(OTf)$_2$] in $CDCl_3$ directly in the NMR tube afforded very complex ^{1}H- and ^{31}P-NMR spectra suggesting the presence of several species, possibly in dynamic equilibrium. Heating and/or increasing of the building blocks concentrations, did not change or simplify the overall pattern of the NMR spectra.

A second preliminary attempt to prepare metallacyclic parallelepiped assemblies was made using [Re(CO)$_5$Br] as metal fragment. Compared to Pd(II), Re(I) is known to form kinetically and thermodynamically more stable bonds with

pyridyl ligands, leading to the formation of stable discrete cyclic structures. The chemistry of the $[Re(CO)_5X]$ (X = Cl^- or Br^-) complex in the formation of stable 4+4 metallacycles with *trans*-di-4-pyridylporphyrins has been pioneered by J.T. Hupp [5, 12]. The strong labilizing effect of CO serves to activate two (and only two) *cis*-carbonyls for substitution, presumably first by solvent molecules (*e.g.* tetrahydrofuran) and then by pyridyl ligands. The reaction is slow and can take up to 2 days for completion under refluxing conditions. We therefore reacted **1b** and $[Re(CO)_5Br]$ in a mixture of THF and toluene under reflux, until the porphyrin starting material was fully consumed. Work-up of the reaction afforded a solid which was scarcely soluble in a variety of solvents. The ^{1}H-NMR spectra of this solid in pyridine-d_5 were difficult to interpret, although a DOSY experiment suggested the presence of a single species in solution (Figure S20 of the Supplemental Material) [13]**.** Once again, variation of the temperature did not lead to any simplification of the NMR spectrum, which would be expected if a highly symmetrical assembly had formed. Most likely, the very low solubility of reagents and intermediates hampers the instauration of a fast thermodynamic equilibrium, that should lead to the desired metallacyclic product, and consequently the porphyrin dimer gets consumed in the formation of undesired oligomeric coordination open-species. The difficulty to identifying a single 4+8 supramolecular adduct with a di-4-pyridylporphyrin dimer and a Re(I) complex when the porphyrin dimer bears a triphenyl bridge has been also reported by Hupp et al. and was attributed to unacceptably slow conversion of "wrong" kinetic intermediate products [9b].

EXPERIMENTAL

General

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*. Analytical thin layer chromatography (TLC) was carried out on *Merck* aluminium backed silica gel plates (thickness 0.25 mm). Flash column chromatography (FCC) was carried out on *Merck* silica gel 60 (230–400 Mesh).

NMR spectra were recorded on a Varian 500 MHz spectrometer (operating at 500 MHz for ^{1}H and at 125 MHz for ^{13}C). Chemical shifts are reported as parts per million (ppm) relative to the solvent residual signal as internal reference. [$CDCl_3$: δ_H, ppm 7.27; δ_C, ppm 77.36; CD_3OD: δ_H, ppm 3.31; δ_C, ppm 49.00; pyridine-d_5: δ_H, ppm 8.74; δ_C, ppm 150.30].

IR spectra were recorded on a *Perkin Elmer* System 2000 NIR spectrophotometer with the KBr pellet technique and only major peaks are reported. UV-Vis spectra were recorded on a *Perkin Elmer* Lambda 35 spectrophotometer. Fluorescence emission spectra were recorded on a *Varian* Cary Eclypse spectrofluorimeter. Electrospray ionization mass spectra (ESI-MS) were performed on a *Perkin Elmer* API I at 5600 eV.

1,4-diethynylbenzene was purchased from Aldrich. 5-(4-Pyridyl)dipyrromethane [14], $[ReBr(CO)_5]$ [15] and $[Pd(dppp)(OTf)_2]$ [16] were prepared as reported previously.

Abbreviations used in the text: AcOEt = ethyl acetate; DCM = dichloromethane; PE = petroleum ether; Py = pyridine; TBAF = tetra-n-butylammonium fluoride; THF = tetrahydrofurane; n-Hx = n-hexane; DMF = dimethylformamide; TEA = triethylamine; TFA = trifluoroacetic acid; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; DIAD = diisopropylazodicarboxylate; dppp = 1,3-bis-(diphenylphosphino)propane; TMEDA = tetramethylethylendiamine; TMSA = trimetylsilylacetylene; dba = tris-dibenzylideneacetone; tol = tolyl; MS = molecular sieves; µWave = microwave; TLC = thin layer chromatography; FCC = flash column chromatography; CC = column chromatography.

Synthesis of A_2BC porphyrins 2a-2c and 3a-3c

4-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]benzaldehyde (TegPhCHO) [8c]

Triphenylphosphine (5.5 g, 21.0 mmol) was dissolved in 70 mL of anhydrous THF under Ar atmosphere and the solution was cooled to 0 °C. DIAD (2.0 mL, d = 1.420 g/mL, 14.0 mmol) was then added dropwise. The solution became pale yellow and a fine white precipitate was formed. Then a solution of triethylenglycolmonomethylether (THF solution, 2.20 mL, d = 1.048 g/mL, 14.0 mmol) and of *p*-hydroxybenzaldehyde (1.71 g, 14.0 mmol) in anhydrous THF was added dropwise. The reaction mixture was stirred under inert atmosphere for 4 hours at room temperature. The solvent was removed under vacuum and the mixture was purified by FCC (AcOEt/n-Hx from 2/3 to 1/1 v/v) giving a pale yellow oil. Yield 2.24 g (60%). R_f = 0.26 (SiO_2, AcOEt/n-Hx 3/2 v/v). ^{1}H-NMR (500 MHz; CD_3OD): δ_H, ppm 9.82 (1H, s, CHO), 7.83 (2H, d, *J* = 9.0 Hz, H_1-Ph), 7.07 (2H, d, *J* = 8.5 Hz H_2-Ph), 4.20 (2H, m, PhOC*H*$_2$CH$_2$O), 3.84 (2H, m, OCH$_2$C*H*$_2$O), 3.68 (2H, m, OC*H*$_2$CH$_2$O), 3.61–3.59 (4H, s, OC*H*$_2$C*H*$_2$O), 3.50 (2H, m, OCH$_2$C*H*$_2$OCH$_3$), 3.32 (3H, s, OCH_3). ^{13}C-NMR (125 MHz; CD_3OD): δ_C, ppm 191.3, 164.1, 131.7, 130.0, 114.7, 71.5, 70.4, 70.2, 70.0, 69.2, 67.7, 57.7. MS (ESI): *m/z* 269, 291 (calcd. for $[C_{14}H_{20}O_5 + H]^+$ 269.13, $[C_{14}H_{20}O_5 + Na]^+$ 291.12).

Porphyrins 2a-2c

The reaction was conducted under Ar atmosphere and in the dark. 5-(4-Pyridyl)dipyrromethane (580 mg, MW = 223.27, 2.60 mmol) and 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (263 mg, MW = 202.32, 1.30 mmol) were dissolved in anhydrous DCM (270 mL). A solution of TegPhCHO (349 mg, MW = 268.306, 1.30 mmol) in 30 mL of anhydrous DCM was added and the mixture was cooled to 0 °C with an ice bath. Then TFA (5.99 mL, d = 1.535 g/mL, 80.6 mmol) was added dropwise and the reaction kept under stirring for 1.5 hours. The reaction mixture was let to reach room temperature and with no more inert atmosphere, DDQ (885 mg, 3.90 mmol) was added and the reaction was stirred for further 2 hours. The crude mixture was directly washed three times with a saturated solution of $NaHCO_3$ and once with water. The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under vacuum. The crude mixture was re-dissolved in 250 mL of DCM and TBAF (1.0 M in THF) (26 mL, d = 0.903 g/mL, 26.0 mmol) was added. After stirring for 2.5 hours at room temperature, the reaction mixture was washed twice with water and the organic phase was dried over Na_2SO_4 and filtered. The solvent was removed under vacuum and the mixture was purified by CC on silica gel ($CHCl_3$/EtOH from 100/0 to 97/3 v/v). The fractions containing the three porphyrins were further purified by another CC on silica gel ($CHCl_3$/EtOH from 100/0 to 98/2). Each product was then obtained as a violet solid by precipitation from $CHCl_3$/MeOH. Yield: **2a** 12%, **2b** 7%, **2c** 3%. Total porphyrins yield 22.0%.

5,15-Bis-(4-pyridyl)-10-(4-ethynylphenyl)-20-(4-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl)porphyrin (2a): R_f = 0.53 (SiO_2, $CHCl_3$/MeOH 97/3 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.04 (4H, d, *J* = 5.6 Hz, H_a-Py), 8.94 (2H, d, *J* = 4.7 Hz, β-H), 8.88 (2H, d, *J* = 4.7 Hz, β-H), 8.82 (4H, m, β-H), 8.17 (6H, s, H_b-Py and H_4-Ph), 8.10 (2H, d, *J* = 8.5 Hz, H_1-Ph), 7.91 (2H, d, *J* = 8.0 Hz, H_3-Ph), 7.32 (2H, d, *J* = 8.5 Hz, H_2-Ph), 4.44 (2H, m, PhOC*H*$_2$CH$_2$O), 4.07 (2H, m, OCH$_2$C*H*$_2$O), 3.89 (2H, m, OC*H*$_2$CH$_2$O), 3.80 (2H, m, OCH$_2$C*H*$_2$O), 3.75 (2H, m, OC*H*$_2$CH$_2$O), 3.62 (2H, m, OCH$_2$C*H*$_2$O), 3.43 (3H, s, OCH_3), 3.33 (1H, s, CCH), –2.84 (2H, br, NH). ^{13}C-NMR (125 MHz; $CDCl_3$): δ_C, ppm 159.0, 150.3, 148.5, 142.4, 135.7, 134.6, 134.2, 130.8, 129.5, 122.1, 121.3, 119.7, 117.3, 113.2, 83.6, 78.7, 72.1, 71.1, 70.9, 70.8, 70.0, 67.9, 59.2. MS (ESI): *m/z* 803, 825, 841 (calcd. for $[C_{51}H_{42}N_6O_4 + H]^+$ 803.33, $[C_{51}H_{42}N_6O_4 + Na]^+$ 825.31, $[C_{51}H_{42}N_6O_4 + K]^+$ 841.29). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 419 (100), 515 (4.7), 549 (2.3), 590 (1.6), 649 (1.5). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 652, 718. IR (KBr): ν, cm^{-1} 2923, 2853, 1637, 1384, 1281, 1248, 1109, 801.

5,15-Bis-(4-pyridyl)-10,20-bis-(4-ethynylphenyl)porphyrin (2b): R_f = 0.47 (SiO_2 $CHCl_3$/MeOH 97/3 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.05 (4H, d, *J* = 5.5 Hz, H_a-Py), 8.89 (4H, d, *J* = 4.7 Hz, β-H), 8.83 (4H, d, *J* = 4.6 Hz, β-H), 8.18 (8H, os, H_b-Py and H_a-Ph), 7.91 (4H, d, *J* = 8.0 Hz, H_b-Ph), 3.34 (2H, s, CCH), –2.86 (2H, br, NH). ^{13}C-NMR (125 MHz; $CDCl_3$): δ_C, ppm 150.2, 148.5, 142.3, 134.57, 130.8, 129.5, 122.2, 120.1, 117.5, 83.6, 78.7, 77.1. MS (ESI): *m/z* 665.2 (calcd. for $[C_{46}H_{28}N_6 + H]^+$ 665.24). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 418 (100), 514 (4.8), 549 (2.0), 589 (1.6), 645 (1.0). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 650, 716. IR (KBr): ν, cm^{-1} 2924, 2854, 1641, 1592, 968, 800, 728.

5,15-Bis-(4-pyridyl)-10,20-bis-(4-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl) porphyrin (2c): R_f = 0.46 (SiO_2, $CHCl_3$/MeOH 95/5 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.04 (4H, dd, *J* = 6.0, 1.5 Hz, H_a-Py), 8.92 (4H, d, *J* = 4.5 Hz, β-H), 8.80 (4H, d, *J* = 5.0 Hz, β-H), 8.17 (4H, dd, *J* = 6.0, 2.0 Hz, H_b-Py), 8.1 (4H, d, *J* = 8.5 Hz, H_1-Ph), 7.32 (4H, d, *J* = 8.5 Hz, H_2-Ph), 4.44 (4H, m, PhOCH_2CH$_2$O), 4.07 (4H, m, OCH$_2$CH_2O), 3.89 (4H, m, OCH_2CH$_2$O), 3.80 (4H, m, OCH$_2$CH_2O), 3.75 (4H, m, OCH_2CH$_2$O), 3.62 (4H, m, OCH$_2$CH_2OCH$_3$), 3.42 (6H, s, OCH$_3$), –2.83 (2H, br, NH). ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C, ppm 159.0, 150.4, 148.4, 135.7, 134.3, 129.5, 126.6, 122.4, 120.8, 120.3, 117.0, 113.1, 111.7, 72.1, 71.1, 70.9, 70.8, 70.0, 67.9, 59.2. MS (ESI): *m/z* 963 (calcd. for $[C_{56}H_{56}N_6O_8 + Na]^+$ 963.40). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 419 (100), 516 (5.2), 550 (3.0), 592 (1.9), 651 (2.7). Fluorescence Emission (**(**CH_2Cl_2, λ_{exc} 426 nm): λ_{em}, nm 655, 719. IR (KBr): ν, cm^{-1} 3078, 2922, 2860, 1637, 1593, 1449, 1404, 1384, 1351, 1286, 1246, 1175, 1108, 967, 788, 737.

Porphyrins 3a-3b

The reaction was conducted under Ar atmosphere and in the dark. 5-(4-Pyridyl)dipyrromethane (594 mg, MW = 223.27, 2.66 mmol) and 4-iodobenzaldehyde (309 mg, MW = 232.02, 1.33 mmol) were dissolved in anhydrous DCM (270 mL). A solution of TegPhCHO (381 mg, MW = 268.306, 1.33 mmol) in 30 mL of anhydrous DCM was added and the mixture was cooled to 0 °C with an ice bath. Then TFA (6.12 mL, d = 1.535 g/mL, 82.5 mmol) was added dropwise and the reaction was kept under stirring for 1.5 hours. The reaction mixture was let to reach room temperature and with no more inert atmosphere DDQ (1.21 g, 5.32 mmol) was added and the reaction was stirred for further 2 hours. The crude mixture was directly washed three times with a saturated solution of $NaHCO_3$ and once with water. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by CC on silica gel ($CHCl_3$/EtOH from 100/0 to 97/3 v/v). The fractions containing the three porphyrins were further purified by another CC on silica gel ($CHCl_3$/EtOH from 100/0 to 98/2). Each product was then obtained as a violet solid by precipitation from $CHCl_3$/MeOH. Yield: **3a** 17%, **3b** 8.0%, **2c** 5%. Total porphyrins yield 30%.

5,15-Bis-(4-pyridyl)-10-(4-iodophenyl)-20-(4-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl)porphyrin (3a): R_f = 0.49 (SiO_2, $CHCl_3$/MeOH 97/3 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.06 (4H, d, *J* = 5.5 Hz, H_a-Py), 8.95 (2H, d, *J* = 5.0 Hz, β-H), 8.89 (2H, d, *J* = 4.5 Hz, β-H), 8.82 (4H, m, β-H), 8.18 (4H, d, *J* = 5.5 Hz, H_b-Py), 8.12 (4H, s, H_1-Ph and H_a-PhI), 7.95 (4H, d, *J* = 8.0 Hz, H_b-Ph), 7.33 (4H, d, *J* = 9.0 Hz, H_2-Ph), 4.45 (2H, m, PhOCH_2CH$_2$O), 4.08 (2H, m, OCH$_2$CH_2O), 3.90 (2H, m, OCH_2CH$_2$O), 3.81 (2H, m, OCH$_2$CH_2O), 3.76 (2H, m, OCH_2CH$_2$O), 3.64 (2H, m, OCH$_2$CH_2OCH$_3$), 3.44 (3H, s, OCH$_3$), –2.85 (2H, br, NH). ^{13}C-NMR (125 MHz; $CDCl_3$): δ_C, ppm 158.9, 150.2, 148.3, 141.3, 136.1, 136.0, 135.6, 134.1, 129.4, 121.2, 119.1, 117.1, 113.0, 94.4, 72.0, 71.0, 70.8, 70.7, 70.0, 67.8, 59.2. MS (ESI): *m/z* 905, 927 (calcd. for $[C_{49}H_{41}IN_6O_4 + H]^+$ 905.23, $[C_{49}H_{41}IN_6O_4 + Na]^+$ 927.21). UV-vis spectrum (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 419 (100), 515 (4.8), 550 (2.2), 591 (1.5), 651 (1.8). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 655, 717. IR (KBr): ν, cm^{-1} 2922, 2853, 1636, 1593, 1472, 1384, 1283, 1248, 1105, 968, 799, 732.

5,15-Bis-(4-pyridyl)-10,20-bis-(4-iodophenyl)porphyrin (3b) [17]: R_f = 0.67 (SiO_2, $CHCl_3$/MeOH 97/3 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.07 (4H, dd, *J* = 5.5, 1.5 Hz, H_a-Py), 8.90 (4H, d, *J* = 4.5 Hz, β-H), 8.84 (4H, d, *J* = 5.0 Hz, β-H), 8.17 (4H, dd, *J* = 6.0, 2.0 Hz, H_b-Py), 8.13 (4H, d, *J* = 8.0 Hz, H_a-PhI), 7.95 (4H, d, *J* = 8.0 Hz, H_b-PhI), –2.89 (2H, br, NH). ^{13}C-NMR (125 MHz; $CDCl_3$): δ_C, ppm 150.0, 148.3, 141.1, 136.1, 136.0, 129.3, 119.5, 117.3, 94.5. MS (ESI): *m/z* 869 (calcd. for $[C_{42}H_{26}I_2N_6 + H]^+$ 869.04). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 418 (100), 514 (4.3), 548 (1.5), 590 (1.1), 650 (1.0). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 656, 716. IR (KBr): ν, cm^{-1} 2921, 1637, 1591, 14783, 1384, 967, 796, 783, 725.

Synthesis of porphyrin dimers 1a-c

Dimer 1a

Anhydrous THF, anhydrous DMF and TEA were degassed for 1 hour with Ar. A solution of **2a** (21 mg, MW = 802.9, 0.026 mmol) in 1 mL of anhydrous THF was prepared and kept under Ar atmosphere. Porphyrin **3a** (21.7 mg, MW = 904.79, 0.024 mmol) was placed in the microwave reactor vessel and set under inert atmosphere. Then DMF (1.2 mL) and TEA (0.8 mL) were added and the mixture was degassed for 15 minutes with Ar. Lastly, keeping the vessel under inert atmosphere, $Pd(PPh_3)_4$ (1.4 mg, MW = 1154.56, 0.0012 mmol) was added and the mixture was degassed for further 15 minutes. Keeping the vessel under Ar, the solution of **2a** was added. The reaction was stirred for 1 hour at 120°C under microwave irradiation (ramping time = 10 min, P = 300 W). The crude mixture was passed through a very short Celite® 521 pad washing with $CHCl_3$/MeOH 9/1. The organic solvent was then extracted twice with distilled water to remove the DMF, dried with Na_2SO_4 and finally the solvent was removed under reduced pressure. Purification of the crude by CC ($CHCl_3$/EtOH from 98/2 to 97:3 v/v) afforded a purple solid. Yield 9.1 mg (24%). R_f = 0.43 (SiO_2, $CHCl_3$/MeOH 95/5 v/v). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H, ppm 9.08 (8H, d, *J* = 5.5 Hz, H_a-Py), 9.00 (4H, d, *J* = 4.5 Hz, β-H), 8.97 (4H, d, *J* = 4.5 Hz, β-H), 8.89 (4H, d, *J* = 5.0 Hz, βH), 8.84 (4H, d, *J* = 5.0 Hz, β-H), 8.31 (4H, d, *J* = 8.0 Hz, H_4-Ph), 8.21 (8H, dd, *J* = 6.0, 3.0 Hz, H_b-Py), 8.14 – 8.11 (8H, ov, H_1-Ph and H_3-Ph), 7.35 (4H, d, *J* = 8.5 Hz, H_2-Ph), 4.46 (4H, m, PhOC*H*$_2$CH$_2$O), 4.09 (4H, m, OCH$_2$C*H*$_2$O), 3.91 (4H, m, OC*H*$_2$CH$_2$O), 3.82 (4H, m, OCH$_2$C*H*$_2$O), 3.77 (4H, m, OC*H*$_2$CH$_2$O), 3.65 (4H, m, OCH$_2$C*H*$_2$O), 3.44 (6H, s, OCH_3), –2.80 (4H, br, NH). ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C, ppm 159.3, 150.6, 148.7, 142.4, 135.9, 135.0, 134.4, 130.6, 130.1, 129.8, 123.4, 121.5, 120.1, 117.5, 113.4, 91.0, 72.4, 71.3, 71.2, 71.0, 70.3, 68.1, 59.5. MS (ESI): *m/z* 1577 (calcd. for $[C_{100}H_{82}N_{12}O_8 - H]^-$ 1577.63). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 423 (100), 516 (5.2), 551 (2.5), 591 (1.2), 649 (0.9). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 654, 718. IR (KBr): ν, cm^{-1} 2919, 1853, 2361, 1719, 1637, 1592, 1473, 1384, 1282, 1247, 1106, 1072, 968, 800, 732.

Dimer 1b

CuCl (5.3 mg, 0.0054 mmol) was inserted in a round bottom flask and TMEDA (24.0 µL, d = 0.78, 0.162 mmol) was added under stirring. Then 1.0 mL of anhydrous DCM and activated molecular sieves (4Å, ~380 mg) were added in sequence. Lastly a solution of **2a** (87 mg, MW = 802.9, 0.108 mmol) in 3.5 mL of anhydrous DCM was added and the reaction was stirred for 16 hours, at room temperature, under air pressure. The reaction was quenched with 3 mL of H_2O, then the organic layer was washed three times with water, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude was purified by CC (silica gel, $CHCl_3$/EtOH from 99/1 to 95/5 v/v) giving a purple solid. Yield 66 mg (76%). R_f = 0.30 (SiO_2, $CHCl_3$/MeOH 98/2 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.07 (8H, d, *J* = 5.4 Hz, H_a-Py), 8.95 (4H, d, *J* = 5.1 Hz, β-H), 8.93 (d, *J* = 4.8 Hz, βH), 8.86 (4H, d, *J* = 4.5 Hz, β-H), 8.82 (4H, d, *J* = 4.4 Hz, β-H), 8.25 (4H, d, *J* = 8.1 Hz, H_4-Ph), 8.18 (8H, d, *J* = 5.6 Hz, H_b-Py), 8.11 (4H, d, *J* = 8.4 Hz, H_1-Ph), 8.04 (4H, d, *J* = 8.1 Hz, H_3-Ph), 7.33 (4H, d, *J* = 8.6 Hz, H_2-Ph), 4.46 (4H, m, PhOC*H*$_2$CH$_2$O), 4.07

(4H, m, OCH_2CH_2O), 3.90 (4H, m, OCH_2CH_2O), 3.81 (4H, m, OCH_2CH_2O), 3.76 (4H, m, OCH_2CH_2O), 3.63 (4H, m, OCH_2CH_2O), 3.43 (6H, s, OCH_3), –2.82 (4H, br, NH). ^{13}C-NMR (125 MHz; $CDCl_3$): δ_C, ppm 159.3, 150.5, 148.7, 143.3, 135.9, 135.0, 134.4, 131.4, 129.7, 125.7, 121.9, 121.6, 119.7, 117.6, 113.4, 82.4, 75.7, 72.4, 71.3, 71.1, 71.0, 70.3, 68.1, 59.5. MS (ESI): *m/z* 1603, 1626 (calcd. for $[C_{102}H_{82}N_{12}O_8 + H]^+$ 1603.64, $[C_{102}H_{82}N_{12}O_8 + Na]^+$ 1626.63). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 423 (100), 516 (5.7), 551 (3.5), 591 (2.1), 649 (1.8). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 655, 718. IR (KBr): ν, cm^{-1} 2921, 2853, 2361, 1717, 1636, 1592, 1384, 1284, 1247, 1108, 799.

Dimer 1c

A solution of 1,4-diethynylbenzene (2.1 mg, 0.016 mmol) in 1 mL of anhydrous THF was prepared and kept under Ar atmosphere. **3a** (31.4 mg, 0.035 mmol) was placed in a microwave reactor vessel and set under inert atmosphere. Then DMF (1 mL) and TEA (3 mL) were added and the mixture was degassed for 15 minutes with Ar. Lastly, keeping the vessel under inert atmosphere, $Pd(PPh_3)_4$ (4 mg, 0.0035 mmol) was added and the mixture was degassed for further 15 minutes. Keeping the vessel under Ar, the solution of 1,4-diethynylbenzene was added. The reaction was stirred for 1 hour at 120°C under microwave irradiation (ramping time = 10 min, P = 300 W). The crude mixture was passed through a very short Celite® 521 pad washing with $CHCl_3$. The organic solvent was extracted three times with distilled water to remove DMF. The organic phase was dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by two CC ($CHCl_3$/EtOH from 100/0 to 97/3 v/v) to give dark purple solid. Yield 16 mg (62%). R_f = 0.36 ($CHCl_3$/MeOH 97/3 v/v). ^{1}H-NMR (500 MHz; $CDCl_3$): δ_H, ppm 9.07 (8H, d, J = 4.0 Hz, H_a-Py), 8.96 – 8.94 (8H, ov, β-H), 8.86 (4H, d, J = 4.5 Hz, β-H), 8.83 (4H, d, J = 5.0 Hz, β-H), 8.25 (4H, d, J = 7.5 Hz, H_4-Ph), 8.19 (8H, d, J = 5.0 Hz, H_b-Py), 8.12 (4H, d, J = 8.5 Hz, H_1-Ph), 8.00 (4H, d, J = 7.5 Hz, H_3-Ph), 7.77 (4H, s, H_5-Ph), 7.34 (4H, d, J = 8.5 Hz, H_2-Ph), 4.46 (4H, m, $PhOCH_2CH_2O$), 4.09 (4H, m, OCH_2CH_2O), 3.90 (4H, m, OCH_2CH_2O), 3.81 (4H, m, OCH_2CH_2O), 3.76 (4H, m, OCH_2CH_2O), 3.64 (4H, m, OCH_2CH_2O), 3.44 (6H, s, OCH_3), –2.81 (4H, br, NH). ^{13}C-NMR (125 MHz; $CDCl_3$): δ_C, ppm 159.3, 150.6, 148.7, 142.4, 135.9, 135.0, 134.5, 132.7, 132.2, 130.5, 129.8, 121.5, 120.1, 117.5, 113.4, 110.4, 91.6, 72.4, 71.3, 71.1, 71.0, 70.3, 69.1, 59.5. MS (ESI): *m/z* 1680 (calcd. for $[C_{108}H_{86}N_{12}O_8 + H]^+$ 1679.67). UV-vis (CH_2Cl_2): λ_{max}, nm (relative intensity, %) 421 (100), 516 (5.2), 551 (3.0), 591 (1.7), 650 (1.8). Fluorescence Emission (CH_2Cl_2, λ_{exc} 420 nm): λ_{em}, nm 655, 719. IR (KBr): ν, cm^{-1} 2923, 2853, 1639, 1593, 1247, 1108, 800, 732.

Supplemental Material

^{1}H-NMR and ^{13}C-NMR spectra of porphyrins **2a-c** and **3a**,**b** and of dimers **1a-c**. ^{1}H-DOSY experiments. UV-vis and fluorescence emission spectra of porphyrins **2a-c** and **3a**,**b**.

CONCLUSION

In conclusion, a small library comprising three different porphyrin dimers was successfully prepared *via* either Glaser-Hay or Sonogashira coupling. The various systems, together with their monomer precursors, were fully characterized by NMR techniques and their UV-vis and fluorescent properties were assessed as well. Although not very successful, the preliminary experiments for the formation of metallacyclic assemblies with a parallelepiped shape gave us good insights on the complexity of this ambitious project. From this stand point, different metal complexes will be tried as alternatives 90° metal fragments in order to overcome the major issues encountered in this report.

ACKNOWLEDGEMENTS

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13. Given the inert nature of the Re–nitrogen bond at room temperature, we exclude that pyridine-d_5 is competing with the already formed Re–nitrogen bonds, even though at least a partial competition cannot be excluded for prolonged exposure times.
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FIGURES AND SCHEMES CAPTIONS

Fig. 1. Structures of the *trans*-di-(4-pyridyl)porphyrin dimers prepared in this work.

Fig. 2. Structures of the *trans*-di-(4-pyridyl)porphyrin monomers prepared in this work.

Scheme 1. Synthetic route to porphyrins **2a-c**.

Scheme 2. Synthesis of dimer **1b**.

Scheme 3. Synthesis of dimers **1a** and **1c**.

Fig. 3. Expansion of the downfield region of the ^{1}H-NMR spectrum ($CDCl_3$) of the reference monomer porphyrin **2a**, and of the dimers **1a-1c**; the asterisk in the spectrum of **1b** indicates a chloroform satellite.

Fig. 4. ^{1}H-DOSY (500 MHz; $CDCl_3$, 298 K) of porphyrin **2c**, and of the dimer **1a**. The 1D trace of **1a** is also shown.

Fig. 5. UV-vis spectra (CH_2Cl_2) of the reference porphyrin **2a** (2 μM), and of the dimers **1a-1c** (1 μM): λ_{max}, nm 419 (**2a**), 423 (**1a**), 423 (**1b**), 421 (**1c**).

Fig. 6. Fluorescence emission spectra (CH_2Cl_2, λ_{exc} = 420 nm) of the reference porphyrin **2a** (2 μM), and of the dimers **1a-1c** (1 μM): λ_{em}, nm 652, 718 (**2a**); 654, 718 (**1a**); 655, 718 (**1b**); 655, 719 (**1c**).

Fig. 7. Schematic depiction of the intended metallacyclic assemblies with a parallelepiped shape, in which four dimers **1b** are coordinated *via* the peripheral pyridyl groups to eight 90° metal fragments.

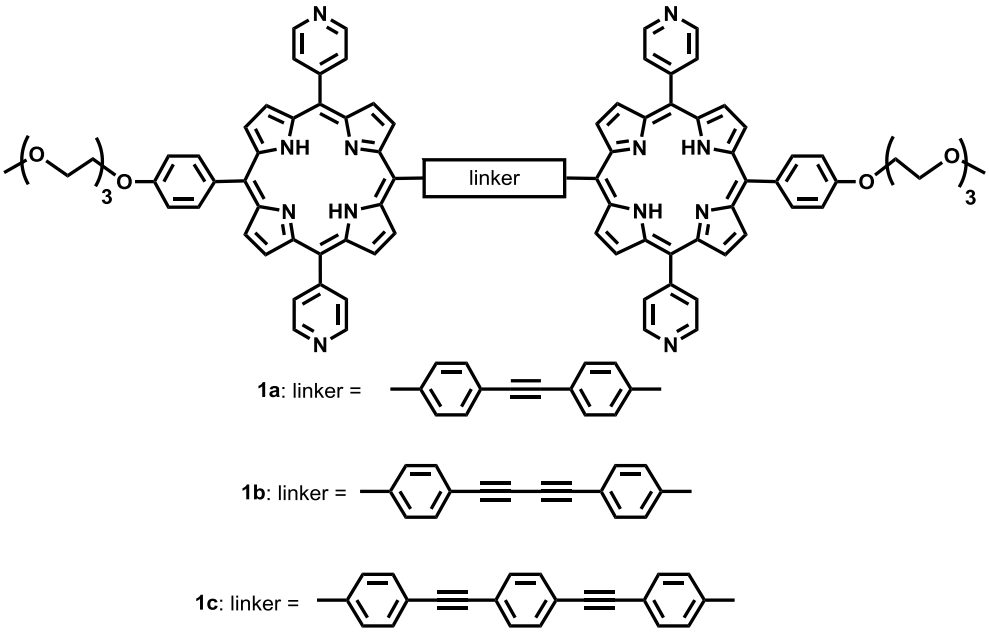
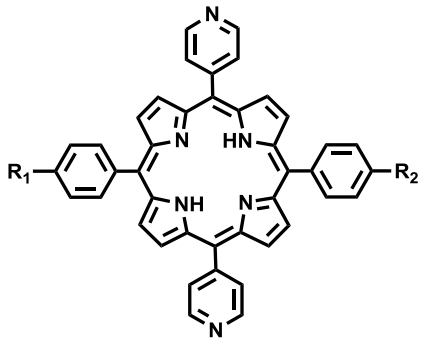


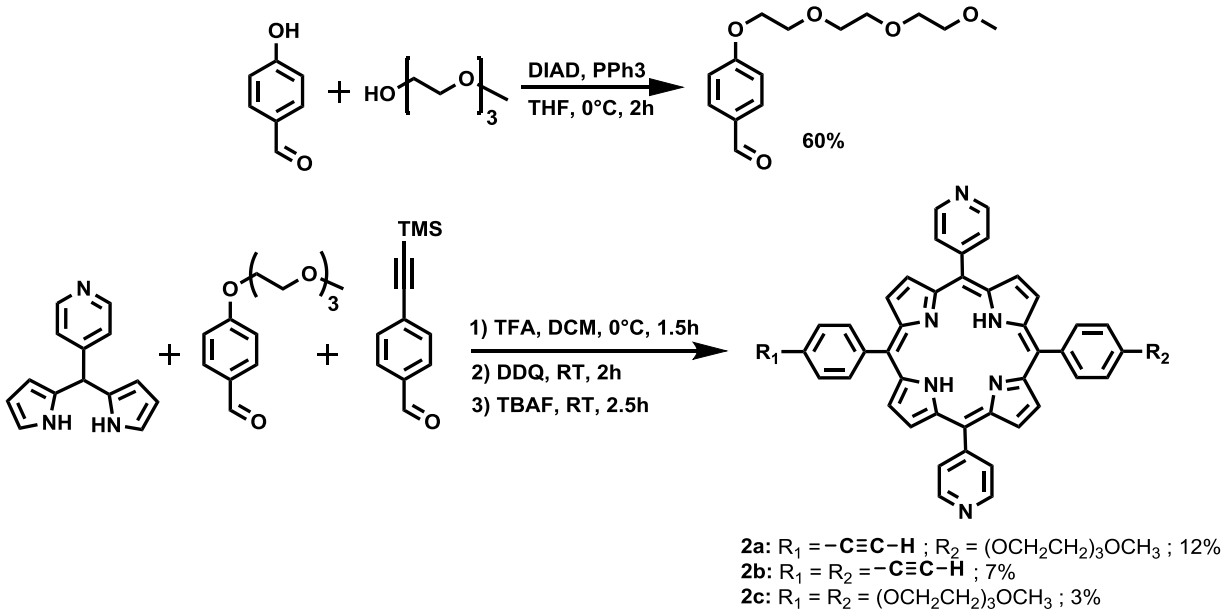
Fig. 1.



2a: R_1 = **—C≡C—H** ; R_2 = $(OCH_2CH_2)_3OCH_3$
2b: R_1 = R_2 = **—C≡C—H**
2c: R_1 = R_2 = $(OCH_2CH_2)_3OCH_3$

3a: R_1 = **I** ; R_2 = $(OCH_2CH_2)_3OCH_3$
3b: R_1 = R_2 = **I**

Fig. 2.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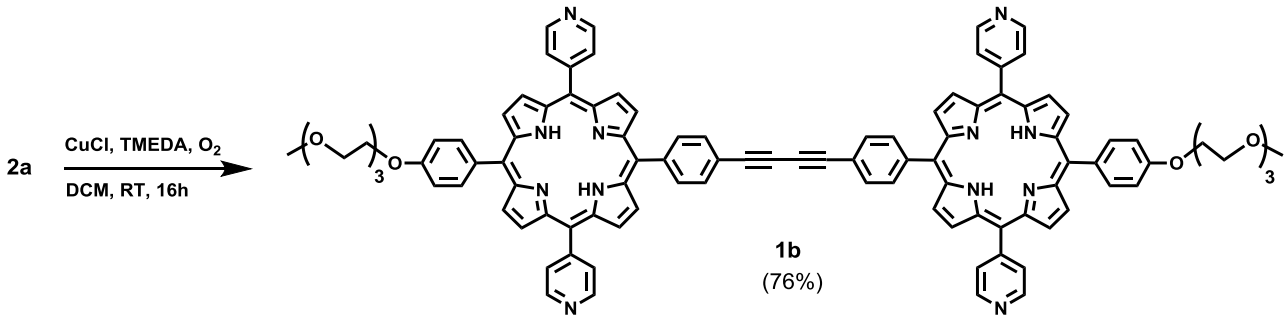
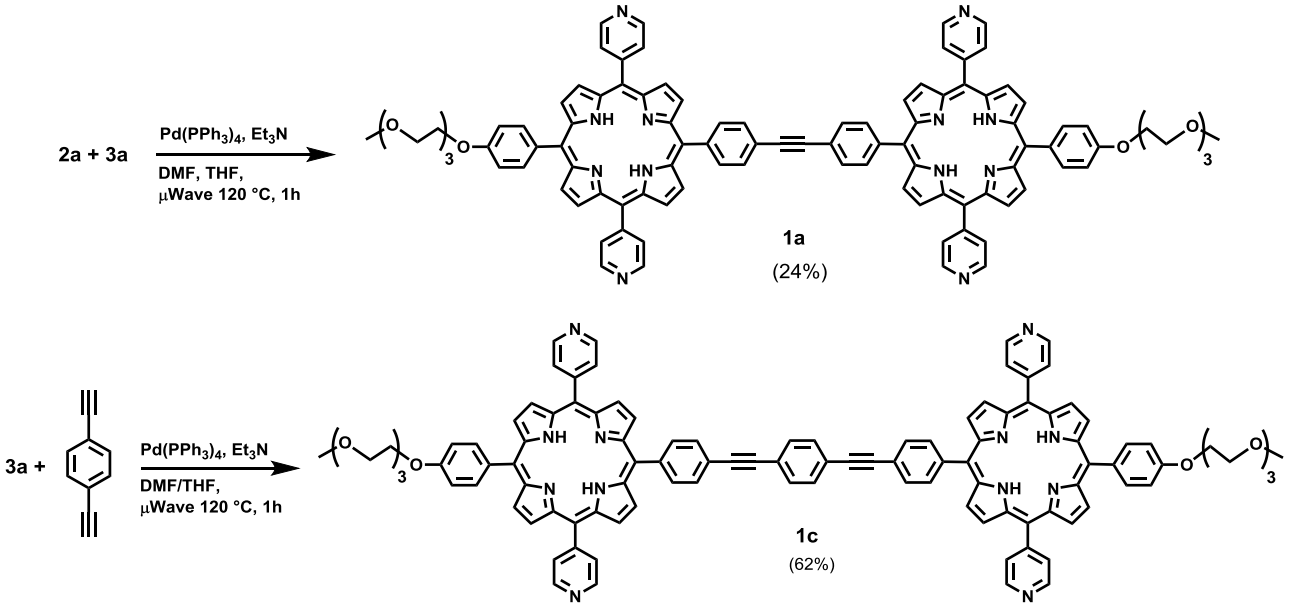
HO
O
3
DIAD, PPh3
THF, 0°C, 2h
60%
TMS
1) TFA, DCM, 0°C, 1.5h
2) DDQ, RT, 2h
3) TBAF, RT, 2.5h
NH
HN
N
R1
R2
2a: R1 = −C≡C−H ; R2 = (OCH2CH2)3OCH3 ; 12%
2b: R1 = R2 = −C≡C−H ; 7%
2c: R1 = R2 = (OCH2CH2)3OCH3 ; 3%

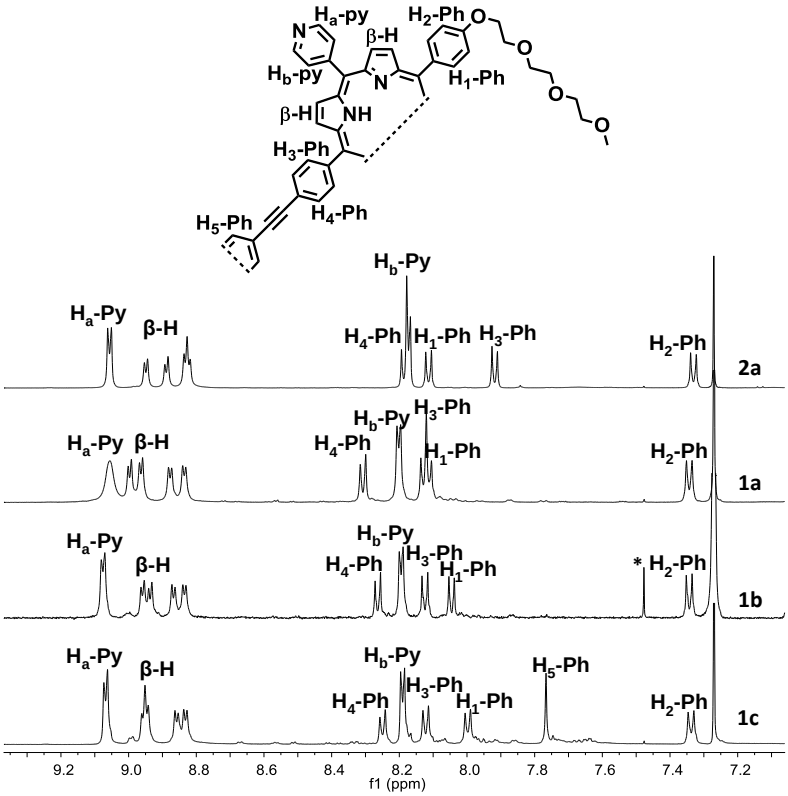
Scheme 1.



Scheme 2.


2a + 3a
Pd(PPh3)4, Et3N
DMF, THF,
μWave 120 °C, 1h
1a
(24%)
3a +
Pd(PPh3)4, Et3N
DMF/THF,
μWave 120 °C, 1h
1c
(62%)

Scheme 3.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H2-Ph
β-H
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NH
H3-Ph
H5-Ph
H4-Ph
Hb-Py
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β-H
H4-Ph
H1-Ph
H3-Ph
H2-Ph
2a
Hb-Py
H3-Ph
Ha-Py
β-H
H4-Ph
H1-Ph
H2-Ph
1a
Hb-Py
Ha-Py
β-H
H4-Ph
H3-Ph
H1-Ph
* H2-Ph
1b
Ha-Py
β-H
Hb-Py
H5-Ph
H4-Ph
H3-Ph
H1-Ph
H2-Ph
1c
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)

Fig. 3.

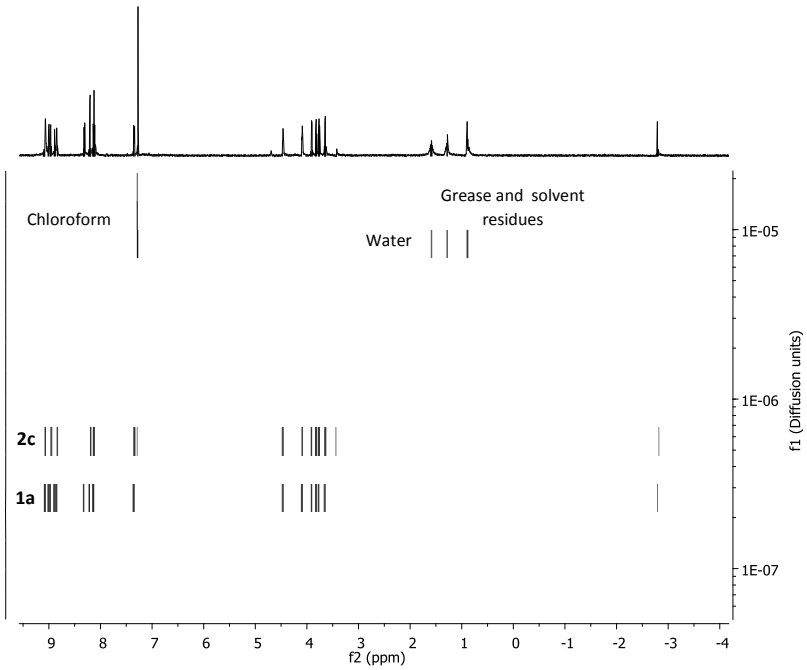
Chloroform
Grease and solvent residues
Water
2c
1a
1E-05
1E-06
1E-07
f1 (Diffusion units)
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f2 (ppm)

Fig. 4.

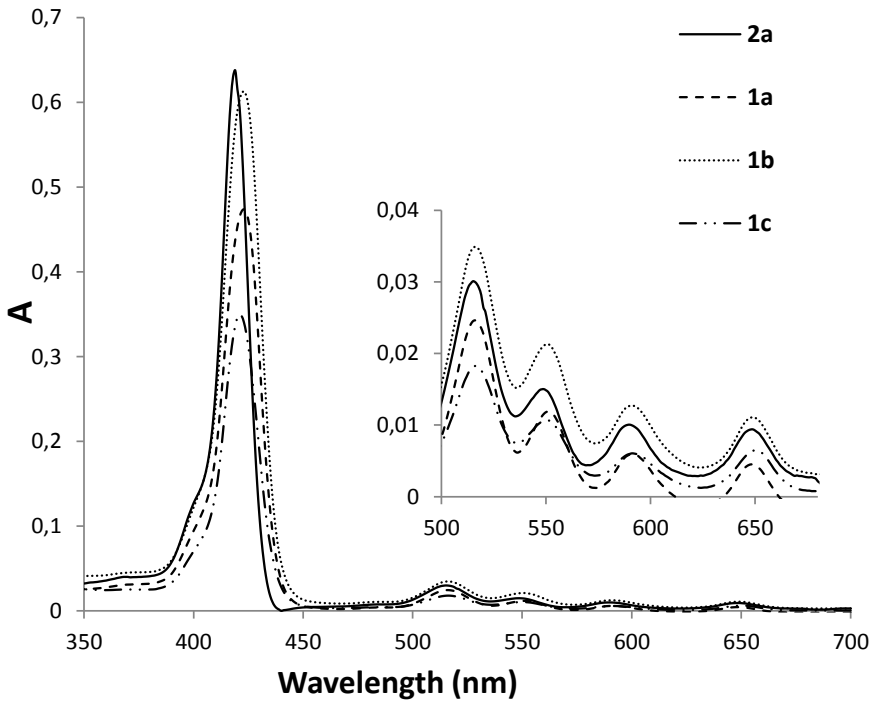
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
A
350
400
450
500
550
600
650
700
Wavelength (nm)
2a
1a
1b
1c
0,04
0,03
0,02
0,01
0
500
550
600
650

Fig. 5.

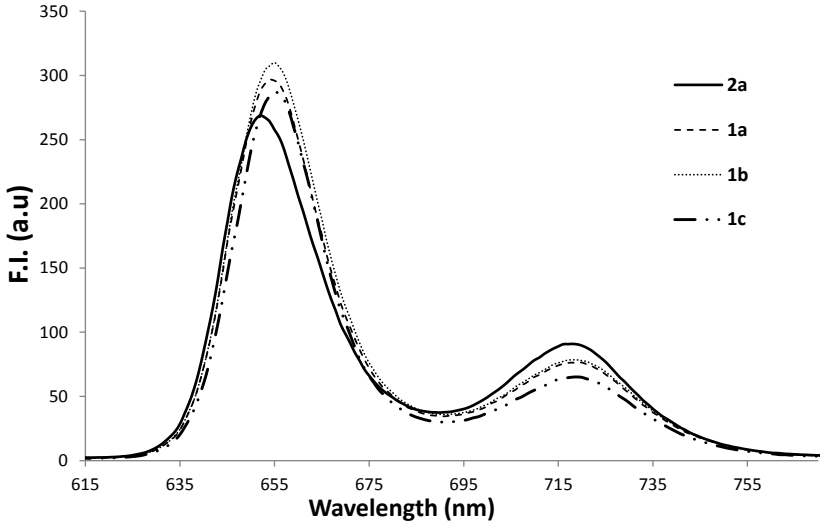
350
300
250
200
150
100
50
0
F.I. (a.u)
615
635
655
675
695
715
735
755
Wavelength (nm)
2a
1a
1b
1c

Fig. 6.

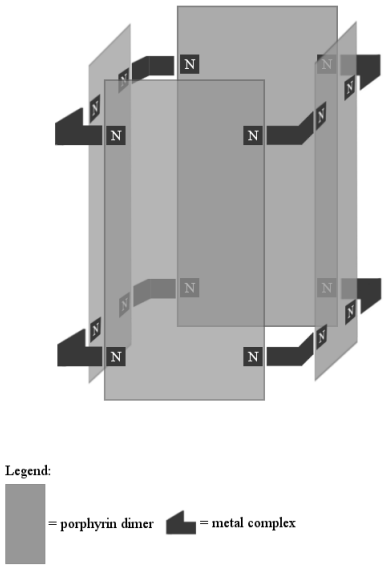

Fig. 7.

GRAPHICAL ABSTRACT

A small library of symmetric *trans*-di-(4-pyridyl)porphyrin dimers have been prepared. The porphyrin dimers are differentiated by a phenyl-alkynyl bridge of increasing length at one *meso* position, while for all the derivatives the two remaining opposite *meso* positions are tailored with a phenyl moiety bearing a short polyether chain.