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Catalytic carbene insertion into an aminoporphyrin and formation of a new chiral supramolecular porphyrin system

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ABSTRACT

The catalytic insertion of ethyl diazoacetate into a porphyrin derivative bearing an NH_2 substituent, in the presence of a Rh-based catalyst, was investigated. The X-ray analysis of one of the isolated products reveals the formation of a chiral supramolecular system.

Researchers in organic synthesis, mainly those working in the area of tetrapyrrolic macrocycles, are constantly looking for new methodologies leading to molecules that might exhibit specific properties.[1] In fact, many synthetic approaches lead to porphyrin derivatives that are used in several applications like photodynamic therapy of cancer cells (PDT),[2] catalysis,[3] electronics or solar cells production. Nowadays, functional self-assembled materials with well-defined three dimensional architectures have attracted much attention owing to their application in electronics, photonics, light-energy conversion and catalysis.[4] Porphyrins and their analogues have already shown their ability to form supramolecular systems to be used in those areas. In fact, even in Nature, porphyrins and chlorophylls are often self-assembled into nanoscale superstructures to perform many essential functions, such as light harvesting and electron transport.[4]

The use of diazo compounds, namely diazocarbonyl compounds, has attracted much attention due to their versatility in several synthetically useful transformations.[5,6] In particular, the catalytic insertion of α-diazocarbonyl compounds into X–H bonds (X=C, N, O, S) is a versatile organic transformation for preparing complex target molecules.[7–10] The concept of metal-carbenoid insertions into X–H bonds (X=C, N, O, S) has been known for more than three decades,[11] but documented studies on the functionalization of porphyrins by catalytic insertion of α-diazocarbonyl compounds into X–H bonds are scarce.[12,13] In 2008, we reported that $Rh_2(OAc)_4$ is able to catalyse the insertion of the carbene generated from ethyl diazoacetate (EDA) into peripheral positions of the zinc complexes of *meso*-tetraarylporphyrins giving rise to cyclopropanation, CH insertion and Büchner ring expansion products.[13]

Following our interest on the development of new synthetic approaches to prepare novel porphyrin derivatives with interesting properties,[14–17] it was decided to investigate the insertion reaction of EDA into porphyrins with N–H bonds in the presence of a Rh(II)-based catalyst. For this study the [5-(4-aminophenyl)-10,15,20-triphenylporphyrinato]zinc(II) **1** was selected; the use of the zinc complex avoids the undesired insertion of the carbene into the inner N–H bonds if a free-base macrocycle would be used. Considering the substituents present in the expected new derivatives it was also aimed at looking at potential intermolecular interactions between the product molecules.

The insertion reaction with porphyrin derivative **1** was performed with EDA, a very reactive commercially available α-diazocarbonyl compound, in the presence of a catalytic amount of $Rh_2(OAc)_4$ (0.1 equiv). The reaction was carried out in refluxing dichloromethane and the EDA (diluted in dichloromethane) was slowly injected (for 10 h) using a syringe pump.[18] The slow addition of the diazo compound minimizes the formation of carbene dimers (Scheme 1).[13] TLC of the reaction mixture shows the formation of three new compounds, one less polar (compound **2**) and other two which are more polar than the starting porphyrin

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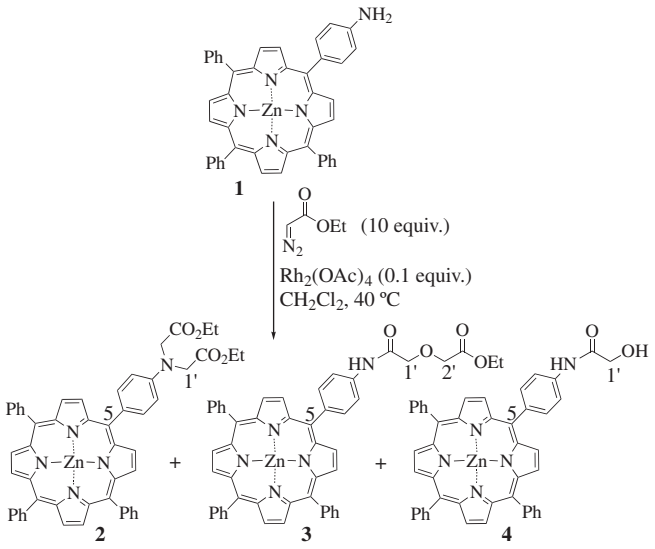


Scheme 1. Reaction of porphyrin complex **1** with EDA in the presence of $Rh_2(OAc)_4$.

(compounds **3** and **4**). Compounds **2**, 3 and **4** were isolated in 14%, 12% and 16% yield, respectively.[19]

The structure of compound **2** corresponds to the insertion of two carbene units, generated from EDA, into the N–H function of porphyrin **1**. Its molecular formula was confirmed by ESI-HRMS (*m/z* 863.2445 (M^+)) and its structure was elucidated by NMR. In the ^1H NMR spectrum the integration of the signals due to the inserted EDA moieties also confirmed the double insertion. The proton resonances of the ethyl groups appear as a quartet and as a triplet at, respectively, 4.33 and 1.37 ppm (J = 7.1 Hz). The signal due to the CH_2-1′ protons appears as a singlet at 4.38 ppm. It is important to notice that from the HMBC spectrum of **2** connectivities were found between the CH_2-1′ protons and the carbons of the carbonyl group and also with the *para*-carbon of the 5-phenyl group (δ 147.3 ppm) (Fig. 1a).

The molecular formula of compound **3** was confirmed by its ESI-HRMS where a peak at *m/z* 853.2131 (M^+) is observed. The aliphatic region of the ^1H NMR spectrum shows the typical profile due to the resonances of the ethyl protons (a quartet at 4.30 ppm and a triplet at 1.34 ppm) and also two singlets due to the resonances of two protons each at 3.79 ppm (CH_2-1′) and at 4.16 ppm (CH_2-2́), unequivocally assigned through the HMBC correlations (Fig. 1b). Contrary to what is observed for compound **2,** (Fig. 1a), this 2D NMR spectrum did not show any correlation between CH_2-1′ and the carbons of the 5-phenyl group. This fact confirms that we are in the presence of an amide derivative and not in the presence of an N-substituted amine derivative. In the aromatic region of the spectrum it is observed the resonance due to the NH proton of the amide group, as a singlet at 9.13 ppm, together with the resonances of the β-pyrrolic and of the *meso*-aryl protons.

The ESI-HRMS spectrum of **4** shows a peak at *m/z* 749.1764 (M^+) in agreement with its molecular formula. In the HMBC spectrum of **4** the CH_2-1′ protons do not correlate with any carbon of the 5-phenyl ring, indicating that compound **4** is also an amide derivative. In fact, the resonance of the NH proton of the amide group was detected as a singlet at 8.93 ppm.

The formation of the unexpected amides **3** and **4** seems to imply the formation of ethyl glycolate by the reaction of EDA with a water molecule present in the reaction medium, as suggested by Afonso et al.[20] Assuming the presence of ethyl glycolate in the reaction medium, its reaction with porphyrin **1** can explain the formation of amide **4**. Therefore, an O–H insertion reaction of EDA in this hydroxyamide can easily justify the formation of compound **3**. To confirm this hypothesis, we performed two complementary experiments (Scheme 2). The first one involved the reaction of porphyrin **1** with commercially available ethyl glycolate. As expected, amide **4** was formed. The second experiment involved the reaction of amide **4** with EDA in the presence of $Rh_2(OAc)_4$. Compound **3** was obtained, and its formation supports the proposed mechanism.

Amide derivative **3** was successfully crystallised as small red prisms by layering hexane over a solution in dichloromethane, at room temperature and over a period of two months. The crystallographic details were unveiled from single-crystal X-ray diffraction, showing that compound **3** crystallises at 150 K in the non-centrosymmetric, chiral $P2_1$ space group (see Table 1, Supplementary data). The asymmetric unit is composed of a whole molecular unit of **3** as depicted in Figure 2a. The substituent pendant group does not seem to impose a significant steric pressure on the central porphyrin ring, with all the four crystallographically independent pyrrole units lying approximately on the same average plane: the mean planes of each pair of consecutive pyrrole rings subtend mutual dihedral angles which only vary between ca. 2.6° and 11.3° (Fig. 2a). These results agree well with the geometrical features usually observed for this type of compounds as revealed by a systematic search in the Cambridge Structural Database (CSD, Version 5.31, November 2009 with four updates until August 2010)[21]: from 3335 crystal determinations of porphyrin derivatives, nearly 82% exhibit analogous dihedral plane angles, all smaller than ca. 12.2°. The central Zn^{2+} cation exhibits a slightly distorted $\{ZnN_4O\}$ square pyramidal coordination environment. The basal plane is formed by the four N-atoms of the porphyrin ring [Zn–N bond lengths ranging from 2.043(4) to 2.069(4) Å; see Table 2 in the Supplementary data], with the Zn^{2+} cation being raised by only ca. 0.24 Å from the average plane containing the *N*-pyrrole units. The apical position is occupied by a carbonyl *O*-atom from the pendant group of a neighbouring molecular unit [Zn–O bond length of 2.152(4) Å] (Fig. 2b). The internal *cis*-angles of the coordination polyhedron vary between 88.63(16)° and 99.36(16)°, with the latter angle being significantly larger than the remaining ones (see Fig. 3b and also Table 2 in the Supplementary data) mainly because of the polymeric nature of the com-

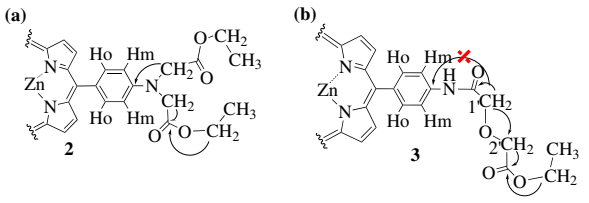
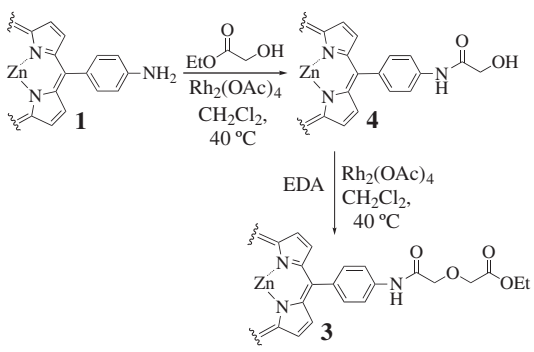


Figure 1. (a) and) (b) Correlations observed in the HMBC spectra of **2** and **3**.



Scheme 2. Reaction of porphyrin **1** with ethyl glycolate and O–H insertion reaction of EDA into porphyrin **4** to afford compound **3**.

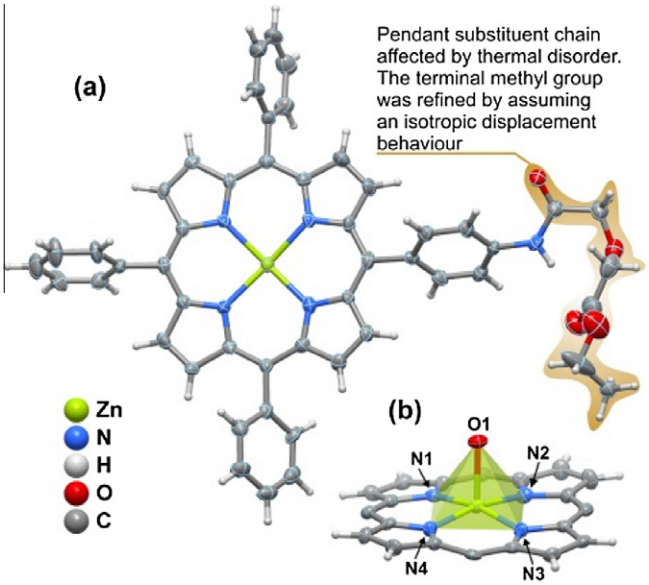


Figure 2. (a) Schematic representation of the molecular unit of metalloporphyrin **3**. (b) Detailed view of the slightly distorted square pyramidal $\{ZnN_4O\}$ coordination environment of the central Zn^{2+} cation, showing the labelling scheme for all atoms composing the coordination sphere. In both representations, while non-hydrogen atoms are represented as thermal ellipsoids drawn at the 50% probability level (except for the terminal $-CH_3$ moiety whose carbon atom is drawn as a sphere), hydrogen atoms are instead represented as small spheres with an arbitrary radius. For bond lengths (in Å) and angles (in degrees) for the $\{ZnN_4O\}$ coordination environment see Table 2 in the Supplementary data.

pound. Indeed, because the carbonyl group of an adjacent molecular unit coordinates to Zn^{2+}, this creates a small steric pressure on the resulting polymer which is minimized by a small tilt of the coordination polyhedron; this occurrence is ultimately reflected in a slightly larger N–Zn–O angle. Even though five-coordinated Zn^{2+} cations are relatively common among metalloporphyrins, only a handful are polymeric and, usually, a solvent molecule occupies the fifth coordinative position. The exception to date is the structure reported by Senge and Smith in the early nineties, in which the apical position of Zn^{2+} is occupied by a nitro group.[22]

The most remarkable structural feature of **3** concerns the presence of a 1D coordination polymer running parallel to the *b*-axis, as depicted in Figure 3. A search in the literature and in the CSD reveals that polymeric metalloporphyrins are not abundant, being less than ca. 9% of all known crystal structures of this family of compounds. The encapsulation of metallic centres into the porphyrin central ring leads to a maximum of two available coordinating *exo*-positions, which may allow the rational design of supramolecular architectures,[23] many of which exhibit interesting properties,[24] such as conductivity.[25] Most of this design is focused in the use of the metalloporphyrins with an auxiliary bridging ligand capable of effectively establishing connections between adjacent units, leading to "shish-kebab" coordination polymers. Recent notable examples come from the Sanders group.[26] Compound **3** is clearly distinct from the "shish-kebab" family of compounds because the bridges between units are instead ensured by the substituent pendant group of the organic moiety: as described above, the carbonyl of the amide group coordinates to the Zn^{2+} centre of an adjacent molecule, with this being in the genesis of the 1D polymer (Fig. 3a). In **3** this arrangement occurs in a spiral fashion, leading to the formation of a right-handed chiral helix (Fig. 3b) with a pitch of ca. 10.4 Å running parallel to the *b*-axis of the unit cell (Fig. 3a and c). It is also worth noting that the crystal structure determination clearly ensured the presence of an enantiomerically pure compound (see the Supplementary data). Remarkably, a search in the

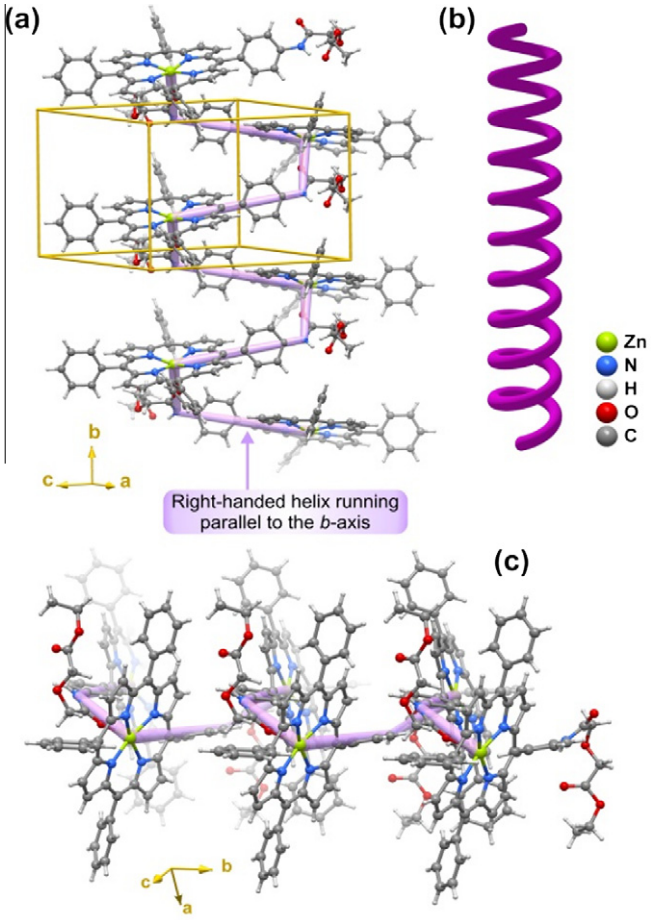


Figure 3. Schematic representation of the one-dimensional, chiral supramolecular metalloporphyrin chain running parallel to the *b*-axis.

literature revealed the existence of only a handful of chiral polymeric metalloporphyrins, usually determined in the $P2_1$[27] or $P2_12_12_1$[28] space groups.

The crystal structure of **3** can be essentially described by the close packing in the *ac* plane of the aforementioned chiral 1D polymers mediated by van der Waals contacts (see Fig. S1 in the Supplementary data). Indeed, the zigzag nature of the polymer and the absence of a significant number of donors to promote a network of structure-directing hydrogen bonding interactions lead to a simple geometrical packing. The only relevant hydrogen bond is of intramolecular nature within the pendant substituent group (not shown): there is a N–H···O interaction connecting the N–H moiety of the amide to the ester group [$d_{D\cdots A}$ of 3.114(7) Å, and <(DHA) of ca. 144°].

In summary, it is reported here the first study on the functionalization of porphyrins by catalytic insertion of ethyl diazoacetate into N–H bonds. The porphyrin with the NH_2 group **1** affords the insertion product **2** plus the amide derivatives **3** and **4**. In the solid state, amide **3** forms an unusual chiral supramolecular metalloporphyrin chain, forming a right-handed helix and being an enantiomeric pure aggregate. This fact allows us to conclude that the catalytic insertions of diazocarbonyl compounds can be considered a new synthetic approach to new supramolecular systems based on porphyrinic arrays.

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Supplementary data

Supplementary data (crystal structure of compound **3** in CIF format and the corresponding check CIF report are presented) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.06.120.

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18. Reaction of porphyrin **1** with EDA: To a dry dichloromethane (6 mL) solution of porphyrin **1** (50 mg, 72.0 μmol) and $Rh_2(OAc)_4$ (3.2 mg, 7.2 μmol, 0.1 equiv), at 40 °C, under a nitrogen atmosphere, was added dropwise a solution of EDA (75.7 μL, 0.72 mmol, 10 equiv) in dichloromethane (5 mL) during 10 h using a syringe pump. The reaction mixture was further stirred at the same temperature for 8 h. The solvent was then evaporated under reduced pressure and the residue was fractionated by column chromatography (silica gel) using CH_2Cl_2 as the eluent. The obtained fractions were further purified by preparative TLC using a mixture of hexane and ethyl acetate (4:1) as the eluent.
19. Compound **2**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 and 8.97 (AB, J = 4.7 Hz, 4H, H-2,3 and H-7,8), 8.93 (br s, 4H, H-12,13 and H-17,18), 8.23–8.21 (m, 6H, H*o*-Ph-10,15,20), 8.07 (d, J = 8.6 Hz, 2H, H*o*-Ph-5), 7.77–7.71 (m, 9H, H*m,p*-Ph-10,15,20), 6.97 (d, J = 8.6 Hz, 2H, H*m*-Ph-5), 4.38 (s, 4H, CH_2-1′), 4.33 (quart, J = 7.1 Hz, 4H, OCH_2CH$_3$), 1.37 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1 (C═O), 150.7, 150.1, 150.0, 147.3 (C*p*-Ph-5), 142.9, 135.4 (C*o*-Ph-5), 134.4 (C*o*-Ph-10,15,20), 132.7, 132.2 and 131.88 and 131.86 and 131.7 (β-C), 127.4 and 126.5 (C*m,p*-Ph-10,15,20), 121.5, 120.9, 120.7, 110.7 (C*m*-Ph-5), 61.3 (CH2-1′), 53.7 (OCH$_2$CH$_3$), 14.3 (OCH$_2$CH$_3$). UV–vis ($CHCl_3$): λ_{max} (log ε) 420 (5.14), 505 (3.39), 548 (3.86), 587 (3.35) nm. HRMS-ESI: m/z 863.2445. Calcd. for $C_{52}H_{41}N_5O_4Zn$ (M^+) 863.2450.
Compound **3**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (s, 1H, N*H*), 9.95–8.93 (m, 8H, H-2,3,7,8,12,13,17,18), 8.24–8.21 (m, 6H, H*o*-Ph-10,15,20), 8.13 (d, J = 8.4 Hz, 2H, H*o*-Ph-5), 7.77–7.72 (m, 9H, H*m,p*-Ph-10,15,20), 7.69 (d, J = 8.4 Hz, 2H, H*m*-Ph-5), 4.30 (quart, J = 7.1 Hz, 2H, OCH_2CH$_3$), 4.16 (s, 2H, C*H*2-2′), 3.79 (s, 2H, CH_2-1′), 1.34 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (CO_2Et), 167.1 (CONH), 150.2, 150.1, 142.8, 138.9, 136.5, 134.8 (C*o*-Ph-5), 134.4 (C*o*-Ph-10,15,20), 132.0 (β-C), 131.9 (β-C), 127.4 and 126.5 (C*m,p*-Ph-10,15,20), 121.1, 121.0, 120.4, 117.8, 117.7 (C*m*-Ph-5), 71.7 (CH_2-1′), 69.3 (CH_2-2′), 61.6 (OCH_2), 14.2 (OCH$_2$CH_3). UV–vis ($CHCl_3$): λ_{max} (log ε) 423 (5.59), 517 (3.47), 552 (4.26), 595 (3.72) nm. HRMS-ESI: m/z 835.2131. Calcd. for $C_{50}H_{37}N_5O_4Zn$ (M^+) 835.2137.
Compound **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.35 (s, 1H, N*H*), 8.89–8.87 (m, 8H, H-2,3,7,8,12,13,17,18), 8.24–8.19 (m, 6H, H*o*-Ph-10,15,20), 7.97 (d, J = 7.9 Hz, 2H, H*o*-Ph-5), 7.79–7.70 (m, 11H, H*m,p*-Ph-5,10,15,20), 4.30 (s, 2H, CH_2-1′). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.7 (C═O), 150.3, 150.3, 150.2, 150.1, 142.8, 135.0, 134.4, 131.9, 131.9, 127.4, 127.4, 127.4, 126.5, 121.1, 121.1, 29.7 (CH_2-1′). UV–vis ($CHCl_3$): λ_{max} (log ε) 418 (5.71), 510 (3.46), 546 (3.82), 584 (3.35) nm. HRMS-ESI: m/z 749.1764. Calcd. for $C_{46}H_{31}N_5O_2Zn$ (M^+) 749.1769.
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