Supplementary Materials: Highly Cost-Efficient Method for Unsymmetrical meso-Aryl Porphyrins Synthesis Using NaY Zeolite as Inorganic Acid Catalyst

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S1. Materials and methods

Commercially available reagents were purchased from Aldrich, Fluorochem and Acros, being used as received. Zeolite NaY was purchased from Zeolyst. All solvents were pre-dried according to standard laboratory techniques. All spectroscopic data from known porphyrins was confirmed (1H-NMR and UV-Vis) and are in agreement with the literature. UV-visible absorption spectra were recorded on a Hitachi U-2010 using quartz cells. The molar absorption coefficients were determined using toluene as solvent. Zeolite acidity measurements were performed using pyridine as probe molecule, followed by Infrared spectroscopy (FTIR); a Nicolet Nexus spectrometer was used for the purpose. 1H NMR spectra were recorded on a 400 MHz Brucker-Amx. The chemical shifts are given in parts per million (ppm) relative to tetramethylsilane at δ 0.00 ppm for proton spectra. Mass spectra were acquired using an Applied Biosystems Voyager DE-STR instrument equipped with a nitrogen laser (λ = 337 nm) or Bruker microTOFQ instrument by Unidade de Masas e Proteomica – Universidade de Santiago de Compostela, Spain. Column chromatographies were performed with silica gel grade 60, 70-230 mesh as stationary phase.

S2. Characterization of acidic properties of NaY zeolite

Acidity measurements were performed using pyridine as probe molecule, followed by Infrared spectroscopy (FTIR); a Nicolet Nexus spectrometer was used for the purpose. In a typical experiment, samples were pressed into thin wafers (10-20 mg/cm²) and heated in an IR glass cell from room temperature up to 450 °C (5 °C.min⁻¹) for 3 h under vacuum (10⁻⁵ mbar). Afterwards, the samples were cooled down to 150 °C and left in contact with pyridine for 10 min. Then, excess probe molecule was removed for 30 min under vacuum and the IR spectra were recorded; 64 scans with a resolution of 4 cm⁻¹ were collected for each spectrum. The concentrations of Brönsted and Lewis sites able to retain the pyridine at 150 °C were determined using the integrated areas.
of the bands at 1541 cm\(^{-1}\) and 1445 cm\(^{-1}\) \cite{1}, respectively, and the extinction coefficients determined by Emeis (Fig. 1) \cite{2}.

![Figure S1. FTIR spectra of NaY obtained after pyridine contact and subsequent desorption under vacuum at 150 °C for 30 min.](image)

**S3. Preparation of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin (1)**

**S3.1. NaY method**

An amount of 1.0 g of NaY zeolite (0.08 mmol) was introduced into a 50 mL round flask, containing a mixture of 4-hydroxybenzaldehyde (0.625 mmol, 76.3 mg), benzaldehyde (1.875 mmol, 0.19 mL) in a glacial acetic acid/nitrobenzene mixture (7 mL/5 mL). Addition of equimolar amount of pyrrole (2.5 mmol, 0.17 mL) was carried out dropwise under stirring and heating (\(\approx 120 °C\)). After complete addition (ca. 3 min), the suspension was heated further till reflux temperature (\(\approx 130 °C\)) and maintained at this temperature for ca. 2 hours. The hot suspension was filtered and the resulting solid material washed with tetrahydrofuran (THF) until no coloured material was collected on the supernatant (250 mL). As alternative Soxhlet extraction with THF can be performed, but in our case we found washing sufficient. The volume of solution was then reduced by rotoevaporation (enough volume to remove the added washing solvent). To induce precipitation, \(n\)-hexane (ca. 50 mL) was added. The Erlenmeyer flask containing the statistical porphyrin mixture was left overnight in the refrigerator and the deposited solid was collected by filtration and then purified by column chromatography using silica gel as stationary phase, starting with \(n\)-hexane:CH\(_2\)Cl\(_2\) (1:3) to collect the first fraction (5,10,15,20-tetraphenyl porphyrin) and then with CH\(_2\)Cl\(_2\) to collect the second band. As this fraction was identified as the porphyrin 1, other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 60 mg (0.0938 mmol) of 1 (16% yield). Characterization data is in accordance with the literature \cite{3}.\(^{3}\)
S3.2. Adler-Longo method [4]

A mixture of 4-hydroxybenzaldehyde (3.75 mmol, 0.458 g) and benzaldehyde (11.25 mmol, 1.13 mL) was introduced into a 250 mL round flask containing propionic acid (100 mL). Addition of equimolar amount of pyrrole (15 mmol, 1.03 mL) was carried out dropwise under stirring and heating (≈130 °C). After complete addition (ca. 10-12 min), the suspension was heated further till reflux temperature (≈150 °C) and maintained at this temperature for ca. 2 hours. The flask condenser was substituted by a distillation apparatus and the solvent mixture was removed by vacuum, under heating. The obtained solid was redissolved in CH₂Cl₂ (30 mL) and the solution washed with saturated NaHCO₃ solution (3 x 25 mL). The solution was concentrated to dryness in a rotoevaporator and purified by column chromatography using silica gel as stationary phase, starting with n-hexane:CH₂Cl₂ (1:3) to collect the first fraction (5,10,15,20-tetraphenyl porphyrin) and finally with CH₂Cl₂ to collect the second band, contaminated with the corresponding chlorin (close Rf). Other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 142 mg (0.225 mmol) of 1 plus its corresponding chlorin (~10%), in an approximated 6% yield.

S3.3. Gonsalves-Pereira method [5]

A mixture of 4-hydroxybenzaldehyde (3.75 mmol, 0.458 g) and benzaldehyde (11.25 mmol, 1.13 mL) was introduced into a 100 mL round flask containing a glacial acetic acid/nitrobenzene mixture (50 mL/25 mL). Addition of equimolar amount of pyrrole (15 mmol, 1.03 mL) was carried out dropwise under stirring and heating (≈120 °C). After complete addition (ca. 10-12 min), the suspension was heated further till reflux temperature (≈130 °C) and maintained at this temperature for ca. 1 hour. The flask condenser was substituted by a distillation apparatus and the solvent mixture was removed by vacuum, under heating. The deposited solid was purified by column chromatography using silica gel as stationary phase, starting with n-hexane to remove nitrobenzene traces, then n-hexane:CH₂Cl₂ (1:3) to collect the first fraction (5,10,15,20-tetraphenyl porphyrin) and finally with CH₂Cl₂ to collect the second band. As this fraction was identified as the porphyrin 1, other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 166 mg (0.263 mmol) of 1 (7% yield).

S3.4. Lindsey method [6]

A mixture of pyrrole (0.25 mL, 3.75 mmol), 4-hydroxybenzaldehyde (114 mg, 0.938 mmol) and benzaldehyde (0.275 mL, 2.75 mmol) in CHCl₃ (250 ml) was bubbled with N₂ for 30 min, and TFA
(0.13 mL, 2.0 mmol) was added. The mixture was stirred at room temperature under N₂ for 1 hr. DDQ (625 mg, 3.75 mmol) was added and the mixture was stirred for 12 hr with protection from light. Triethylamine (2.5 ml, 19 mmol) was added and stirred for 30 min, and the solvent was removed by rotary evaporation. The residue was then suspended in CH₂Cl₂, placed on the top of a dry column of Al₂O₃, and eluted with CH₂Cl₂. The eluted solution was evaporated and then purified by chromatography on silica gel, starting with n-hexane:CH₂Cl₂ (1:4) to collect the first fraction (5,10,15,20-tetraphenyl porphyrin) and finally with CH₂Cl₂ to collect the second band. As this fraction was identified as the porphyrin 1, other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 89 mg (0.14 mmol) of 1 (15% yield).

**S4. Porphyrin yield as function of the amount of zeolite NaY used**

Ratio was calculated as the quotient between the number of moles of NaY used per sum of moles of pyrrole and aldehydes (reagents). For instance, when the reaction (see above, point 2) was performed using 1 g NaY (0.08 mmol) per 5 mmol reagents, the ratio was 0.032 *i.e.*, NaY was present in 3.2% of all reagents. When ratio was 0.032, the yield obtained was ca. 16%. The yields obtained using different ratios of NaY per amount of reagents is presented in Table S1 and Figure S2.

**Table S1.** Isolated yields of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin (1) vs amount of NaY used.

| NaY ratio | Isolated yield (%) |
|-----------|--------------------|
| 0         | 7                  |
| 0.013     | 9                  |
| 0.021     | 11                 |
| 0.032     | 16                 |
| 0.043     | 16                 |
Figure S2: Isolated yields of porphyrin 1 vs NaY amount. Note: when amount NaY = 0, it represents the isolated yields using the nitrobenzene method.

S5. Catalyst recycling

The catalyst zeolite NaY was tested in successive cycles to evaluate the reutilisation process in the synthesis of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1. Using the best determined conditions, after the first cycle, the selected catalyst was collected by filtration and washed with chloroform and tetrahydrofuran, following drying of the solid overnight, at 150 °C under vacuum. The second, third, fourth and fifth and sixth cycles were carried out with the recovered solid and reactivation procedure was followed for each reutilisation.

Table S2: Reutilisation of NaY on the synthesis of porphyrin 1

| Number of cycles in NaY reutilisation | Isolated yields of porphyrin 1 (%) |
|--------------------------------------|-----------------------------------|
| 1                                    | 16                                |
| 2                                    | 15                                |
| 3                                    | 16                                |
| 4                                    | 16                                |
| 5                                    | 15                                |
| 6                                    | 12                                |

S6. Calculation of sustainability E Factors

Density of liquid chemicals used for the calculation of residues (d = density)

- Propionic acid d= 990 g/L
- Nitrobenzene d= 1200 g/L
- Acetic acid d= 1050 g/L
- Dichloromethane d= 1330 g/L
Chloroform d= 1489 g/L
Trifluoroacetic acid d= 1489 g/L
n-Hexane d= 655 g/L
Water d= 1000g/L
Triethylamine d= 725.5 g/L
Saturated sodium bicarbonate solution d= 2200 g/L

S6.1. Calculation of E Factor for the preparation of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1, considering the preparation of 10 mmol of end product

*Adler-Longo method*

\[ E = \frac{(4356 \text{ g propionic acid} + 1771.6 \text{ g dichloromethane} + 7392.6 \text{ g sodium bicarbonate} + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane})}{6.3 \text{ g porphyrin}} \]
\[ E = 6793 \]

*Gonsalves-Pereira method*

\[ E = \frac{(1995 \text{ g nitrobenzene} + 1140 \text{ g acetic acid} + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane})}{6.3 \text{ g porphyrin}} \]
\[ E = 4233 \]

*Lindsey method (J. Org. Chem. 1987, 52, 827-836)*

\[ E = \frac{(29184.4 \text{ g chloroform} + 15.2 \text{ g TFA} + 142.2 \text{ g triethylamine} + 49 \text{ g DDQ} + 2000 \text{ g Al}_2\text{O}_3 + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane})}{6.3 \text{ g porphyrin}} \]
\[ E = 7090 \]

*Lindsey method (J. Org. Chem. 1994, 59, 579–587)*

\[ E = \frac{(3720 \text{ g dichloromethane} + 160 \text{ g BF}_3\text{Et}_2\text{O} + 160 \text{ g TCQ} + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane})}{6.3 \text{ g porphyrin}} \]
\[ E = 2750 \]

*This method was not reproduced but calculations assuming similar yields obtained and similar purification procedures as for the other methodologies were performed.*

*NaY method**

\[ 784 \text{ g nitrobenzene} + 641 \text{ g acetic acid} + 2000 \text{ g silica} + 9410 \text{ g dichloromethane} + 1970 \text{ g n-hexane})}{6.3 \text{ g porphyrin}} \]
E = 2350

**Since NaY is reusable, it is not included in the calculations**

**S7. Price evaluation related to the synthesis of porphyrin 1**

Notes: Market prices were calculated on basis of laboratory scale acquisition at Sigma-Aldrich company and available at www.sigmaaldrich.com, excluding NaY, whose prices were calculated from Zeolyst International company. Prices do not reflect reagents and solvents acquisitions on a large scale, but at a laboratory scale, just following Sigma-Aldrich website prices. Amounts of solvents and reagents used for the preparation of 10 mmol product were calculated simply by multiplying the amounts used in preparations according to the experimental above, considering obtained yields.

**Table S3** Price calculation for the preparation of 10 mmol 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1 using Adler-Longo method.

| Solvents/Reagents     | CAS Number   | Market Prices\(^a\) (€) | Amount used (10 mmol product) | Price (10 mmol product) |
|-----------------------|--------------|--------------------------|-------------------------------|-------------------------|
| Propionic acid        | 79-09-4      | 1L = 69 €                | 4.44 L                        | 306.36 €                |
| 4-hydroxybenzaldehyde | 123-08-0     | 50g = 34.7 €             | 20.34 g                       | 14.12 €                 |
| benzaldehyde          | 100-52-7     | 100mL = 60 €             | 50.17 mL                      | 30.06 €                 |
| Pyrrole               | 109-97-7     | 100mL = 64.7 €           | 45.73 mL                      | 29.59 €                 |
| NaHCO\(_3\)           | 144-55-8     | 500g = 39.1 €            | 130 g                         | 10.17 €                 |
| Silica gel            | 112926-00-8  | 1Kg = 143 €              | 2 Kg                          | 286 €                   |
| n-hexane              | 110-54-3     | 2.5L = 84 €              | 3 L                           | 100.8 €                 |
| dichloromethane       | 75-09-2      | 2.5L = 104 €             | 7 L                           | 291.2 €                 |
| **Total**             | ****         | **                      | **                            | **1068.3 €**            |
| Solvents/Reagents          | CAS     | Market Prices (€) | Amount used (10 mmol product) | Price (10 mmol product) |
|---------------------------|---------|-------------------|-------------------------------|-------------------------|
| acetic acid               | 64-19-7 | 1 L = 69 €        | 1.9 L                         | 131.1 €                 |
| nitrobenzene              | 98-95-3 | 0.5 L = 73.0 €    | 0.95 L                        | 138.7 €                 |
| 4-hydroxybenzaldehyde     | 123-08-0| 50 g = 34.7 €     | 17.40 g                       | 12.08 €                 |
| benzaldehyde              | 100-52-7| 100 mL = 60 €     | 42.94 mL                      | 25.76 €                 |
| Pyrrole                   | 109-97-7| 100 mL = 64.7 €   | 39.14 mL                      | 25.32 €                 |
| Silica gel                | 112926-00-8| 1 Kg = 143 €       | 2 Kg                          | 286 €                   |
| n-hexane                  | 110-54-3| 2.5 L = 84 €      | 3 L                           | 100.8 €                 |
| dichloromethane           | 75-09-2 | 2.5 L = 104 €     | 7 L                           | 291.2 €                 |
| **Total**                 |         |                   |                               | **1010.96 €**           |
Table S5 Price calculation for the preparation of 10 mmol 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1 using Lindsey method.

| Solvents/Reagents | CAS Number | Market Prices (€) | Amount used (10 mmol product) | Price (10 mmol product) |
|-------------------|------------|--------------------|------------------------------|-------------------------|
| chloroform        | 67-66-3    | 2.5 L = 104 €      | 19.6 L                       | 815.36 €                |
| 4-hydroxybenzaldehyde | 123-08-0   | 50 g = 34.7 €      | 8.94 g                       | 6.2 €                   |
| benzaldehyde      | 100-52-7   | 100 mL = 60 €      | 21.56 mL                     | 12.94 €                 |
| Pyrrole           | 109-97-7   | 100 mL = 64.7 €    | 19.6 mL                      | 12.68€                  |
| Trifluoracetic acid | 76-05-1    | 100 mL = 58.1 €    | 10.19 mL                     | 5.92 €                  |
| 2,3-Dichloro-5,6-dicyano-p-benzoquinone | 84-58-2 | 10 g = 30.2 € | 49 g | 147.98 € |
| triethylamine     | 121-44-8   | 1 L = 52 €         | 196 mL                       | 10.19 €                 |
| Al2O3             | 1344-28-1  | 1 Kg = 94 €        | 2 Kg                         | 188.0 €                 |
| Silica gel        | 112926-00-8| 1 Kg = 143 €       | 2 Kg                         | 286.0 €                 |
| n-hexane          | 110-54-3   | 2.5 L = 84 €       | 3 L                          | 100.8 €                 |
| dichloromethane   | 75-09-2    | 2.5 L = 104 €      | 10 L                         | 416.0 €                 |
| **Total**         |            |                    |                              | **2002.07 €**           |
Table S6 Price calculation for the preparation of 10 mmol 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1 using “NaY” method.

| Solvents/Reagents          | CAS        | Market Prices (€) | Amount used (10 mmol product) | Price (10 mmol product) |
|---------------------------|------------|-------------------|--------------------------------|------------------------|
| acetic acid               | 64-19-7    | 1 L = 69 €        | 746.7 mL                       | 51.52 €                |
| nitrobenzene              | 98-95-3    | 0.5 L = 73.0 €    | 533.4 mL                       | 38.94 €                |
| 4-hydroxybenzaldehyde     | 123-08-0   | 50 g = 34.7 €     | 8.14 g                         | 5.65 €                 |
| benzaldehyde              | 100-52-7   | 100 mL = 60 €     | 20.05 mL                       | 12.03 €                |
| Pyrrole                   | 109-97-7   | 100 mL = 64.7 €   | 18.13 mL                       | 11.73 €                |
| NaY                       | 1318-02-1  | 0.5 Kg = 220 €    | 106.7 g                        | 46.95 €                |
| Silica gel                | 112926-00-8| 1 Kg = 143 €      | 1.75 Kg                        | 250.2 €                |
| n-hexane                  | 110-54-3   | 2.5 L = 84 €      | 2.5 L                          | 84 €                   |
| dichloromethane           | 75-09-2    | 2.5 L = 104 €     | 6 L                            | 249.6 €                |
|                           |            |                   |                                | **Total 750.62 €**      |
**Table S7** Price calculation for the preparation of 10 mmol 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1, disregarding the contribution of reaction solvents (when not mixtures) and chromatography solvents.

| Solvents/Reagents          | Market Prices (€) | Amount (price) used per reaction (Adler)a | Amount (price) used per reaction (Pereira)a | Amount (price) used per reaction (Lindsey)a | Amount (price) used per reaction (NaY)a |
|----------------------------|-------------------|------------------------------------------|--------------------------------------------|--------------------------------------------|----------------------------------------|
| acetic acidb               | 1 L = 69 €        | 250 mL (17.25 €)                         |                                             | 175 mL (12 €)                              |                                        |
| nitrobenzeneb              | 0.5 L=73 €        | 125 mL (18.25€)                          |                                             | 125 mL (18.25€)                            |                                        |
| Propionic acid a           | 1L=69 €           | 0.4 L (27.6€)                            |                                             |                                            |                                        |
| Chloroform a               | 2.5 L = 104 €     | 1.25 L (52€)                             |                                             |                                            |                                        |
| NaY a                      | 0.5 Kg=220 €      |                                            |                                            |                                            | 25 g (11€)                              |
| 4-hydroxy-benzaldehydeb    | 50g=34.7 €        | 2.284 g (1.6€)                           | 2.284 g (1.6€)                             | 0.57 g (0.4€)                              | 1.9 g (1.3€)                            |
| benzaldehydeb              | 100mL=60 €        | 5.65 mL (3.1€)                           | 5.65 mL (3.1€)                             | 1.375 mL (0.8€)                            | 4.7 mL (2.8€)                           |
| pyrroleb                   | 100mL=65 €        | 5.15 mL (3.3€)                           | 5.15 mL (3.3€)                             | 1.25 mL (0.8€)                             | 4.25 mL (2.8€)                          |
| TFA b                      | 100 mL=58 €       |                                            |                                            | 0.65 mL (0.4€)                             |                                        |
| DDQ b                      | 10 g = 30 €       |                                            |                                            | 3.125 g (10€)                              |                                        |
| Triethylamineb             | 1 L = 52 €        |                                            |                                            | 12.5 mL (0.65€)                            |                                        |
| NaHCO3b                    | 500g=39.1 €       | 15 g (1.2€)                              |                                            |                                            |                                        |
| Al2O3 b                    | 1 Kg = 94 €       |                                            |                                            | 0.15 Kg                                    |                                        |
| silica gel | 1 kg = 143 € | 0.3 kg (42.8 €) | 0.3 kg (42.8 €) | 0.2 kg (28.6 €) | 0.25 kg (36 €) |
|------------|--------------|----------------|----------------|----------------|----------------|
| n-hexane  | 2.5 L = 84 € | 0.5 L (16.8 €) | 0.5 L (16.8 €) | 0.4 L (13.4 €) | 0.4 L (13.4 €) |
| dichloromethane | 2.5 L = 104 € | 3.5 L (145.6 €) | 3.5 L (145.6 €) | 3.2 L (133.1 €) | 3.2 L (133.1 €) |
| Yield | 1.125 mmol | 1.315 mmol | 0.7 mmol | 2.35 mmol |
| Factor for 10 mmol | x 8.89 | x 7.6 | x 14.3 | x 4.26 |
| total | 652 € | 741 € | 995 € | 504 € |

*items which do not need multiplication by Factor, since they are recoverable

**not recoverable items

**Table S8** E Factors and prices calculated for the synthesis of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin 1 using several methods.

| Method           | E Factor | Price (10 mmol product) | Price (10 mmol product) |
|------------------|----------|-------------------------|-------------------------|
|                  |          | considering solvent reutilization |
| Adler-Longo      | 6793     | 1068.30 €               | 652 €                   |
| Gonsalves-Pereira| 4233     | 1010.96 €               | 741 €                   |
| Lindsey          | 7090     | 2002.07 €               | 995 €                   |
| NaY              | 2350     | 750.62 €                | 504 €                   |

S9. Synthesis of unsymmetrical meso-substituted porphyrins 2 – 6
S9.1. General procedure

An amount of 1.0 g of NaY zeolite (0.08 mmol) was introduced into a 50 mL round flask, containing a 1:3 mixture of aldehydes (0.625 mmol:1.875 mmol) in a glacial acetic acid/nitrobenzene mixture (7 mL/5 mL). Addition of equimolar amount of pyrrole (2.5 mmol, 0.17 mL) was carried out dropwise under stirring and heating (~120 °C). After complete addition (ca. 3 min), the suspension was heated further till reflux temperature (~130 °C) and maintained at this temperature for ca. 2 hours. The hot suspension was filtered and the resulting solid material washed with tetrahydrofuran (THF) until no coloured material was collected on the supernatant (250 mL). As alternative Soxhlet extraction with THF can be performed, but in our case we found washing sufficient. The volume of solution was then reduced by rotoevaporation (enough volume to remove the added washing solvent). To induce precipitation, n-hexane (ca. 50 mL) was added. The Erlenmeyer flask containing the statistical porphyrin mixture was left overnight in the refrigerator and the deposited solid was collected by filtration and then purified by column chromatography using silica gel as stationary phase, starting with n-hexane:CH$_2$Cl$_2$ (1:3) and then increasing polarity using appropriate gradients of n-hexane:CH$_2$Cl$_2$, then pure CH$_2$Cl$_2$ and finally CH$_2$Cl$_2$:ethanol gradients if necessary to collect fraction 2 (the target compound). This fraction was then evaporated to dryness and the resulting solid was dried under vacuum and weighed.

S9.2. 5-(4-hydroxyphenyl)-10,15,20-tris(4-ethylhexyloxyphenyl) porphyrin (2)
Benzaldehydes used: 4-hydroxybenzaldehyde (0.625 mmol, 76.3 mg) and 4-ethylhexyloxybenzaldehyde\(^7\) (1.875 mmol, 439 mg). Column chromatography was carried out using as eluent \(n\)-hexane:CH\(_2\)Cl\(_2\) (1:3) to collect the first fraction (A\(_4\) product) followed by CH\(_2\)Cl\(_2\) to collect porphyrin 2. We obtained 95 mg of porphyrin 2 (15% yield). Characterisation data is in agreement with the literature.\(^7,8\)

**S9.3. 5-(4-carboxyphenyl)-10,15,20-tris(phenyl) porphyrin (3)**

Benzaldehydes used: 4-carboxybenzaldehyde (0.625 mmol, 94 mg) and benzaldehyde (1.875 mmol, 200 mg). Column chromatography was carried out using as eluent \(n\)-hexane:CH\(_2\)Cl\(_2\) (1:3) to collect the first fraction (A\(_4\) product) followed by ethanol:CH\(_2\)Cl\(_2\) (1:200) to collect porphyrin 3. We obtained 70 mg of porphyrin 3 (17% yield). Characterisation data is in agreement with the literature.\(^3\)

**S9.4. 5-(4-carboxyphenyl)-10,15,20-tris(2,6-difluorophenyl) porphyrin (4)**

Benzaldehydes used: 4-carboxybenzaldehyde (0.625 mmol, 94 mg) and 2,6-difluorobenzaldehyde (1.875 mmol, 267 mg). Column chromatography was carried out using as eluent \(n\)-hexane:CH\(_2\)Cl\(_2\) (1:3) to collect the first fraction (A\(_4\) product) followed by ethanol:CH\(_2\)Cl\(_2\) (1:100) to collect porphyrin 4. We obtained 62 mg of porphyrin 4 (13% yield). Characterisation data is in agreement with the literature.\(^9\)

**S9.5. 5-(4-acetylaminophenyl)-10,15,20-tris(2,6-difluorophenyl) porphyrin (5)**

Benzaldehydes used: 4-acetylaminobenzaldehyde (0.625 mmol, 102 mg) and 2,6-difluorobenzaldehyde (1.875 mmol, 267 mg). Column chromatography was carried out using as eluent \(n\)-hexane:CH\(_2\)Cl\(_2\) (1:3) to collect the first fraction (A\(_4\) product) followed by ethanol:CH\(_2\)Cl\(_2\) (1:100) to collect porphyrin 5. We obtained 78 mg of porphyrin 5 (16% yield).

\(^1\)H NMR (CDCl\(_3\), 400 MHz), \(\delta_H\), ppm: 8.90-8.83 (m, 8H, \(\beta\)-H), 8.17 (d, \(J = 8.0\) Hz, 2H, Ph(Ac)-H), 7.90 (d, \(J = 8.0\) Hz, 2H, Ph(Ac)-H), 7.89-7.76 (m, 3H, Ph-H), 7.49-7.36 (m, 6H, Ph-H), 2.36 (s, 3H, CH\(_3\)), -2.75 (s, 2H, NH).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta_C\), ppm: 134.9, 130.8, 129.1, 119.7, 118.0, 111.5, 111.2, 24.6.

\(^19\)F NMR (376.5 MHz, CDCl\(_3\)) \(\delta_F\), ppm: -108.2, -108.3.

HRMS (ESI-FIA-TOF): Calcd. for C\(_{46}\)H\(_{28}\)F\(_6\)N\(_5\)O: 780.2193; Found \(m/z\) = 780.2202 [M]+

UV-vis (toluene): \(\lambda_{max}\), nm (\(\epsilon\), M\(^{-1}\)cm\(^{-1}\)) 420 (3.5x10\(^5\)), 515 (2.3x10\(^4\)), 546 (6.2x10\(^3\)), 591 (6.9x10\(^3\)), 656 (4.3x10\(^3\)).

EA: Anal. Calcd for C\(_{46}\)H\(_{28}\)F\(_6\)N\(_5\)O: C, 70.86; H, 3.49; N, 8.98. Found: C, 70.87; H, 3.49; N, 8.97.
S9.6. 5-(4-acetylaminophenyl)-10,15,20-tris(2,6-dichlorophenyl) porphyrin (6)

Benzaldehydes used: 4-acetylaminobenzaldehyde (0.625 mmol, 102 mg) and 2,6-dichlorobenzaldehyde (1.875 mmol, 328 mg). Column chromatography was carried out using as eluent n-hexane:CH2Cl2 (1:3) to collect the first fraction (A4 product) followed by ethanol:CH2Cl2 (1:100) to collect porphyrin 6. We obtained 71 mg of porphyrin 6 (13% yield).

1H NMR (400 MHz, CDCl3), δH = ppm 8.85 (d, J = 4.5 Hz, 2H, β-H), 8.66 – 8.62 (m, 6H, β-H), 8.12 (d, J = 8.0 Hz, 2H, Ph(Ac)-H), 7.85 (d, J = 7.9 Hz, 2H, Ph(Ac)-H), 7.79-7.65 (m, 9H, Ph-H), 2.31 (s, 3H, CH3), -2.56 (s, 2H, NH).

13C NMR (101 MHz, CDCl3) δC = ppm 135.1, 131.2, 129.2, 124.6, 119.7, 117.6, 111.6, 111.4, 24.8.

MS (MALDI-TOF): m/z = 879.039 [M]+

UV-vis (toluene): λmax, nm (ε, M⁻¹ cm⁻¹) 420 (3.6x10⁵), 514 (2.3x10⁴), 545 (6.1x10⁴), 591 (6.9x10⁴), 656 (4.4x10⁴).

EA: Anal. Calcd. for C₄₆H₂₇F₆N₅O: C, 62.89; H, 3.10; N, 7.97. Found: C, 62.85; H, 3.08; N, 7.99.

S9.7. NMR spectra of compounds 4 and 5.

Figure S3 ¹H NMR spectrum of compound 5, recorded in CDCl3.
**Figure S4** $^{13}$C NMR spectrum of compound 5, recorded in CDCl$_3$.

**Figure S5** $^{19}$F NMR spectrum of compound 5, recorded in CDCl$_3$. 
**Figure S6** $^1$H NMR spectrum of compound 6, recorded in CDCl$_3$.

**Figure S7** $^{13}$C NMR spectrum of compound 6, recorded in CDCl$_3$. 
S10. Mass Spectra of compounds 5 and 6.

Figure S8 Mass spectrum of compound 5.
Figure S9 Mass spectrum of compound 6.

S11. UV-Vis Spectra of compounds 5 and 6.

Figure S10. Absorption spectrum of compound 5, recorded in toluene.
Figure S11. Absorption spectrum of compound 6, recorded in toluene.

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