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PAPER

Triazole- and triazolium-containing porphyrin-cages for optical anion sensing†

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Triazole and triazolium groups have been integrated into a zinc(II) metalloporphyrin-based structural framework to produce two porphyrin-cages for anion sensing applications. UV/visible spectroscopic titration investigations reveal both host systems exhibit strong anion binding affinities, with the positively-charged triazolium-porphyrin cage capable of colorimetric sensing halides, fluoride and chloride, and oxoanions in acetone–water solvent mixtures.

Introduction

The fundamental importance of negatively-charged species in biological processes and medical diseases as well as the detrimental environmental impact of anions such as nitrate and phosphate is well-known. The need for suitable methods of anion detection and extraction is therefore acute and as a consequence, the field of anion supramolecular chemistry has grown rapidly over recent decades.[1] In particular, examples of anion receptor molecular frameworks with integrated optical and redox reporter groups for sensing applications is ever increasing.

The porphyrin macrocycle is endowed with inherent optical and redox properties that can be exploited for signalling anion recognition *via* a measurable physical response.[2] Indeed, we[3] and others[4] have reported several porphyrin-based host systems containing integrated amide, urea, pyrrole, ammonium and imidazolium hydrogen-bond donor groups capable of recognising and sensing anions *via* spectro- and/or electrochemical methodologies.

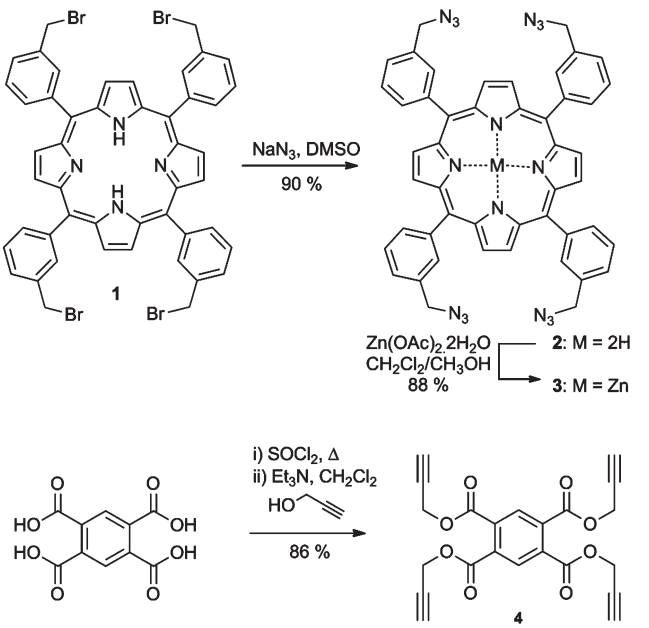
Recently, the capability of neutral triazole units to bind anions in organic solvents by C–H···anion type hydrogen bonding has been demonstrated.[5] In particular, Flood has incorporated multiple triazole groups into a macrocycle leading to strong chloride anion recognition in dichloromethane.[6]

With one notable recent exception of a tetra-triazole-appended "picket-fence" zinc(II) porphyrin receptor which senses halide anions in organic solvents,[7] porphyrin molecules incorporating triazole and triazolium groups for anion recognition are unprecedented. Herein we describe the first examples of triazole- and triazolium-containing zinc(II) metalloporphyrin-cage systems which combine C–H···anion hydrogen bonding and Lewis acidity for the optical colorimetric sensing of anions in polar organic and organic–aqueous solvent mixtures.

Results and discussion

Syntheses

The target triazole-containing zinc(II) metalloporphyrin-cage receptor **5** was prepared *via* modification of Crossley's synthetic procedure[8] which involves a copper(I)-catalysed azide-alkyne cycloaddition (CuAAC) reaction[9] between a tetra-*meso*-substituted azide-functionalised porphyrin and a capping aryl-alkyne (Scheme 1).



Scheme 1 Synthesis of tetra-azide-porphyrin **3** and capping group **4**.

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†Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra and ESI mass spectra of porphyrins **5** and **6·(PF$_6$)$_4$** and ^{1}H–^{1}H TOCSY and ^{1}H–^{1}H ROESY spectra for compound **5**; titration protocols and UV/visible binding curves. CCDC reference number 863074. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30124e

3-(Bromomethyl)benzaldehyde was prepared by reduction of commercially available 3-(bromomethyl)benzonitrile using D*i*BAL-H in toluene.[10] Reaction with pyrrole in the presence of catalytic boron trifluoride etherate afforded 5,10,15,20-tetrakis (α-bromo-*m*-tolyl)porphyrin, **1**, in 30% yield *via* a modification of the Lindsey protocol.[11] Stirring porphyrin **1** with sodium azide in DMSO gave tetra-azide porphyrin **2** which upon metallation using $Zn(OAc)_2{\cdot}2H_2O$ in $CH_2Cl_2 : CH_3OH$ (v/v 9 : 1) gave the zinc-porphyrin derivative **3** in 80% yield over two steps. The required tetra-alkyne aryl capping group **4** was prepared by condensation of ten equivalents of propargyl alcohol with benzene-1,2,4,5-tetracarbonyl chloride formed from benzene-1,2,4,5-tetracarboxylic acid and thionyl chloride (Scheme 1).[8]

Zinc-porphyrin cage **5** was prepared *via* a copper(I)-catalysed alkyne-azide cycloaddition (CuAAC) reaction between 5,10,15,20-tetrakis(α-azido-*m*-tolyl)zinc porphyrin **3** and capping group **4** in the presence of copper-tetrakisacetonitrile hexafluorophosphate and triethylamine in DMF. After purification using preparative thin layer chromatography, the zinc-porphyrin-cage compound **5** was isolated in 17% yield (Scheme 2).

The novel tetra-triazolium cage receptor **6·(PF$_6$)$_4$** was prepared in 32% yield *via* reaction of **5** with five equivalents of $Me_3O{\cdot}BF_4$ in anhydrous CH_2Cl_2 followed by anion exchange (Scheme 2).

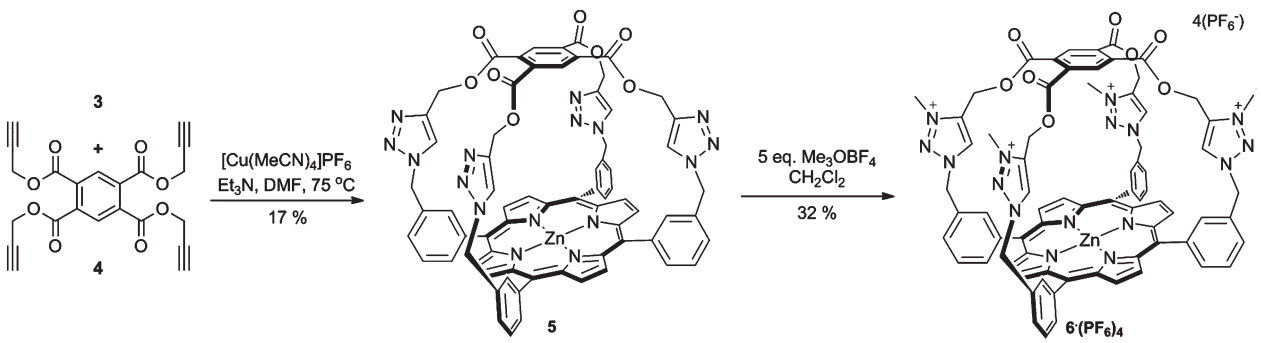
Both porphyrin-cage receptors **5** and **6·(PF$_6$)$_4$** were characterised by NMR spectroscopy, mass spectrometry and UV/Visible spectroscopy (see Experimental section and ESI†).

X-ray crystallography

Crystals of zinc metalloporphyrin cage **5**·5(C_3H_6O) suitable for single crystal X-ray diffraction structural analysis were grown by the slow evaporation of an acetone solution of the cage receptor. The structure (Fig. 1) reveals the open nature of the three-dimensional cavity where an anion can potentially be bound. The four triazole groups are aligned perpendicular to the cage in the solid state but the flexibility of the receptor should allow for strong induced-fit anion binding. It can be seen that the four *meso*-phenyl protons pointing into the cavity, together with the triazole protons provide a suitable binding pocket for anion coordination to the porphyrin-bound zinc(II) centre. The presence of five-coordinate zinc(II), with an acetone solvent molecule as the axial-coordinating ligand, is also apparent.

Anion binding studies

A preliminary ^{1}H NMR anion binding investigation of **5** and TBA·Cl was undertaken in acetone-d^6 solution (Fig. 2). Upon



Scheme 2 Synthesis of zinc-porphyrin cage **5** and tetracationic-porphyrin cage **6·(PF$_6$)$_4$**.

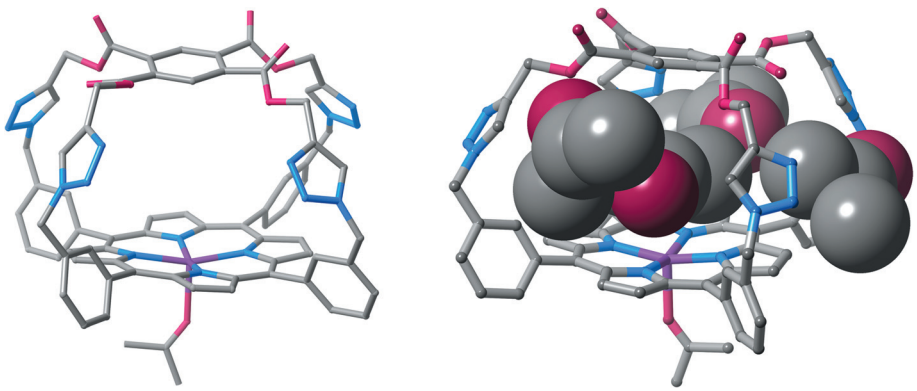


Fig. 1 Capped stick model (left) and space filling representation (right) of the X-ray crystal structure of **5**·5(C_3H_6O). Colour scheme: grey = C; blue = N; red = O; purple = Zn.

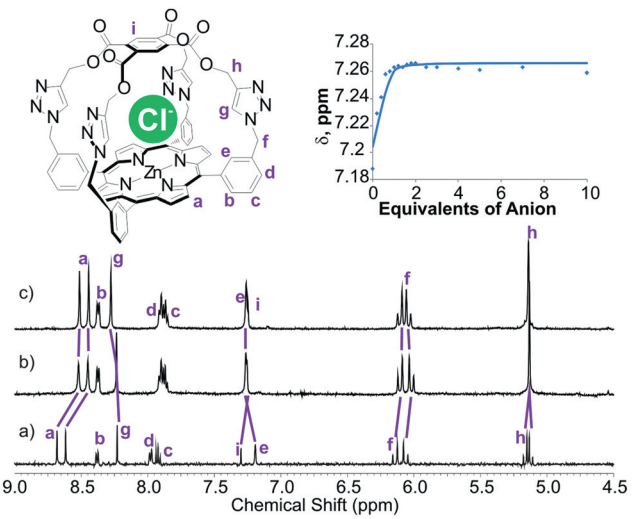


Fig. 2 Partial ^{1}H NMR spectra of a 2 mM solution of porphyrin **5** in the presence of (a) 0, (b) 1 and (c) 10 equivalents of TBA·Cl in acetone-d^6 at 293 K. Left inset: porphyrin **5**. Right inset: changes in chemical shift of proton *e* on addition of TBA·Cl. (Square data points represent experimental data; continuous line represents theoretical binding isotherm).

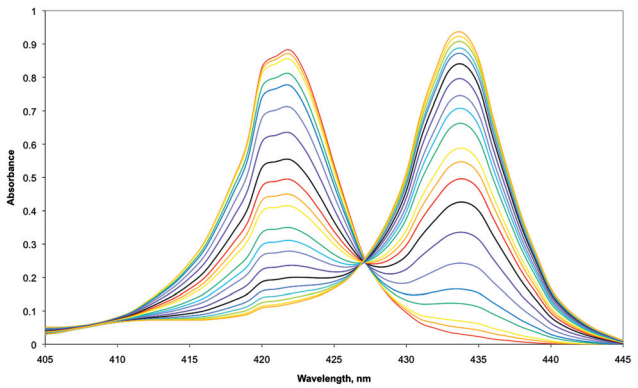


Fig. 3 Changes in the Soret band component of the UV/visible absorption spectrum of a 2 μM solution of porphyrin **5** upon addition of TBA·Cl in acetone at 293 K.

addition of chloride significant downfield shifts in the receptor's triazole, *g*, and *ortho*-phenyl, *e*, cavity protons were observed. This suggests the chloride anion is binding within the cage, co-ordinating to both the triazole and phenyl C–H groups. WinEQNMR2[12] analysis of the titration data gave an association constant, $K > 10^4$ M^{-1} following the *ortho*-phenyl proton, *e*.

The anion recognition and sensing properties of cage porphyrins **5** and **6·(PF$_6$)$_4$** were investigated by UV/visible spectroscopic titrations. Both receptors exhibit characteristic metalloporphyrin absorption spectra with strong Soret band absorbances in the 400–450 nm region as well as weaker Q band absorbances in the 500–650 nm region.

Anion titration experiments in acetone and acetone–water solvent mixtures revealed significant perturbations of the respective porphyrin receptor's Soret band as a function of concentration of TBA anion salts. In a typical titration experiment (Fig. 3), upon addition of chloride, a bathochromic shift in the maxima of the absorbance bands is observed. This arises from

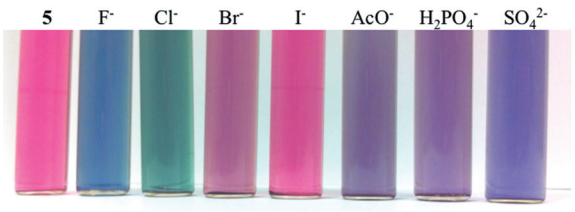


Fig. 4 Colour of receptor **5** before (left) and after addition of 10 equivalents of anions in acetone.

the axial ligation of the halide anion to the Lewis acidic zinc centre.[13] An isobestic point is observed with increasing anion concentration which corresponds to a 1 : 1 receptor : anion binding stoichiometry. It is noteworthy that acetone solutions of zinc receptor **5** are pink in colour and addition of anions resulted in the solutions changing colour (Fig. 4).‡

Job plot analyses[14] confirmed a 1 : 1 host : guest binding stoichiometry for both cage receptors. The anion binding properties of zinc tetraphenylporphyrin[15] (ZnTPP) were also investigated as a control, in order to elucidate the contribution of the triazole-capping framework of receptor **5** to anion binding strength and selectivity. Association constants for 1 : 1 stoichiometric complexes were determined using the Specfit® computer program[16] and are reported in Tables 1 and 2.

Neutral cage host **5** was found to bind anions strongly in acetone, with large association constant values for F^- and SO_4^{2-} in particular. Indeed, the receptor is shown to be selective for F^- over other halide anions, despite its small size. This is likely to be a result of fluoride's greater basicity and possibly it is bound as the trihydrate complex. Receptor **5** exhibits low binding affinity for larger, more diffuse Br^- and I^- anions. Sulfate is bound very strongly by porphyrin **5** with an association constant an order of magnitude higher than for the other basic oxoanions, which is presumably a consequence of the sulfate anion's higher charge. Amongst the singly-charged anions, the anion selectivity trend displayed by **5** in general correlates with anion basicity $AcO^- \sim H_2PO_4^- \gg Cl^- > Br^- > I^-$.

The data in Table 1 also highlight a significant increase in anion binding strength for cage receptor **5** compared with acyclic ZnTPP, particularly for F^- and Cl^-, where additional hydrogen-bond-donating triazole units provide a complementary binding cleft for harder, spherical anions (Fig. 2).

The anion recognition properties of the positively-charged, tetra-triazolium zinc porphyrin cage **6·(PF$_6$)$_4$** were also probed using UV/visible spectroscopy and the association constants for complex formation in 5% water : acetone are reported in Table 2. As anticipated, even in the presence of water, the tetracationic cage **6·(PF$_6$)$_4$** is a superior anion complexant to host **5**. In this aqueous medium the binding affinity of positively-charged caged receptor **6·(PF$_6$)$_4$** for F^- and Cl^- is of similar magnitude and is significantly larger than with Br^- or I^-. All oxoanions are bound strongly in 5% water : acetone and receptor **6·(PF$_6$)$_4$** demonstrates a clear preference (~5-fold) for the sulfate dianion.

‡For positively-charged receptor **6·(PF$_6$)$_4$** in acetone–water mixtures, however, the concentrations required for naked-eye anion sensing resulted in precipitation of the complex from solution.

Table 1 Association constants, K (M^{-1}), for 1 : 1 complexes of porphyrin host **5** and ZnTPP with various anions[a]

Anion	**5**	ZnTPP
F^-	79 707 (8989)	20 850 (988)
Cl^-	12 191 (159)	8092 (318)
Br^-	255 (13)	149 (5)
I^-	<50	<50
AcO^-	22 202 (893)	18 971 (786)
$H_2PO_4^-$	21 657 (989)	23 691 (801)
SO_4^{2-}	100 785 (4858)	91 537 (2556)

[a] K values calculated by analysis of the anion induced changes in the Soret band using Specfit® software. All anions added as their TBA salts. Solvent: acetone. Temperature: 293 K.

Table 2 Association constants, K (M^{-1}), for 1 : 1 complexes of porphyrin host **6·(PF$_6$)$_4$** with various anions[a]

Anion	**6·(PF$_6$)$_4$** [b]	**6·(PF$_6$)$_4$** [c]
F^-	8666 (312)	[d]
Cl^-	7449 (112)	[d]
Br^-	<50	—
I^-	<50	—
AcO^-	134 214 (1060)	[d]
$H_2PO_4^-$	123 452 (12 221)	[d]
SO_4^{2-}	517 726 (73 517)	252 988 (1426)

[a] K values calculated by analysis of the anion induced changes in the Soret band using Specfit® software. All anions added as their TBA salts. Temperature: 293 K. [b] Solvent: 5% water : acetone. [c] Solvent: 15% water : acetone. [d] Soret band perturbations too small to determine an association constant.

The optical anion sensing properties of **6·(PF$_6$)$_4$** were also assessed in 15% water : acetone for F^-, Cl^-, AcO^-, $H_2PO_4^-$ and SO_4^{2-} (Table 2). Porphyrin **6·(PF$_6$)$_4$** exhibits strong and selective sulfate binding whereas with the singly-charged anions minimal perturbations of the Soret band were observed which suggests these anions are not bound in this more competitive aqueous solvent mixture.

Conclusions

The anion binding properties of a neutral tetra-triazole zinc(II) metalloporphyrin cage receptor and a novel positively-charged triazolium cage host system have been investigated by UV/visible spectroscopy. With strongly bound anions a distinctive naked-eye colorimetric response is observed. UV/visible anion titration experiments reveal that both host systems exhibit strong anion binding affinities forming 1 : 1 stoichiometric complexes with a range of halides and oxoanions in acetone and acetone–water mixtures. Specifically, the positively-charged triazolium porphyrin cage displays a marked preference for sulfate in 15% water–acetone.

Experimental

Unless otherwise stated, commercially available solvents (HPLC grade) and reagents were used without further purification. Triethylamine was distilled from KOH and stored over 3 Å molecular sieves. Pyrrole was distilled over CaH_2, under reduced pressure and stored at −25 °C under N_2. $TBA_2{\cdot}SO_4$ was azeotroped with toluene and stored in a dessicator containing P_2O_5. TBA salts of Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ were stored in a dessicator and $TBAF{\cdot}3H_2O$ was used immediately after purchase from Sigma-Aldrich. Water was deionised and micro-filtered using a Mill-Q® Millipore machine. Where anhydrous solvents were used, they were degassed with N_2, and dried by passing through an MBraun MSPS-800 column.

^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded on a Varian Mercury-VX 300, a Varian Unity Plus 500 or a Bruker AVII500 with cryoprobe at 293 K. Mass spectra were obtained using a micromass LCT (ESMS) instrument. Electronic absorption spectra were recorded on a PG instruments T60U spectrometer. Melting points were recorded on a Gallenkamp capillary melting point apparatus and are uncorrected.

5,10,15,20-Tetrakis(α-bromo-*m*-tolyl)porphyrin, 1[17]

3-(Bromomethyl)benzaldehyde (4.50 g, 22.6 mmol) and pyrrole (1.57 mL, 22.6 mmol) were dissolved in anhydrous, degassed CH_2Cl_2 (2.5 L) in a 3-necked, 3 L round bottomed flask. EtOH (17.0 mL) was added and the solution was purged with N_2 for 10 min and wrapped in foil. $BF_3{\cdot}OEt_2$ (0.93 mL, 7.54 mmol) was added *via* syringe and the reaction mixture stirred in the dark at r.t. for 70 min whilst continuously degassing with N_2. Et_3N (1.26 mL, 9.04 mmol) was added, followed by *p*-chloroanil (4.17 g, 17.0 mmol) and the reaction mixture was refluxed for 1 h. After cooling to r.t., all volatiles were removed *in vacuo*. The residue was redissolved in CH_2Cl_2 and passed through a plug of silica, eluting with CH_2Cl_2 to give compound **1** as a purple solid (0.66 g, 0.67 mmol, 30%). λ_{max}(acetone)/nm: 415 (ε/dm^3 mol^{-1} cm^{-1} 631 500) 512 (23 920), 546 (11 380), 589 (8360), 644 (6060); δ_H (300 MHz, $CDCl_3$) 8.87 (8H, s, pyrrole-Ar*H*), 8.27 (4H, s, phenyl-H^2), 8.17 (4H, d, ^3J = 7.5 Hz, phenyl-H^6), 7.84 (4H, d, ^3J = 7.5 Hz, phenyl-H^4), 7.75 (4H, t, ^3J = 7.5 Hz, phenyl-H^5), 4.79 (8H, s, –CH_2–), −2.80 (2H, s, pyrrole-N*H*). *m*/*z* (ES): 987.0 ([M + H]$^+$. $C_{48}H_{35}Br_4N_4$ requires 987.0).

5,10,15,20-Tetrakis(α-azido-*m*-tolyl)porphyrin, 2

Compound **1** (500 mg, 0.507 mmol) was dissolved in DMSO (100 mL). NaN_3 (329 mg, 5.05 mmol) was added and the reaction stirred at r.t. under N_2 for 16 h. After cooling to 0 °C, H_2O (100 mL) was added and the mixture extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with H_2O (100 mL), dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude residue was purified by column chromatography (SiO_2, CH_2Cl_2 : 60–80 petroleum ether (v/v 3 : 2)) to give **2** as a purple solid (382 mg, 0.485 mmol, 90%). Mp: 192–194 °C; λ_{max}(acetone)/nm: 415 (ε/dm^3 mol^{-1} cm^{-1} 271 000) 512 (19 940), 545 (8280), 589 (5660), 645 (3880); δ_H (300 MHz, $CDCl_3$) 8.86 (8H, s, pyrrole-Ar*H*), 8.22 (4H, d, ^3J = 6.5 Hz, phenyl-H^6), 8.19 (4H, s, phenyl-H^2), 7.83–7.76 (8H, m, phenyl-H^4,-H^5), 4.66 (8H, s, –CH_2–), −2.79 (2H, s, pyrrole-N*H*); δ_C (75.5 MHz, $CDCl_3$) 142.6, 134.4, 134.3, 133.8, 131.2, 127.8, 127.3, 119.6, 54.8; *m*/*z* (ES): 835.3223 ([M + H]$^+$. $C_{48}H_{35}N_{16}$ requires 835.3225).

[5,10,15,20-Tetrakis(α-azido-*m*-tolyl)porphyrin]zinc(II) complex, 3

Compound **2** (382 mg, 0.485 mmol) was dissolved in CH_2Cl_2 : CH_3OH (v/v 9 : 1, 20 mL) and $Zn(OAc)_2{\cdot}2H_2O$ (502 mg, 2.29 mmol) was added. The reaction was stirred under N_2 at r.t. for 16 h. The solvent was removed *in vacuo*, the residue redissolved in CH_2Cl_2 (100 mL) and washed with water (5 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude residue was purified using column chromatography (SiO_2, CH_2Cl_2) to give **3** as a purple solid (360 mg, 0.401 mmol, 88%). Mp: decomposed > 200 °C; λ_{max}(acetone)/nm: 428 (ε/dm^3 mol^{-1} cm^{-1} 485 000) 560 (20 120), 599 (9120); δ_H (300 MHz, $CDCl_3$) 8.93 (8H, s, pyrrole-Ar*H*), 8.21 (4H, d, ^3J = 7.5 Hz, phenyl-H^6), 8.14 (4H, s, phenyl-H^2), 7.78 (4H, t, ^3J = 7.5 Hz, phenyl-H^5), 7.72 (4H, d, ^3J = 7.5 Hz, phenyl-H^4), 4.55 (8H, s, –CH_2–); δ_C (300 MHz, DMSO-d^6) 149.3, 143.0, 134.3, 133.9, 131.6, 129.5, 127.8, 127.1, 120.0, 53.6; *m*/*z* (ES): 931.1984 ([M + Cl]$^-$. $C_{48}H_{32}ClN_{16}Zn$ requires 931.1981).

Tetra(prop-2-yn-1-yl) benzene-1,2,4,5-tetracarboxylate, 4

1,2,4,5-Benzenetetracarboxylic acid (1.00 g, 3.93 mmol) was suspended in $SOCl_2$ (20 mL) and DMF (5 drops, cat.) was added. The reaction mixture was heated to reflux and stirred under N_2 for 16 h until the solution became homogenous. The $SOCl_2$ was removed by distillation and the residue dissolved in anhydrous CH_2Cl_2 (20 mL). This was added dropwise to a solution of propargyl alcohol (2.30 mL, 39.3 mmol) and Et_3N (6 mL, 43 mmol) in anhydrous CH_2Cl_2 (100 mL). The reaction mixture was stirred under N_2 at r.t. for 16 h after which it was washed with water (3 × 100 mL), dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude residue was purified by column chromatography (SiO_2, CH_2Cl_2 : CH_3OH (v/v 95 : 5)) to give **4** as a white solid (1.37 g, 3.67 mmol, 86%). Mp: 113–115 °C; δ_H (300 MHz, $CDCl_3$) 8.17 (2H, s, Ar*H*), 4.96 (8H, d, ^4J = 2.5 Hz, –CH_2–), 2.58 (4H, t, ^4J = 2.5 Hz, alkyne-C*H*); δ_C (75.5 MHz, $CDCl_3$) 164.7, 133.8, 130.0, 76.6, 76.0, 53.8; *m*/*z* (ES): 429.0582 ([M + Na]$^+$. $C_{22}H_{14}NaO_8$ requires 429.0581).

Porphyrin cage 5

Porphyrin **3** (90.0 mg, 0.100 mmol), $[Cu(NCCH_3)_4]PF_6$ (8.00 mg, 21.5 μmol), and Et_3N (60.0 μL, 0.4 mmol) were dissolved in anhydrous DMF (200 mL). Capping group **4** (40.0 mg, 0.100 mmol) was added and the reaction mixture was stirred under N_2 at 75 °C for 3 days. The reaction mixture was then cooled, the solvent reduced to 3 mL *in vacuo*. The reside was redissolved in CH_2Cl_2 (100 mL) and EtOAc (100 mL) and washed with water (2 × 100 mL), filtered, washed with water (2 × 100 mL), dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo*. The crude residue was purified by preparative thin layer chromatography (SiO_2, 95 : 5 CH_2Cl_2 : CH_3OH) to give **5** as a purple solid (22.6 mg, 0.0173 mmol, 17%). Mp: decomposed >245 °C; λ_{max}(acetone)/nm: 422 (ε/dm^3 mol^{-1} cm^{-1} 439 500), 553 (5140), 592 (1600); δ_H (500 MHz, $CDCl_3$) 8.75 (4H, s, pyrrole-Ar*H*), 8.71 (4H, s, pyrrole-Ar*H*), 8.43 (4H, d, ^3J = 7.8 Hz, phenyl-H^6), 7.86 (4H, t, ^3J = 7.8 Hz, phenyl-H^5), 7.79 (4H, d, ^3J = 7.8 Hz phenyl-H^4), 7.67 (4H, s, triazole-*H*), 7.36 (2H, s, Ar*H*), 7.10 (4H, s, phenyl-H^2), 5.95 (4H, d, ^2J = 16.4 Hz, –OCH_2–), 5.80 (4H, d, ^2J = 16.4 Hz, –OCH_2–), 5.15 (4H, d, ^2J = 12.8 Hz, –NCH_2–), 5.06 (4H, d, ^2J = 12.8 Hz, –NCH_2–). δ_C (125.8 MHz, 9 : 1 $CDCl_3$:CD_3OD) 164.9, 149.6, 149.4, 144.1, 141.0, 133.1, 133.0, 132.4, 132.4 (*sic*), 129.0, 126.8, 125.9, 125.5, 119.5, 58.2, 53.4. *m*/*z* (ES): 1325.2888 ([M + Na]$^+$. $C_{70}H_{46}NaN_{16}O_8Zn$ requires 1325.2868).

Porphyrin cage 6·$(PF_6)_4$

Porphyrin cage **5** (22.0 mg, 0.0169 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL), $Me_3O{\cdot}BF_4$ (12.6 mg, 0.0852 mmol) was added and the reaction mixture stirred under N_2 at r.t. for 3 days. CH_3OH : Et_3N (v/v 1 : 1) was added and the volatiles were removed *in vacuo*. Following purification using preparative thin layer chromatography (SiO_2, CH_3CN : H_2O : sat. $KNO_{3(aq)}$ (v/v 14 : 2 : 1)) the crude reside was dissolved in acetone : H_2O : sat. $NH_4PF_{6(aq)}$ (v/v 100 : 2 : 1). The acetone was removed *in vacuo* and the resulting purple precipitate was isolated by filtration as **6·$(PF_6)_4$** (10.7 mg, 5.5 μmol, 32%). Mp: decomposed > 281 °C; λ_{max}(acetone)/nm: 425 (ε/dm^3 mol^{-1} cm^{-1} 409 000), 554 (14 900), 593 (4440); δ_H (500 MHz, CD_3CN) 8.76 (4H, s, pyrrole-Ar*H*), 8.72 (4H, s, pyrrole-Ar*H*), 8.55–8.53 (8H, m, triazolium-*H* & phenyl-H^6), 7.97 (4H, t, ^3J = 7.7 Hz, phenyl-H^5), 7.93 (4H, d, ^3J = 7.7 Hz, phenyl-H^4), 7.37 (2H, s, Ar*H*), 7.24 (4H, s, phenyl-H^2), 6.153 (8H, s, –OCH_2–), 5.34 (4H, d, *J* = 14.4 Hz, –NCH_2–), 5.14 (4H, d, *J* = 14.4 Hz, –NCH_2–), 4.11 (12H, s, –NCH_3); δ_C (125.8 MHz, CD_3CN) 163.6, 149.8, 144.0, 137.4, 133.6, 132.7, 132.3, 132.0, 131.9, 131.9 (*sic*), 131.2, 129.6, 127.4, 126.8, 119.6, 56.9, 54.1, 38.61; δ_F (282.4 MHz, CD_3CN) −72.9 (d, ^1J = Hz, 709 Hz, PF_6); δ_P (121.6 MHz, $CDCl_3$) −139.3 (sept, ^1J = 709 Hz, *P*F_6). *m*/*z* (ES): 1797.2874 ([M − PF_6]$^+$. $C_{74}H_{58}F_{18}N_{16}O_8P_3Zn$ requires 1797.2835).

X-ray crystallography

Single crystals of **5**·5(C_3H_6O) were grown by slow evaporation of an acetone solution of **5**. X-ray diffraction data were collected using graphite monochromated Cu Kα radiation (λ = 1.54184 Å) on a Oxford Diffraction SuperNova diffractometer. The diffractometer was equipped with a Cryostream N_2[18] open-flow cooling device, and the data were collected at 150(2) K. Series of ω-scans were performed in such a way as to collect all unique reflections to a maximum of 0.80 Å. Cell parameters and intensity data (including inter-frame scaling) were processed using CrysAlis Pro.[19] The structure was solved by charge-flipping methods using SUPERFLIP[20] and refined using full-matrix least-squares on F^2 within the CRYSTALS suite.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generally visible in the difference map and their positions and displacement parameters were refined using restraints prior to inclusion into the model using riding constraints.[22]

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