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A Highly Sterically Congested Bis-Zinc-Porphyrin Containing a Single Buta-1,3-diyne Linkage: From a Serendipitous Finding to Supramolecular Encapsulation

Kamil Kupietz,^[a] Jonathan Trouvé,^[a] Thierry Roisnel,^[a] Samia Kahlal,^{*[a]} and Rafael Gramage-Doria^{*[a]}

[a] Dr. K. Kupietz, Dr. J. Trouvé, Dr. T. Roisnel, Dr. S. Kahlal, Dr. R. Gramage-Doria
Univ Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France
E-mail: samia.kahlal@univ-rennes1.fr; rafael.gramage-doria@univ-rennes1.fr

Supporting information (NMR, UV-vis, X-ray, and computational data) for this article is given via a link at the end of the document.

Abstract: A unique example of a bis-zinc-porphyrin chemical system in which both macrocycles are covalently connected with a single, short 1,3-butadiyne linkage placed at the *ortho* sites of the *meso* phenyl rings is presented. This dimeric compound resulted from an homo-coupling side-reaction taking place during a copper-catalyzed click reaction between an alkyne porphyrin and 2-azidopyridine derivatives. Its unexpected formation was rationalized by control experiments and an improved synthesis was achieved under copper-catalyzed Glaser-Hay coupling reaction conditions. This highly sterically congested bis-zinc-porphyrin derivative behaved as a supramolecular host for encapsulating ditopic molecular guests such as 1,4-diazabicyclo[2.2.2]octane (DABCO) with association constant $K_{1,1}$ in the order of 10^6 M⁻¹. This value is comparable to current systems that typically feature several connecting linkages between the two zinc-porphyrin sites resulting in (supra)molecular cages ensuring a high pre-organization. As such, the requirements to take benefit from supramolecular encapsulation can be reduced to a highly rigid, minimal covalent linkage of four atoms between zinc-porphyrins as herein described.

Introduction

Supramolecular chemistry is a well-established field in chemical sciences that study, in particular, the ability of chemical systems to undergo molecular recognition via non-covalent interactions.^[1] As such, different technologies have been disclosed by merging supramolecular approaches with other physicochemical processes.^[2] For instance, artificial molecular machineries enabling processes similar to those occurring in living organisms have been developed.^[3] In parallel to that, supramolecular catalysts featuring substrate pre-organization features or switchable properties have been shown as powerful systems to circumvent reactivity limitations displaying enhanced activities and atom-precise selectivities impossible to reach with non-supramolecular versions.^[4]

Aside these possibilities, supramolecular encapsulation appears to be an important topic since it plays a major role in biology and its exploitation in artificial systems has been a source of remarkable contributions in both molecular sensing and catalysis.^[5] In this context, hydrogen bonding and the hydrophobic effect have been mainly utilized for designing systems that enable the supramolecular encapsulation of different guests via shape and size complementarity.^[6] Another type of interaction that has been utilized for the design of chemical systems featuring

supramolecular encapsulation is the dative coordination of heteroatom-containing organic molecules to zinc-porphyrins derivatives via X...Zn binding (X = N, O, S, etc.).^[7] The simplest cases of study are the formation of dimeric zinc-porphyrin hosts linked through peripheral linkages in order to get an appropriate distance between both zinc sites to encapsulate a specific ditopic organic guest.^[8] These compounds are generally referred to as "porphyrin tweezers".^[7,8]

Consequently, the design of zinc-porphyrin-based chemical systems enabling supramolecular encapsulation is very attractive and may provide access to new emerging properties. Herein, we present a rare bis-zinc-porphyrin dimer (**2**) in which both zinc-porphyrin scaffolds are linked through a rigid 1,3-butadiyne moiety placed at the highly sterically congested *ortho* position of one *meso*-phenyl ring (Figure 1). It is worthy to note that zinc-porphyrins have been connected each other through alkyne units, but only in the more spatially accessible *meta* or *para* position, respectively.^[9] The corresponding chemical systems either linear, cyclic, dimeric, trimeric or oligomeric have been found to display unique supramolecular properties.^[10] Interestingly, dimer **2** was found as a homo-coupled side-product in a copper-catalyzed azide-alkyne cycloaddition reaction, which is so far unprecedented as regards of the high selectivity and efficiency encountered for click reactions.^[11] Control experiments enabled to identify the truly active species for this side-reaction and reaction conditions derived from the Glaser-Hay coupling enabled exclusive formation of dimer **2**. The conformational structure of **2** together with its ability for encapsulating ditopic molecular guests such as 1,4-diazabicyclo[2.2.2]octane (DABCO) was studied by experimental (NMR, DOSY, UV-vis, X-ray) and computational (DFT, QTAIM, EDA) studies.

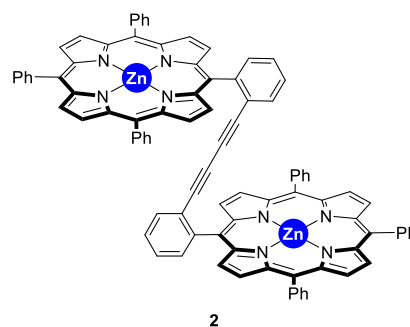
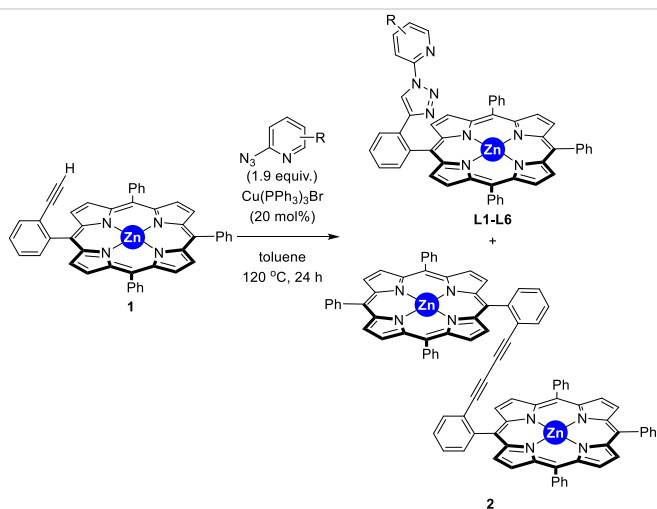


Figure 1. Compound of interest in this study.

Results and Discussion

Recently, we have described a general experimental protocol to obtain a supramolecular ligand of formula **L** (Table 1) which contains a peripheral triazolopyridine backbone that coordinates to a catalytically active iridium center whilst a zinc-porphyrin unit enables molecular recognition towards heterocyclic substrates, typically pyridine derivatives.^[12,13] Unexpectedly, during the formation of the supramolecular ligands **L** under copper-catalyzed click reaction conditions starting from the alkyne porphyrin **1**, we identified the formation of dimeric species **2** in yields that vary depending on the nature of the triazolopyridine reagent being employed (Table 1).^[13] Notably, when employing the 2-azido-4-*tert*-butyl-pyridine, up to 26% yield of **2** was obtained. As regards of the exotic character of this highly sterically demanding species, we decided to explore in detail the origin of this unexpected reactivity and its eventual molecular recognition properties.

Table 1. Synthesis of supramolecular ligands **L** and formation of by-product **2**.^[a]

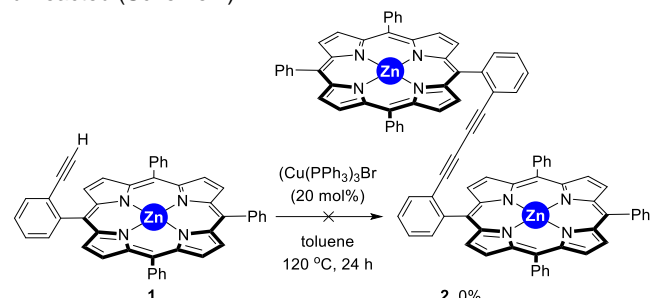


Entry	L	R	Conv. 1 (%) ^[b]	Yield L (%) ^[b]	Yield 2 (%) ^[b]
1 ^[c]	L1	H	>99	95	<5
2	L2	4- <i>t</i> -Bu	>99	74	26
3	L3	4-Me	>99	92	8
4	L4	6-Me	>99	95	<5
5	L5	4-OMe	>99	90	10
6	L6	4-CF ₃	>99	>99	0

[a] Reaction conditions: **1** (0.320 g, 0.5 mmol, 1 equiv.), 2-azidopyridine derivative (0.75 mmol, 1.5 equiv.), Cu(PPh₃)₃Br (0.106 mg, 0.2 mmol, 0.2 equiv.), dry toluene (20 mL), 120 °C, 24 h. [b] Conversion and yields estimated by ¹H NMR spectroscopy studies. [c] 1.9 equiv. of 2-azidopyridine derivative were used. Note: the synthesis and characterization of **L1-L6** have been reported in reference [13].

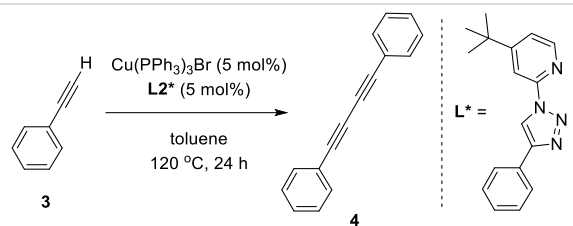
Initially, in view to understand the unexpected formation of dimer **2**, we wondered whether the copper pre-catalyst Cu(PPh₃)₃Br,^[14] which is known to outperform state-of-the-art copper catalysts for selective triazole synthesis,^[15] was productive enough for the formation of **2**. To our surprise, the homo-coupling reaction of **1** did not proceed in the presence of catalytic amounts

of Cu(PPh₃)₃Br and the starting material **1** was fully recovered unreacted (Scheme 1).



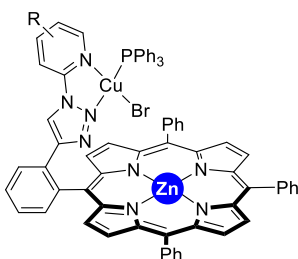
Scheme 1. Attempts to synthesize **2** starting from **1** with Cu(PPh₃)₃Br as the pre-catalyst.

The above-described observation indicates that the supramolecular triazolopyridine compounds (**L**) formed as a major product in Table 1 could play a role by activating/coordinating to the copper species that truly promote the homo-coupling side-reaction towards formation of **2**. To address this point, we evaluated a model reaction (Table 2), namely the homo-coupling of phenylacetylene (**3**) in the presence of Cu(PPh₃)₃Br as the pre-catalyst and an additional ligand **L**^{*} that corresponds to the triazolopyridine fragment belonging to the supramolecular ligand **L2** that displays the highest yield of dimer **2** (26%, Table 1, entry 2). Under these reaction conditions, the corresponding homo-coupled product 1,4-diphenylbutadiyne (**4**) formed in 65% isolated yield. Importantly, the reaction in the absence of **L**^{*} led to no product formation (Table 2, entry 2). Moreover, replacing the copper salt Cu(PPh₃)₃Br by CuI and addition of PPh₃ ligand to the reaction mixture was completely ineffective (Table 2, entries 3-5). These findings strongly suggest that the formation of the bis-zinc-porphyrin **2** under copper catalysis in Table 1 is likely due to the formation of catalytically active triazolopyridine-coordinated copper species (Cu-**L**, Figure 2) while Cu(PPh₃)₃Br is the truly active catalyst for the selective triazole synthesis that yields the supramolecular ligands **L** (Table 1). Overall, this is a rare example relevant for the copper-catalyzed click chemistry in which the triazole compound formed drives the system towards an unprecedented side-reaction so far, in this case the homo-coupling of the alkyne starting material. It is relevant to note that, in general, the triazole compound formed during copper-catalyzed azide-alkyne cycloaddition reactions behaves as a ligand to accelerate the catalysis in an autocatalytic fashion as shown in the early work of Whitesides.^[16] Whether formation of monomeric or dimeric copper species are responsible for one product selectivity or the other one remains to be addressed.^[17] On another side, the activity of the copper triazolopyridine species (Cu-**L**, Figure 2) is dependent on the pyridine electron density, as regards of the yields of **2** obtained in Table 1, thereby indicating a reaction enhancement by electron donating groups. The ability of heteroaromatic *N,N*-chelating ligands to coordinate to [Cu(PPh₃)Br] motifs is well reported in the literature.^[18]

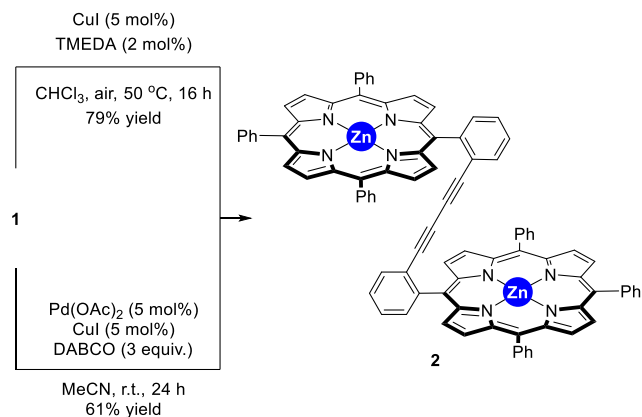
Table 2. Evaluation of the homo-coupling of phenylacetylene under copper catalysis relevant to understand the formation of **2**.^[a]


Entry	Deviation from above conditions	Yield 4 (%) ^[b]
1	none	65
2	w/o L*	<5
3	with CuI instead of Cu(PPh ₃) ₃ Br	0
4	w/o L* and with CuI instead of Cu(PPh ₃) ₃ Br	0
5	as entry 4 plus PPh ₃	<5

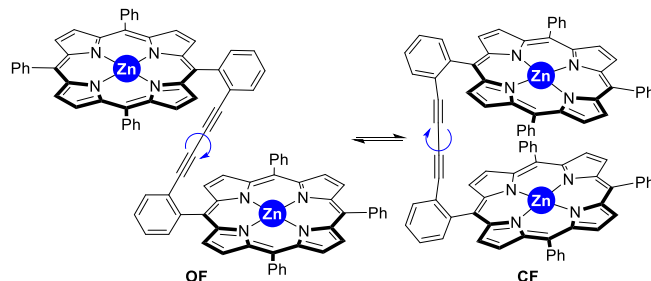
[a] Reaction conditions: **3** (0.100 g, 0.98 mmol), Cu(PPh₃)₃Br (0.046 g, 0.049 mmol), L* (0.014 g, 0.049 mmol), toluene (20 mL), 120 °C, 24 h. [b] Isolated yield after purification by column chromatography.

**Figure 2.** Postulated copper species responsible for the formation of the side-product, homo-coupled product **2** during the synthesis of the supramolecular ligands **L** in Table 1.

Next, we envisioned the high-yielding synthesis of **2** by performing a copper-catalyzed Glaser-Hay homo-coupling.^[19] Indeed, treatment of **1** with catalytic amounts of both CuI and *N,N*-tetramethylethylenediamine (TMEDA) in chloroform solvent at 50 °C during 16 hours afforded the bis-zinc-porphyrin **2** in 79% isolated yield after purification by column chromatography (Scheme 2, top). Alternatively, the homo-coupled product **2** was also synthesized by a palladium-catalyzed homo-coupling reaction in the presence of CuI and DABCO in acetonitrile at room temperature.^[20] In this case, the isolated yield of **2** dropped slightly to 61% (Scheme 2, bottom).

**Scheme 2.** Synthesis of **2** starting from **1** under copper catalysis (top) and under palladium/copper catalysis (bottom).

HRMS and multinuclei NMR unambiguously confirmed the formation of species **2** (see Supporting Information). In fact, the relatively simple and symmetric ¹H and ¹³C NMR spectra of **2** indicate that the two zinc-porphyrin backbones freely rotate along the buta-1,3-diyne axis despite the highly constrained environment around this doubly triple bond. Additional ¹H NMR studies at low temperatures (up to 208 K) did not reveal major differences as compared to the room temperature analysis (Figure S1 in the Supporting Information). However, we noted the appearance and disappearance of a broad signal in the negative area at δ ca. -1 ppm values, which we tentatively attributed to water bound to zinc.^[21] As such, dimer **2** likely exists as a mixture of two interconverting species, namely a closed form (**CF**), in which both zinc-porphyrin backbone stuck each other, and an open form (**OF**), in which the zinc-porphyrins reach the maximal distance between both zinc atoms by pointing to opposite directions (Scheme 3). This interconversion is fast in the NMR timescale in order to be detected. Density functional theory (DFT) calculations at the PBE0/TZ2P/D3BJ level support the existence of two isomers for **2** (see Computational Details in the Supporting Information). Their optimized geometries are shown in Figure 3. The open form (**OF**) is found in fact more intricate than that drawn on the left side of Scheme 3, with the C-C single bond of the bis-alkynyl unit somewhat sandwiched between the two porphyrinic planes and the two metal centers separated by 8.17 Å. The **CF** structure, with a shorter Zn...Zn distance of 5.78 Å as one could expect, was found more stable than **OF** one by 0.29 eV.

**Scheme 3.** Plausible extreme cases of an open form (**OF**, left) and a closed form (**CF**, right) for species **2**.

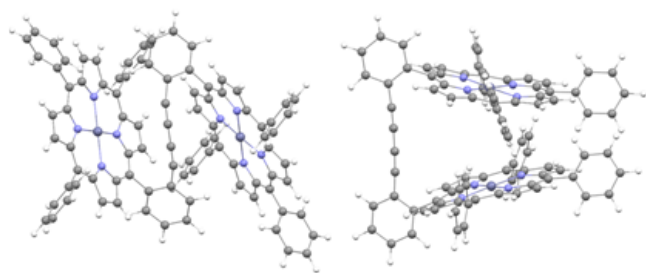


Figure 3. DFT-optimized geometries of the open form (**OF**, left) and close form (**CF**, right) of **2**.

In addition, we managed to grow single crystals suitable for X-ray diffraction studies from a concentrated solution of **2** in a mixture of ethanol and chloroform solvents which further unambiguously supports the proposed dimeric structure of **2**. In the solid state, dimer **2** adopts an open conformation (**OF**) with each zinc center being coordinated to the oxygen atom of an ethanol molecule (Figure 4).^[22] The binding of ethanol to dimer **2** was assessed in solution by ¹H NMR spectroscopy upon addition different aliquots of ethanol (up to 13% in volume) to a solution of **2** in CDCl₃ (see details in Figure S7 in the Supporting Information). Only very minor field shifts in the aromatic area were observed while keeping the same multiplicity for all signals. As such, the binding of ethanol to dimer **2** in solution seems to occur at a relatively fast scale to be identified by NMR spectroscopy.

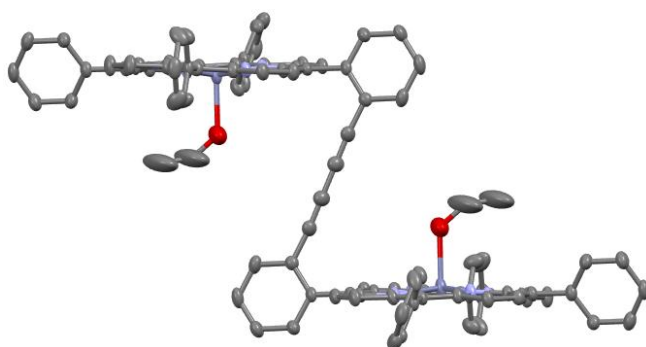
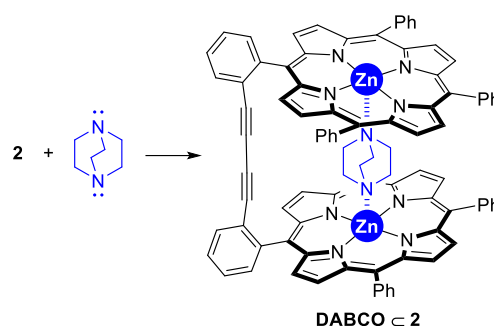


Figure 4. X-ray structure of dimer **2** in the presence of two ethanol molecules binding to the zinc centers (ellipsoid representation, chloroform molecules and hydrogen atoms are not displayed for the sake of clarity).

The postulated equilibria between an open form (**OF**, Scheme 3) and a closed form (**CF**, Scheme 3) in **2** was taken as an advantage for the study of the eventual encapsulation of DABCO between both zinc-porphyrins in the closed form of **2**. We anticipated that each nitrogen atom from DABCO could be involved in a Zn...N interaction with each zinc atom from **2** (Scheme 4). Indeed, ¹H NMR spectroscopy studies comprising a mixture of dimer **2** and DABCO in a 1:1 ratio featured a strong up-field shift for the proton signals belonging to DABCO that resonate at -4.64 ppm (Figure S2 in the Supporting Information), value which is in agreement for the encapsulation of DABCO into highly elaborated (supra)molecular cages containing two zinc-porphyrin units.^[23] The addition of excess of DABCO resulted in the disappearance of the chemical shift ascribed to the encapsulation and the merger of a new one at a chemical shifts in which free DABCO is in exchange with higher aggregates involving binding

to the zinc-porphyrin.^[24] In addition, DOSY studies revealed that the up-field shifted signal belonging to DABCO are aligned with the proton signals from dimer **2**, thereby indicating formation of a single supramolecular assembly [DABCO ⊂ **2**] in which both the host (**2**) and the guest (DABCO) diffuse together (Figure S3 in the Supporting Information). It is relevant to note that the resonances in the porphyrin beta region of the ¹H NMR dramatically change when DABCO is bound - four (roofed) doublets become 2 singlets of unequal height (4:12 ratio) (Figure S4-S5 in the Supporting Information). We tentatively assign the 4 beta protons to the pyrrolic protons located in close proximity to the bis-alkyne unit. Note that excess of DABCO did not change the NMR fingerprint for the signals of dimer **2** while DABCO signals were identified at δ ca. 47 ppm in the ¹³C{¹H}NMR spectrum (Figure S6 in the Supporting Information), which is in agreement with a molecular encapsulation taking place at a fast rate in the NMR timescale.



Scheme 4. Supramolecular encapsulation of DABCO inside **2**.

In addition, UV-vis titration studies in CHCl₃ solvent enabled to calculate the binding constant which was found to be $K_{1,1} = 7.49 \times 10^5 \text{ M}^{-1}$ with a clear isosbestic point (Figure 5).^[25] Changing the solvent to toluene led to a higher association constant ($K_{1,1} = 1.49 \times 10^6 \text{ M}^{-1}$, see supporting information). These values, which are currently obtained in a system comprising a single linkage between the two zinc-porphyrins, compares well with previous systems exhibiting a 1:1 binding stoichiometry in which the host concerned was a cyclic system bearing at least two linkers to connect both zinc-porphyrin units.^[21,23] Additional experimentation and analysis did not provide evidences of an eventual second binding of DABCO to **2** in solution or it is too small to be measured so far (see supporting information) as it was seen by Ballester and co-workers in a more flexible zinc-porphyrin tweezer.^[7b] However, a solution of **2** containing an excess of DABCO afforded single crystals suitable for X-ray diffraction studies which revealed the presence two DABCO molecules binding each zinc-porphyrin unit within **2** (Figure 6).^[22] As a result, it appears that the 1:1 encapsulation of DABCO with **2** is favored in solution whereas the 2:1 assembly is possible only in the solid state so far. For comparison purposes, UV-vis titrations studies were carried out to evaluate the binding of quinuclidine, which is structurally related to DABCO but contains only one nitrogen donor atom, to dimer **2** (see supporting information). In this case, the solution studies revealed, as it could be expected, the presence of two binding events between the guest (quinuclidine) and the host (dimer **2**) with $K_{1,1} = 1.12 \times 10^5 \text{ M}^{-1}$ and $K_{1,2} = 6.65 \times 10^4 \text{ M}^{-1}$ in toluene solution. ¹H NMR studies involving addition of aliquots (up to 6.44 equiv.) of quinuclidine to a solution of dimer **2** indicate the persistent formation of the open form (**OF**) in a 2:1 assembly according to the NMR fingerprint from the dimer **2** with the

characteristic four, roofed doublets for the pyrrolic protons (Figure S8 in the Supporting Information). Overall, according to NMR and UV-vis studies, the supramolecular behavior of **2** for DABCO encapsulation in solution resembles very much the system reported by Cao comprising a bis(zinc-porphyrin) bridged by a benzo orthocarbonates, although in our case the association constant is two orders of magnitude lower.^[7c]

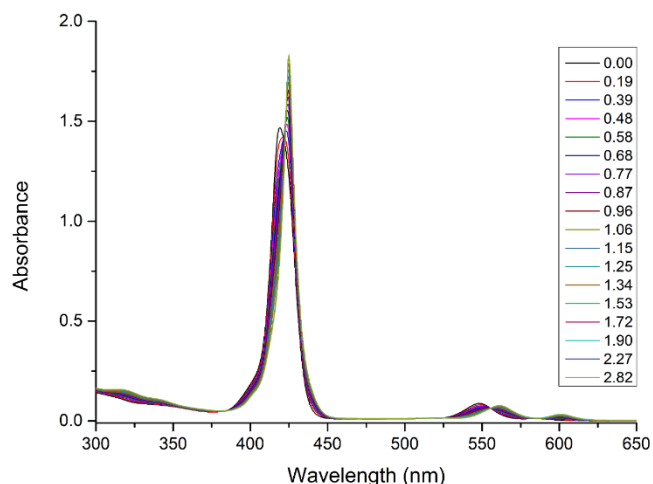


Figure 5. UV-vis titration studies performed with addition of aliquots of the guest (DABCO) to the host (**2**). The rectangle shows the number of equivalents (CHCl_3 , 300 K).

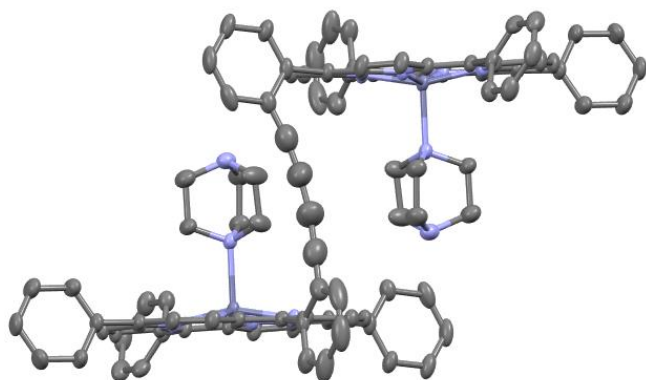


Figure 6. X-ray structure of dimer **2** in the presence of two DABCO molecules binding to the zinc centers (ellipsoid representation, hydrogen atoms are not displayed for the sake of clarity).

DFT computational calculations also indicate the feasibility of the formation of 1:1 assembly between dimer **2** and DABCO. The DFT-optimized geometry of the 1:1 assembly between **2** and DABCO ($[\text{DABCO} \subset \mathbf{2}]$) is shown in Figure 7. It exhibits a rather regular structure close to C_2 symmetry. Selected computed data are given in Table 3. As expected, the $\text{Zn}\cdots\text{N}(\text{porphyrin})$ distances are significantly shorter than their $\text{Zn}\cdots\text{N}(\text{DABCO})$ counterparts (by $\sim 0.14 \text{ \AA}$). The corresponding Wiberg bond indices are reduced by more than 50%, indicating a dramatic decrease of covalency when going from $\text{Zn}\cdots\text{N}(\text{porphyrin})$ to $\text{Zn}\cdots\text{N}(\text{DABCO})$.

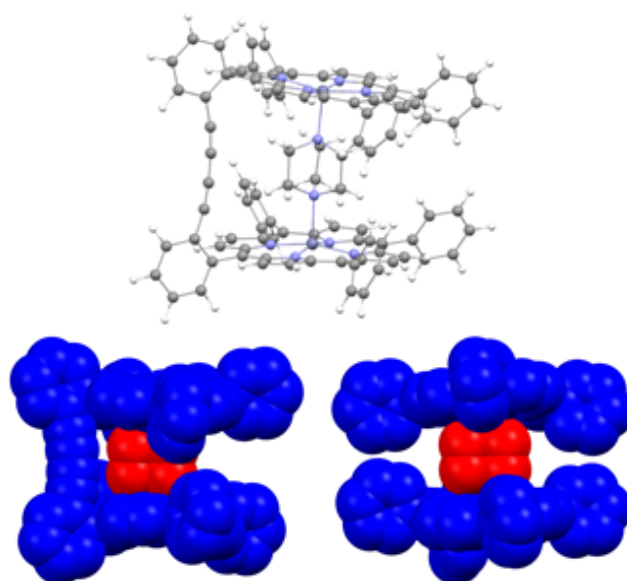


Figure 7. DFT-optimized geometry of the self-assembly $[\text{DABCO} \subset \mathbf{2}]$ (top) and its spacefill representation from two different side views (bottom - DABCO guest is shown in red color and the dimeric zinc-porphyrin in blue color.)

A deeper insight into the nature of the $\text{Zn}\cdots\text{N}$ bonds in $[\text{DABCO} \subset \mathbf{2}]$ can be obtained through a Quantum Theory of Atoms in Molecules (QTAIM) approach.^[26] Selected QTAIM data are collected in Table 3. Bond critical points were found for all $\text{Zn}\cdots\text{N}$ bonds. Looking first at the $\text{Zn}\cdots\text{N}(\text{porphyrin})$ indicators, the positive sign of their Laplacian density, the negative sign of the energy density and the $|V|/G$ ratio larger than 1 are compatible with dative covalent bonding mixed with some ionic character. The $\text{Zn}\cdots\text{N}(\text{DABCO})$ indicators have similar signs but substantially smaller absolute values, indicating both weaker and more ionic bonding.

Table 3. Relevant metrical data, corresponding Wiberg bond indices (WBIs) and QTAIM indicators computed for [DABCO \subset **2**]. ρ , $\nabla^2\rho$, H, V and G are the electron density, Laplacian of ρ density, energy density, potential energy density and kinetic energy density values at the bcp, respectively. δ is the delocalization bond index. All values in a.u.

		Distances (Å)	WBIs	QTAIM indicators					
				ρ	$\nabla^2\rho$	H	V	V /G	δ
Zn...N(porphyrin)	Average	2.063	0.120	0.077	0.306	-0.015	-0.106	1.160	0.386
	range	2.057 / 2.076	0.118 / 0.122	0.075 / 0.078	0.259 / 0.312	-0.014 / -0.015	-0.101 / -0.108	1.158 / 1.162	0.378 / 0.390
Zn...N(DABCO)	Average	2.200	0.051	0.059	0.213	-0.008	-0.069	1.128	0.296
	range	2.199 / 2.201	0.050 / 0.051	0.058 / 0.059	0.212 / 0.213	-0.008 / -0.008	-0.069 / -0.069	1.127 / 1.128	0.296 / 0.297

Another viewpoint on the bonding between **2** and DABCO in [DABCO \subset **2**] is provided by the bond energy decomposition analysis (EDA), according to the Morokuma-Ziegler procedure.^[27] The decomposition of the total bonding energy (TBE) between the **2** and DABCO molecular fragments (with the structure they have in [DABCO \subset **2**]) is provided in Table 4. TBE is expressed as the sum of four components, the Pauli repulsion (E_{Pauli}), the electrostatic interaction energy (E_{elstat}), the orbital interaction energy (E_{orb}) and the component associated with the dispersion (van der Waals) forces (E_{disp}). The E_{orb} component, which is associated with covalency, is rather small, of the same order of magnitude as the dispersion component. It is only 25% of the electrostatic component. Such a situation features a bonding dominated by electrostatic interactions, in agreement with the QTAIM analysis. The non-negligible TBE value (-2.58 eV) is consistent with the stability of [DABCO \subset **2**]. However, owing to the important distortion of **2** when going from its free stable **CF** structure to the one that it adopts in [DABCO \subset **2**], the energy of the reaction **2** + DABCO \rightarrow [DABCO \subset **2**], computed from the energies of the three optimized structures, decreases to -1.58 eV (37 kcal/mol). Finally, it should be noted that the interaction between the bis-porphyrin **2** and DABCO results from the simple addition of two nearly-independent interactions between one porphyrinic ring and one DABCO nitrogen. Indeed, the computed hypothetical model made of a monomer of **2** (one half of the molecule, saturated by an H atom) to which is bonded a DABCO molecule (Figure S25) provided similar QTAIM and EDA indicators as for [DABCO \subset **2**] (Tables S1 and S2). Overall, these calculations further support the encapsulation of DABCO within **2**.

Table 4. EDA analysis associated with the bonding between the **2** and DABCO fragments in [DABCO \subset **2**]. TBE = E_{Pauli} + E_{elstat} + E_{orb} + E_{disp} . All values in eV.

E_{Pauli}	5.72
E_{elstat}	-5.18
E_{orb}	-1.82
E_{disp}	-1.29
TBE	-2.58

Conclusion

Although the encapsulation of small molecules such as DABCO within (supra)molecular cages made from zinc-porphyrins is known, the vast majority of examples concern cyclic systems bearing at least two linkers to connect both zinc-porphyrin units or rather flexible single junctions.^[7,8,28] In the present case, we show that such a strong pre-organization or flexibility is not required for DABCO encapsulation since a simple acyclic and highly rigid bis-zinc-porphyrin system such as **2** is adaptable enough to drive the self-assembly process to a selective 1:1 encapsulation. In addition, this supramolecular system provides a significant space available around the encapsulated guest to further explore new physicochemical processes that are less available for the typical cases in which the highly sophisticated (supra)molecular cages impose little access to additional events. Overall, by rational understanding the formation of an unexpected side-product in a copper-catalyzed click reaction, we have discovered the molecular recognition properties found in a sterically congested bis-zinc-porphyrin scaffold. Metalloporphyrins based on this tweezer chemical design might be ideal constituents for switchable catalysis and/or chemical sensing.^[29]

Experimental Section

General methods. Solvents were purified with an MB SPS-800 purification system. Pyrrole was dried with CaH₂ and distilled prior to use.

CDCl_3 was filtered through alumina and stored under argon over molecular sieves. All the other employed chemicals were purchased from commercial sources and used as received. Unless otherwise specified, all reactions were carried out under argon atmosphere by employing standard Schlenk and vacuum-line techniques. ^1H and ^{13}C NMR spectra were recorded with a Bruker GPX (400 MHz) spectrometer. ^1H NMR spectra were referenced to residual protiated solvent ($\delta = 7.24$ ppm for CDCl_3). ^{13}C NMR spectra were referenced to CDCl_3 ($\delta = 77.0$ ppm). Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, J , were reported in hertz unit (Hz). The reactions were monitored by using a Shimadzu 2014 gas chromatograph equipped with an EquityTM-1 Fused Silica capillary column (30 m x 0.25 mm x 0.25 μm) and an FID detector; conversion and selectivity were determined by using dodecane as internal standard. UV/Vis absorption spectra were recorded with a Specord 205 UV/Vis/NIR spectrophotometer and quartz cuvettes of 1 cm path length. Mass spectroscopy and microanalysis were performed in the laboratories of the Centre Regional de Mesures Physiques de l'Ouest (CRMPO, Université de Rennes 1, Rennes, France). Alkyne porphyrin **1** was prepared following a reported procedure.^[12,13]

Important Note: Azide are sensitive compound that are prone to explosion or decomposition under harsh conditions (high temperature, low pressure...). Careful attention should be taken to prevent any unwanted reactivity as well as safety incident. In the same regard, quenching the remaining aqueous sodium azide at the end of reaction should be carried out for safety and toxicity reason.

Synthesis and characterization of 2-azido-4-*tert*-butylpyridine:

According to the general procedure, 2-bromo-4-*tert*-butylpyridine (0.417 mL, 0.539 g, 2.66 mmol, 1 equiv.), sodium azide (0.345 g, 5.32 mmol, 2 equiv.), CuI (0.050 g, 0.27 mmol, 0.1 equiv.), sodium ascorbate (0.026 g, 0.13 mmol, 0.05 equiv.) and *N,N'*-dimethylethylenediamine (0.04 mL, 0.033 g, 0.40 mmol, 0.15 equiv.) were dissolved in a mixture of EtOH:H₂O (12 mL, *v/v* 7:3). The reaction mixture was stirred for 2 hours at reflux under air atmosphere. Then, the mixture was evaporated to dryness. A mixture of EtOAc and H₂O were added and the aqueous layer was extracted with EtOAc (3 x 50 mL). Then the combined organic layers were washed with water two times and once with brine solution. After drying over MgSO₄ and filtration, the solvents were evaporated under reduced pressure. The product was further purified by column chromatography (SiO_2 , *n*-heptane:EtOAc) affording the analytically pure product as a white powder (0.410 g, 90%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.72$ (dd, $J = 7.3$, 1.0 Hz, 1H), 7.90 (dd, $J = 1.8$, 1.0 Hz, 1H), 7.27 (dd, $J = 7.3$, 1.8 Hz, 1H), 1.41 (s, 9H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 156.7$, 149.0, 124.3, 116.1, 110.2, 35.6, 30.3 ppm. HRMS (ESI, MeOH/DCM : 95/5): m/z calcd for $\text{C}_8\text{H}_{12}\text{N}_4$: 199.0954 [$\text{M}+\text{Na}$]⁺; found: 199.0954 (0 ppm).

Synthesis and characterization of L*:

Into a dried Schlenk tube charged with a stirring bar, 2-azido-4-*tert*-butylpyridine (0.299 g, 1.7 mmol, 1 equiv.) and $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (0.158 g, 0.17 mmol, 0.1 equiv.) were dissolved in dry toluene (12 mL) in a dry Schlenk tube. Then, phenylacetylene (0.208 mg, 0.224 mL, 2 mmol, 1.2 equiv.) was introduced and the reaction mixture was stirred at 120°C immediately for 24 hours. Back at room temperature, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2 , *n*-heptane:EtOAc, 1:0 to 7:3) to afford analytically pure L* (0.142 g, 30% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.80$ (s, 1H), 8.42 (d, $J = 6.0$ Hz, 1H), 8.25 (d, $J = 1.2$ Hz, 1H), 7.95 (dd, $J = 6.0$, 1.2 Hz, 2H), 7.57–7.30 (m, 5H), 1.41 (s, 9H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 164.1$, 149.5, 148.3, 148.0, 132.5, 130.4, 128.9, 128.4, 128.4, 125.9, 120.9, 117.0, 110.9, 35.4, 30.5 ppm. HRMS (ESI, DCM): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}_4$: 301.14237 [$\text{M}+\text{Na}$]⁺; found: 301.1424 (0 ppm).

General protocol for the homo-coupling of phenylacetylene: Into a dried Schlenk tube charged with a stirring bar, phenylacetylene **3** (0.100 g, 0.107 mL 9.8×10^{-4} mol, 1 equiv.), $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (0.046 g, 4.9×10^{-5} mol,

0.05 equiv.), L* (0.014 g, 4.9×10^{-5} mol, 0.05 equiv.) and dry toluene (20 mL) were added. The reaction mixture was stirred for 24 hours at 120°C. GC-MS and GC-FID analysis showed a conversion of 65% and an estimated yield of 54%. Back at room temperature, the solvents were evaporated. The crude mixture was further purified by column chromatography (SiO_2 , *n*-heptane:EtOAc, *v/v* 1:0 to 9:1) affording the homocoupling product **4** as a colourless oil (0.047 g, 47% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.54$ (dd, $J = 7.9$, 1.8 Hz, 4H), 7.41–7.28 (m, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 132.5$, 129.2, 128.4, 121.8, 81.5, 73.9 ppm. The spectral data match those found in the literature.^[30]

Glaser-Hay cross coupling procedure for the synthesis of dimer 2:

Into a dried Schlenk tube charged with a stirring bar, **1** (0.100 g, 0.14 mmol, 1 equiv.), CuI (0.001 g, 0.007 mmol, 0.05 equiv.), dry CHCl_3 (5 mL) and *N,N'*-tetramethylethylenediamine (0.003 g, 4 μL , 0.025 mmol, 0.02 equiv.) were added and the reaction mixture was stirred for 16 hours at 50 °C under air atmosphere. Then the solvents were evaporated and the crude mixture was purified by column chromatography (SiO_2 , *n*-heptane:DCM, *v/v* 1:0 to 7:3) affording the analytically pure bis-alkyne zinc porphyrin **2** as a purple powder (0.079 g, 79% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.93$ (d, $J = 4.6$ Hz, 4H), 8.90 (d, $J = 4.6$ Hz, 4H), 8.65 (d, $J = 4$ Hz, 4H), 8.35 (d, $J = 4.6$ Hz, 4H), 8.26–8.17 (m, 4H), 8.10–8.02 (m, 8H), 7.83–7.58 (m, 20H), 7.35 (td, $J = 7.6$, 1.4 Hz, 2H), 7.21 (m (td), 2H), 6.95 (dd, $J = 7.8$ Hz, 0.9 Hz, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 150.2$, 149.97, 149.94, 149.7, 145.2, 142.9, 142.7, 134.5, 134.4, 134.35, 134.1, 132.1, 132.0, 132.0, 131.8, 131.1, 127.5, 127.4, 127.4, 126.7, 126.5, 126.5, 126.4, 125.2, 121.4, 120.9, 117.8, 81.5, 77.0 ppm. HRMS (ESI): m/z calcd for $\text{C}_{92}\text{H}_{54}\text{N}_8\text{Zn}_2$: 1398.30489 [M]⁺; 1398.3055 (0 ppm).

Palladium/Copper co-catalyzed synthesis of 2:

Into a dried Schlenk tube charged with a stirring bar, **1** (0.100 g, 0.14 mmol, 1 equiv.), CuI (0.001 g, 0.007 mmol, 0.05 equiv.), Pd(OAc)₂ (0.002 g, 0.007 mmol, 0.05), DABCO (0.478 g, 0.426 mmol, 3 equiv.) and dry acetonitrile (5 mL) were added and the reaction mixture was stirred for 16 hours at room temperature under air atmosphere. Then the solvents were evaporated and the crude mixture was purified by column chromatography (SiO_2 , *n*-heptane:DCM, *v/v* 1:0 to 7:3) affording the analytically pure bis-alkyne zinc porphyrin **2** as a purple powder (0.061 g, 61%).

NMR binding studies between bis-alkyne porphyrin 2 and DABCO

(1:1 ratio): **2** (5 mg, 3.57×10^{-3} mmol, 1 equiv.) was placed in an NMR tube and dried under vacuum for few minutes. Then, dry CDCl_3 (0.75 mL) was added and the corresponding ^1H NMR spectrum was recorded. Then, 1 equiv. of a diluted solution of DABCO (0.4 mg, 3.57×10^{-3} mmol, 1 equiv.) was added to the NMR tube containing the host **2** and the corresponding ^1H NMR spectrum was recorded showing strong up-field shifts for the DABCO proton signals. DOSY NMR also showed that both DABCO and **2** diffuse together as one species.

Computational details: DFT calculations were performed using the Amsterdam Density Functional ADF2020 code.^[31,32] Scalar relativistic effects were taken into account via the Zeroth Order Regular Approximation (ZORA).^[33] A triple-zeta basis set augmented with two polarisation function (STO-TZ2P)^[34] was used together with the PBE0 functional^[35,36] and Grimme's empirical DFT-D3BJ corrections^[37] for geometry optimisation. The robust and very widely used PBE0 functional has proven its reliability in, inter alia, ground state calculations,^[38] including metal-porphyrin systems.^[39] When associated with Grimme's corrections for dispersion forces, it is well suited for investigating weak and/or non-covalent interactions at a reasonable computational cost.^[40] Wiberg bond indices were computed with the NBO6.0 program.^[41] Interaction energy between fragments were computed according to the Morokuma-Ziegler energy decomposition analysis (EDA) formalism^[27] implemented in the ADF2019 program. The QAIM analysis^[26] was performed as implemented in the ADF2020 suite.^[42]

Supporting Information

The data that support the findings of this study are available in the supplementary material of this article. Additional references cited within the Supporting Information.^[43–46]

Acknowledgements

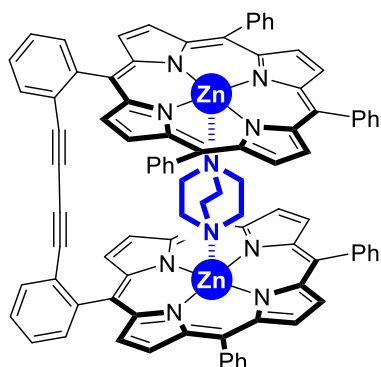
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Two zinc-porphyrin moieties have been covalently attached through a single, rigid buta-1,3-diyne linkage placed at the *ortho* position of a *meso* phenyl ring. Despite of freely rotating around the bis-alkyne axle, such species is adaptable enough to encapsulate a DABCO molecule with a high association constant of $K \approx 10^6 \text{ M}^{-1}$ as supported by in-depth experimental and computational studies.

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