

## A novel porphyrazine ligand tailored to homogeneous metal catalyzed transformations

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### Abstract

A novel centrosymmetric porphyrazine (Pz) **1** decorated with pyrazino-dibenzo[*b,f*]azepine units have been prepared via Linstead macrocyclization reaction of a dinitrile precursor. Accordingly, the peripheral azepine nitrogen offers a chemical handle for subsequent functionalizations. Characterization of the metal complexes (MPzs = Metal Porphyrazines) of **1** was accomplished and good catalytic performances were achieved in the Cu(II)- and Co(II)- catalyzed cyclopropanation with ethyl diazoacetate as a test reaction.

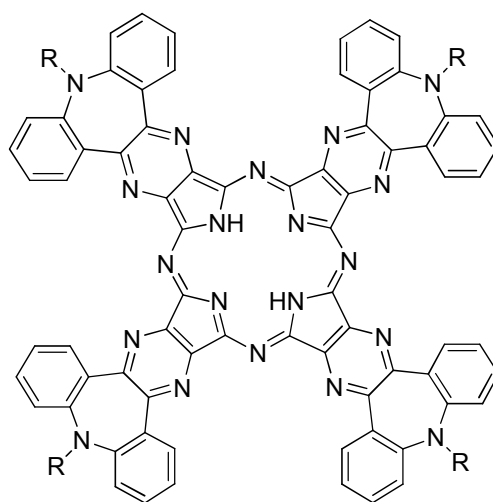
**Keywords:** Porphyrazine, oxcarbazepine, heterocycles, macrocycles, homogeneous catalysis, cyclopropanation

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### Introduction

Phthalocyanines (Pcs) are  $D_{4h}$  symmetry (due to mesomeric averaging as metal complexes, dications or dianions) macrocyclic compounds with aromatic 18  $\pi$ -electrons, closely related to the natural occurring porphyrins. As porphyrins they could host a variety of metal ions inside the central cavity of the system. Pcs *per se* and their metal Pcs (MPCs) offer a wide assortment of extensively functionalized structures with classical application as pigments and dyes and, more recently, in photodynamic therapy, as photonic materials (*e.g.* mesogenics, NLO, optomaterials) and functionalized solids (*e.g.* microporous solids, conductive polymers, ferroelectrics, chemical sensors).<sup>1-4</sup>

In addition to the above mentioned applications, Pcs had found place as ligands in a wide number of metal catalyzed organic transformations (*e.g.* oxidation, synthesis of nitrogen-containing compounds, C-C bond formation, reduction and many other useful synthetic procedures).<sup>5</sup> The application of MPcs as catalysts is an emerging strategy and has attracted broad interests due to their accessibility in terms of the cost and straightforward preparation on a large scale as well as their chemical and thermal stability. Porphyrazines (Pzs) represent a structural analogue of porphyrins in which the *meso* carbons of porphyrins are replaced with N atoms. This structural similarity would make Pzs a good candidate for development of functional dyes, molecular devices and biomedical applications. A peculiar study on porphyrazines and related metal complexes was reported by Ercolani and coworkers.<sup>6</sup> Recently, Pzs has attracted a lot of attention for their intense electronic absorption and emission in their near infrared region. Homogeneous and heterogeneous catalysis with metal porphyrazines (MPzs) has been extensively demonstrated, also their use as biomimetic catalyst was successfully achieved.<sup>7</sup> However, for some of these applications, MPzs are of disappointing use due to their scarce solubility in common organic solvents and this drawback could be overcome by an appropriate decoration of the periphery of the macrocycle.<sup>8</sup>



1  
1b R = hexadecanoyl

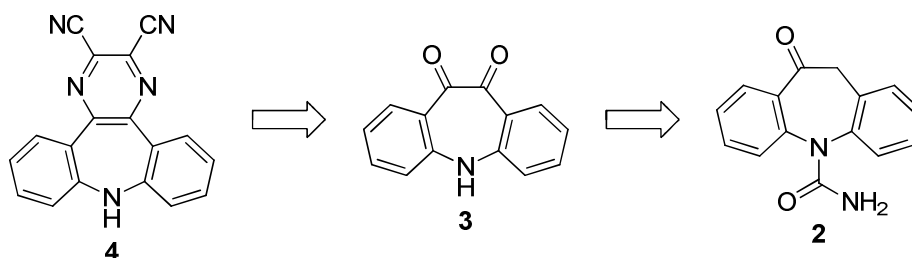
### Figure 1

In this paper we report the synthesis of a novel centrosymmetric Pz system (Figure 1), arising from the formal substitution of four benzo subunits in a Pc by a 9*H*-dibenzo[*b,f*]pyrazino[2,3-*d*]azepine moiety, wherein the peripheral azepine nitrogen atoms offer a chemical handle for subsequent functionalizations (*i.e.*, introduction of lipophilic chains in order to address the above issue as in **1b**). Accordingly, cyclopropanation with ethyl diazoacetate (EDA) catalyzed by the Cu(II)- and Co(II)-metal complexes **11** and **12**,

respectively, of the highly lipophilic *N*-hexadecanoyl porphyrazine **1b** is also reported as test reaction.

## Results and Discussion

There are a number of protocols available for synthesis of porphyrazine macrocycles and, of the particular relevance to our work, were methods based on tetramerization of *ortho*-disubstituted arenes (i.e., phthalic acids and anhydrides, phthalimides, diiminoisoindolines, *o*-cyanobenzamides).<sup>9</sup> Retrosynthetic analysis suggested to pick the 5*H*-dibenzo[*b,f*]azepine-10,11-dione **3** as key intermediate, due to the potential of supplying the required *o*-dinitrile **4** through a [4+2 (CC+NCCN)] cyclocondensation with diaminomaleonitrile as 1,4-bis(nucleophile) (Scheme 1).

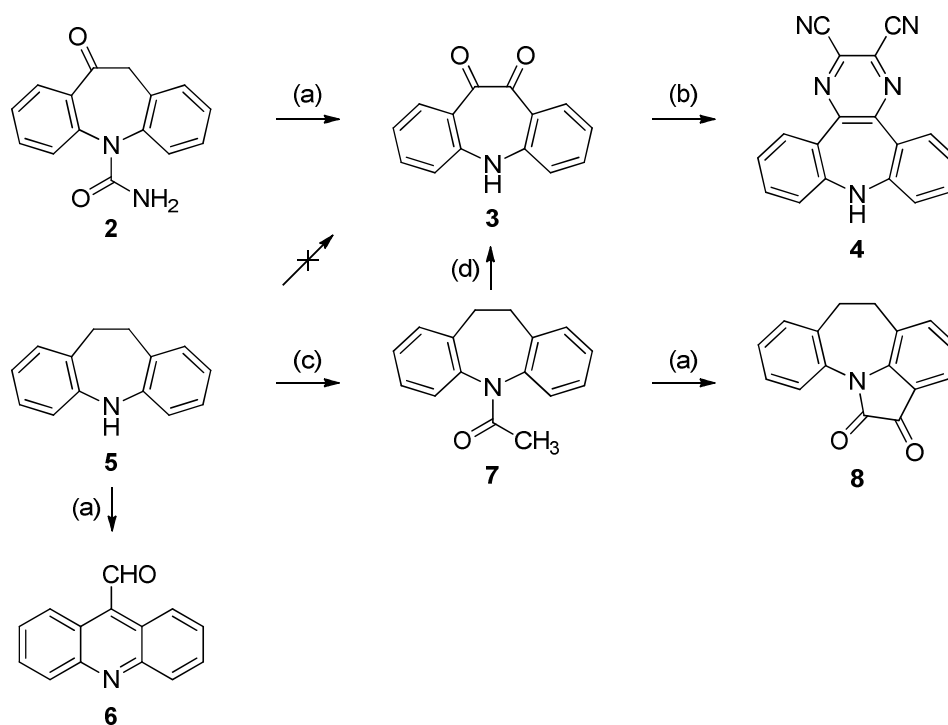


### Scheme 1

With ample supply of oxcarbazepine **2** available, our intention was to effect a one-pot tandem oxidation/*N*-decarbamylation to yield diketone **3** required for the elaboration of porphyrazine ring system (Scheme 2). We initially considered application of a report by Heckendorn describing the transformation of **2** into **3** by a multi-step procedure, entailing  $\alpha$ -carbonyl bromination of **2**, nucleophilic substitution with KOAc followed by aerial oxidation.<sup>10</sup> In our hands, however, yields of **3** remain unsatisfactory, notwithstanding strict adherence to conditions prescribed by Heckendorn. Therefore, we attempted to design a method that would enhance the yields and, possibly, through a shorter synthetic pathway. Several methods currently exist to obtain  $\alpha$ -diketones by oxidation of  $\alpha$ -methylene ketones. Among these are the use of venerable SeO<sub>2</sub> (Riley method),<sup>11</sup> seleninic acids and anhydrides, pyridinium chlorochromate (PCC) or KMnO<sub>4</sub> as oxidant agents. Multi-step approaches have also been reported like Kornblum oxidation of  $\alpha$ -bromo ketones, nitrosation, microwave promoted oxidation or CuBr<sub>2</sub> adsorbed on alumina.<sup>12</sup>

Each method has its advantage and drawbacks in any given situation. For the sake of expediency, we opted for an oxidant able to gain **3** from **2** in only one step. Thus, a survey of oxidants was undertaken and on treatment of **2** with freshly sublimed SeO<sub>2</sub> (2.5 equiv) in refluxing 1,4-dioxane for 7 h, clean tandem oxidation/*N*-decarbamylation pleasingly ensued to produce **3** in 90% yield.<sup>13,14</sup> This compound precipitates directly from the reaction mixture as

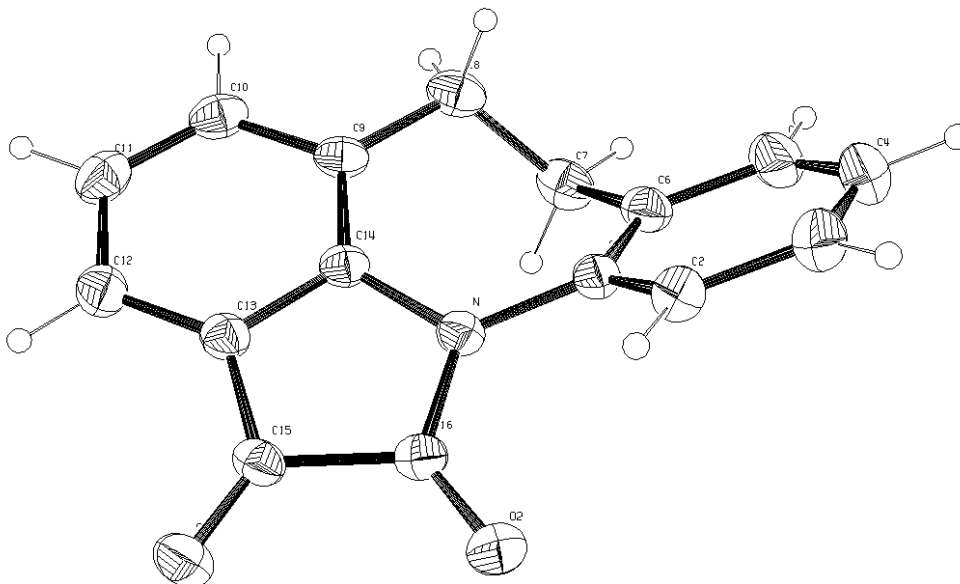
orange solid so that this process proved useful enough to prepare multigram quantities of **3**. The mechanism of *N*-decarbamylation is not clear at this time, but it seems plausible that reaction may commence with nucleophilic attack of amide carbonyl (as carboximidic acid tautomer) on  $\text{SeO}_2$ , followed by proton transfer with formation of a *N*-cyano intermediate and seleninic acid. The subsequent hydrolysis of the former would result in **3**.<sup>15,16</sup>



**Scheme 2.** Reagents and conditions: (a)  $\text{SeO}_2$ , 1,4-dioxane, reflux, 7 h; (b) diaminomaleonitrile, AcOH, reflux, 1 h; (c)  $\text{Ac}_2\text{O}$ , reflux 3 h; (d) BSA, PhCl, reflux, 8 h.

In the approach to **3**, alternatives to Scheme 2 were examined which proved less successful or less direct. Chen and coworkers reported a three-step procedure from iminostilbene (*5H*-dibenzo[*b,f*]azepine) concerning a progressive oxidation of the bridged double bond within an acceptable overall yield of 43%.<sup>17</sup> We checked the possibility to obtain **3** from commercially available 10,11-dihydro-*5H*-dibenzo[*b,f*]azepine **5**. Unfortunately, our initial efforts on this proved to be less straightforward than expected. For instance, use of either  $\text{SeO}_2$  or benzeneseleninic anhydride under conditions identical to those used with **3** proved fruitless because of various side products including the aldehyde **6** (formed by tandem benzylic rearrangement/ oxidative decarboxylation), presumably as a consequence of the unprotected NH. The susceptibility of dibenzazepines toward ring contraction to give acridine derivatives is well documented.<sup>18-20</sup> Thus, reaction of **5** with refluxing  $\text{Ac}_2\text{O}$  (3 h) gave **7**<sup>21</sup> which was converted to **3** in 67% overall yield, upon exposure to benzeneseleninic anhydride (BSA) (2 equiv) in chlorobenzene at 120 °C.<sup>22</sup> In stark contrast, access to **3** from **5** with  $\text{SeO}_2$  in refluxing dioxane

was messy and resulted in a complex mixture of compounds from which the isatin derivative **8**<sup>23</sup> was isolated, albeit in abysmally low yield. The structure of **8** has been established by single-crystal X-ray crystallography (Figure 2).

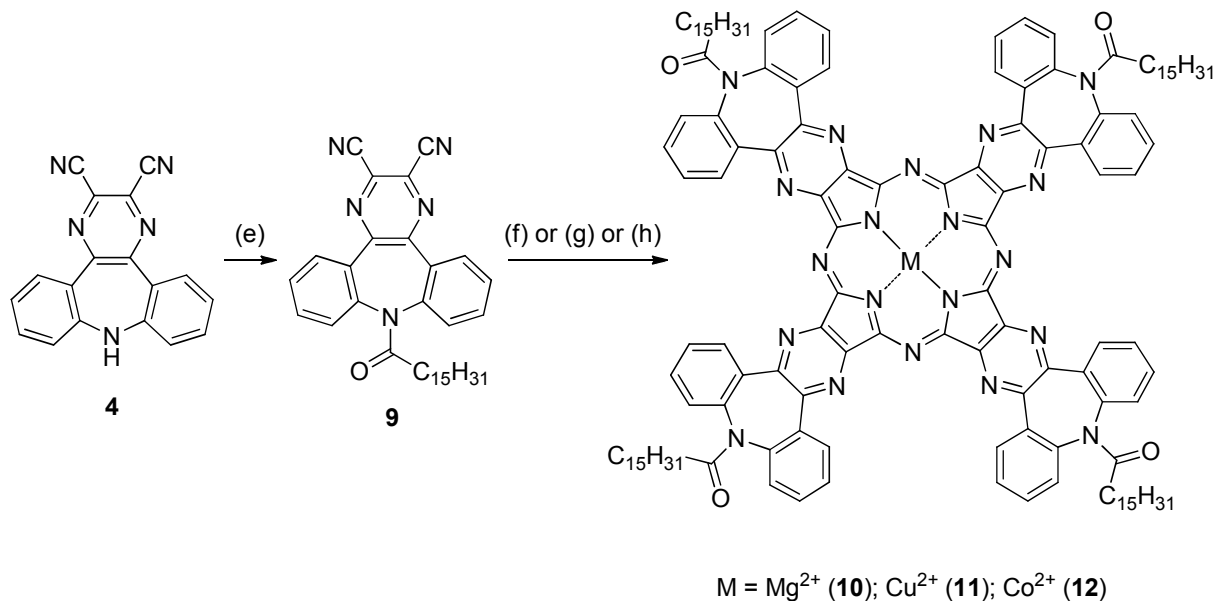


**Figure 2.** ORTEP drawing of the molecular structure of compound **8**, with thermal ellipsoids drawn at the 30% probability level. For sake of clarity, H atoms have been drawn as circles of arbitrary radius.

At this point, to get ready for Linstead macrocyclization step,<sup>24</sup> we only needed to react the 1,2-diketone **3** with diaminomaleonitrile as 1,4-bis(nucleophile) to form the required *o*-dinitrile **4** (Scheme 3), an operation which succeeded readily by refluxing the mixture in AcOH (1 h) (65% yield).

En route to porphyrazine, we were forced to postpone the tetramerization process of **4** owing to its poor solubility, which has hampered the purification. Thus, attempts were made to improve the solubility by incorporation of a long alkyl chain at the azepine *N* atom. After sampling a variety of derivatives (amides and tertiary *N*-alkyl amines), the hexadecanoyl group (i.e., **9**) appeared to be optimal in terms of yield and lipophilicity. Acylation of **4** was performed in anhydrous pyridine at 100 °C with hexadecanoyl chloride (1.1 equiv) in the presence of a catalytic amount of 4-*N,N*-dimethylaminopyridine (DMAP) and resulted in the isolation of **9** in 77% yield (Scheme 3). Finally, compound **9** was converted into its porphyrazine magnesium complex **10** via Linstead's Mg template cyclization. Therefore, Mg(*n*-BuO)<sub>2</sub> was prepared by heating Mg in 1-butanol for 6 h after which the dinitrile **9** was added and the reaction was

allowed to run under reflux for 8 h. After silica gel chromatography the magnesium complex **10** was isolated in 32% yield as a dark green powder.




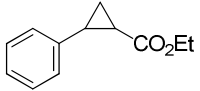

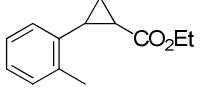

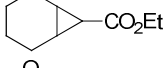

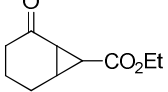

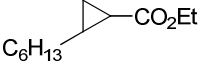

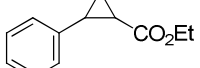

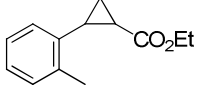

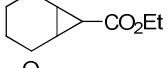

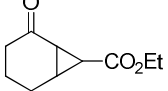

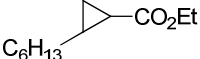
**Scheme 3.** Reagents and conditions: (e) palmitoyl chloride, pyridine, reflux, 6h; (f) 1) Mg, I<sub>2</sub>, n-BuOH, reflux 6 h N<sub>2</sub>, 2) **9**, reflux 8 h; (g) Cu(OAc)<sub>2</sub>, DMAE, DBU, MW 350W 10 min; (h) Co(OAc)<sub>2</sub>, DMAE, DBU, MW 350W 10 min.

With **10** in hand, the conversion into the respective Cu(II) and Co(II) complexes, **11** and **12**, was undertaken by well-known transmetalation procedure.<sup>9</sup> Treatment of **10** with a variety of Bronsted acids (e.g., TFA, AcOH, H<sub>2</sub>SO<sub>4</sub>) followed by subsequent remetalation with either Cu(OAc)<sub>2</sub> or Co(OAc)<sub>2</sub> uniformly resulted in formation of a reaction mixture in which only small quantities of the expected **11** and **12**, respectively, could be isolated. At this juncture, we turned our attention to Linstead's metal template strategy. Gratifyingly, when **9** was irradiated for 10 min in a microwave oven at 175 °C/350 W in freshly distilled 2-(dimethylamino)ethanol (DMAE),<sup>25</sup> in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anhydrous Cu(OAc)<sub>2</sub> or Co(OAc)<sub>2</sub>, the respective Cu and Co porphyrazines **11** and **12** were isolated in 67% and 72% yields, respectively. These two complexes show a good solubility in different classic organic solvents (e.g. CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF, Et<sub>2</sub>O, MeOH).

**Catalytic cyclopropanation.** As benchmark catalysis test we opted for transition metal complex-mediated cyclopropanation of alkenes with diazo compounds, an efficient and selective method for access to synthetically and biologically interesting cyclopropanes.<sup>26</sup> A huge amount of examples concerning the porphyrine metal complexes mediated cyclopropanation of alkenes are reported,<sup>27-29</sup> while few examples of the use of phthalocyanine transition metal complexes

have recently appeared.<sup>30-32</sup> Some of us reported recently studies in cyclopropanation reactions by using transition metal complexes with nitrogen ligands.<sup>33,34</sup>

**Table 1.** Catalytic cyclopropanation of alkenes mediated by **11** and **12** in CH<sub>2</sub>Cl<sub>2</sub> at 40 °C. Yields and ratio were obtained by GC-MS and <sup>1</sup>H NMR using examethylbenzene as internal standard

Entry	Substrate	Catalyst	Yield, %	Product	<i>Trans:Cis</i>	Time, h
1		<b>11</b>	96		2.3	4
2		<b>11</b>	85		2.7	2
3		<b>11</b>	64		4.6	5
4		<b>11</b>	57		5.8	5
5		<b>11</b>	77		3.4	9
6		<b>12</b>	95		2.4	6
7		<b>12</b>	80		2.6	8
8		<b>12</b>	75		4.9	10
9		<b>12</b>	53		6.1	14
10		<b>12</b>	85		5.7	23

*General procedure for catalytic cyclopropanation.* Reactions are carried out by slow addition of a solution of ethyl diazoacetate (EDA) (5.0 mmol in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>) under stirring to a refluxing CH<sub>2</sub>Cl<sub>2</sub> solution (75mL) consisting of alkene (12.5 mmol, 0.2 M) and **11** or **12** (0.005 mmol). Molar ratio catalyst / EDA / alkene = 1 / 1000 / 2500. The reaction was monitored by IR till the complete consumption of EDA [ $\nu_{N=N}$  2110 cm<sup>-1</sup>]. Yields and diastereomeric ratio were obtained by GC-MS and <sup>1</sup>H NMR using examethylbenzene as internal standard.

Our aim was to test the efficacy of the metal-porphyrizine complexes **11** and **12** in activating the diazo precursor (i.e., EDA), via the metal carbenoid specie, to the cyclopropanation reaction of aromatic, aliphatic and carbonyl conjugated alkenes. In this contest we decide to run the catalytic tests (Table 1) with EDA as limiting reagent (ratio

catalyst:EDA:substrate 1:1000:2500), the reactions were considered terminated when no trace of EDA was detected (IR) in the mixture. The reaction was monitored by GC-MS and  $^1\text{H}$  NMR, it was related to maximum % of product formation respect to the quantity of diazo compound loaded into the reactor. The stereochemical *trans:cis* ratios of the cyclopropanes formed were also studied and reported in Table 1.

Good performances were obtained either from Cu(II) complex (**11**) (yield range 57-96 %) and Co(II) complex (**12**) (yield range 53-95 %), even if the latter revealed a slower turnover frequency, in accordance with the data on phthalocyanine-catalyzed cyclopropanation previously reported by Zhou and coworkers.<sup>30</sup> The reactions were run only once and the reported results are therefore unoptimized. The yields and the stereochemical outcomes of the reaction had proved to be substrate dependent, in fact the best result in cyclopropanation products were obtained with styrene (Table 1, entries 1 and 6) and the best *trans* selectivity emerged from the cyclopropanation of cyclohexenone (Table 1, entries 4 and 9).

## Experimental Section

**General.** All reactions were performed using standard glassware and IKA num heating plates. Reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an argon atmosphere. Solvents were used as received without further purifications, unless stated otherwise. All reagents, if not otherwise specified, were used as received and, if necessary, stored under inert gas. Oxcarbazepine was supplied by Trifarma SpA, Ceriano Laghetto, Italy. Silica thin-layer chromatography (TLC) was done on E. Merck plastic or aluminum-backed plates (silica gel 60, F<sub>254</sub>, 0.2 mm). Quantitative analyses of products were performed on a Shimadzu GC-17A gas chromatograph coupled with a QP5000 mass detector. Column chromatography was performed on E. Merck silica gel 60 (70-230 mesh). Microwave heating was performed on a CEM Discover SP instrument with a single-mode microwave cavity providing continuous irradiation at 2.45 GHz and power up to 300W. Melting point determinations were performed by using a Gallenkamp melting point apparatus.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) were recorded on Bruker AV400 spectrometer; chemical shifts ( $\delta$ ) are expressed in parts per million (ppm) downfield from TMS ( $\delta$  0.0) and relative to the signal of  $\text{CDCl}_3$  (i.e.,  $\delta$  7.26 (singlet) and  $\delta$  77.0 (triplet) for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, respectively. Coupling constants are given in hertz (Hz). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dt (doublet of triplet), m (multiplet), br (broad). Infrared spectra were recorded in a Shimadzu Prestige 21 FTIR. UV-Vis spectra were obtained on a Thermo Scientific Evolution 220 instrument. MALDI-TOF-MS were recorded on Buker Multiflex LT spectrometer using  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) as the matrix. Chemical ionization mass spectra ( $^+$ ve mode) ( $\text{CI}^+$ -MS) were performed on a Finnigan-MAT TSQ70 with isobutane as the reactant gas. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400;



the samples were kept under vacuum (0.001 hPa) at 60°C for 3 h before subsequent elemental analysis.

**10,11-Dihydro-5-acetyl-5H-dibenzo[*b,f*]azepine (7).** A solution of 10,11-dihydro-5H-dibenzo[*b,f*]azepine **5** (2.50 g, 12.8 mmol) in acetic anhydride (8 mL) was refluxed for 3h under stirring. The formation of the product was controlled via GC-MS. When the reaction was complete the mixture was dropped into water, extracted with AcOEt and dried in vacuo to give **7** (2.88 g, 95 %) as white solid. The spectroscopic data were in accordance with those reported in the literature.<sup>35</sup>

**5H-Dibenzo[*b,f*]azepine-10,11-dione (3).** Oxcarbazepine (**2**, 5.0 g, 19.82 mmol) and SeO<sub>2</sub> (5.4 g, 48.67 mmol) in dioxane (100 mL) were brought to reflux under vigorous stirring for 7 h. The reaction progress was monitored by TLC analysis (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOH 95:5, *R<sub>f</sub>* **1** = 0.27, *R<sub>f</sub>* **3** = 0.56). After cooling to r.t. the orange precipitate was filtered and dried under vacuum to afford **3** (4.0 g, 90%): the spectroscopic data were in accordance with those reported in the literature.<sup>17</sup>

**5H-Dibenzo[*b,f*]azepine-10,11-dione (3).** A suspension of **7** (300 mg, 1.26 mmol) and benzeneseleninic anhydride (910 mg, 2.52 mmol) in chlorobenzene (5 mL) was refluxed for 8 h, under vigorous stirring. The precipitate was filtered, washed with chlorobenzene (2 mL), Et<sub>2</sub>O (4 mL) and dried in vacuum to afford **3** (200 mg, 68%). The spectroscopic data were in accordance with those reported in the literature.<sup>17</sup>

**9H-Dibenzo[*b,f*]pyrazino[2,3-*d*]azepine-2,3-dicarbonitrile (4).** Compound **3** (100 mg, 0.45 mmol) and diaminomaleonitrile (49 mg, 0.45 mmol) in AcOH (2 mL) were refluxed for 1 h under stirring. The reaction progress was monitored by TLC analysis (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOH 19:1, *R<sub>f</sub>* **3**: 0.54, *R<sub>f</sub>* **4**: 0.73). The reaction mixture was left cooling to r.t., the precipitate was collected by filtration and dried under vacuum to afford **4** (86 mg, 65%) as red solid. The spectroscopic data were in accordance with those reported in the literature.<sup>14</sup>

**9-Hexadecanoyl-9H-dibenzo[*b,f*]pyrazino[2,3-*d*]azepine-2,3-dicarbonitrile (9).** A solution of **4** (950 mg, 3.22 mmol) and hexadecanoyl chloride (1.51 mL, 5.0 mmol) in pyridine (4 mL) was stirred for 10 min at room temperature in the presence of 4-*N,N*-dimethylaminopyridine (122 mg, 1.0 mmol) and then refluxed for 6 h. The mixture was then poured into ice-water, acidified with 5% HCl and extracted with AcOEt (3 x 50 mL). The organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed under reduced pressure. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, *R<sub>f</sub>* 0.15) afforded **9** (1.28 g, 75%) as a reddish glass. IR (KBr) cm<sup>-1</sup>: 2232 (C≡N), 1670 (C=O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07 (d, *J* 7.4 Hz, 2H), 7.72 (d, *J* 7.4 Hz, 2H), 7.61-7.49 (m, 4H), 2.25 (t, *J* 7.0 Hz, 2H), 1.70-1.20 (m, 26H), 0.90 (t, *J* 7.0 Hz 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 173.1, 144.5, 144.1, 133.6, 132.8, 132.4, 129.6, 128.9, 128.3, 113.4, 34.3, 34.2, 32.3, 30.1, 30.0, 30.0, 29.9, 29.8, 29.6, 29.5, 25.3, 25.1, 23.1, 14.5; MS (ESI): *m/z* 534 ([M+H]<sup>+</sup>); Anal. Calcd. for C<sub>34</sub>H<sub>39</sub>N<sub>5</sub>O: C, 76.52; H, 7.37; N, 13.12. Found: C, 76.38; H, 7.45; N, 13.41.

**Tetrakis-2,3-{9-hexadecanoyl-9H-dibenzo[*b,f*]pyrazino[2,3-*d*]azepine}porphyrzinatomagnesium(II) (10).** Magnesium (13 mg, 0.56 mmol), a small crystal of I<sub>2</sub> and 1-butanol (5 mL) were heated to reflux under N<sub>2</sub> for 6 h. After the mixture was cooled to room temperature dinitrile **9**

(75 mg, 0.14 mmol) was added and the solution refluxed for further 8 h. The reaction progress was monitored by TLC analysis (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 19:1, R<sub>f</sub> **10**: 0.28). After being allowed to cool to room temperature the dark green mixture was evaporated with toluene (3 x 5 mL). The mixture was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and filtered through Celite. Evaporation of the solvent gave a green residue which was purified by flash column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 19:1) to afford **10** (24 mg, 32%) as a green powder. mp >200 °C; UV-Vis (THF, c 1·10<sup>-5</sup> mol dm<sup>-3</sup>) λ<sub>max</sub> (ε): 376 (70200), 598 (16600), 660 (132300) nm (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); IR (KBr) cm<sup>-1</sup>: 1668, 1454, 1350, 1253, 1182, 1101, 947, 801, 748; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.25-7.42 (br, 32H), 2.45-2.23 (br, 8H), 1.70-0.75 (br, 116H); MS (MALDI-TOF): *m/z* 2158.4; Anal. Calcd. for C<sub>136</sub>H<sub>156</sub>MgN<sub>20</sub>O<sub>4</sub>: C, 75.65; H, 7.28; N, 12.97. Found: C, 75.32; H, 7.57; N, 13.21.

**Tetrakis-2,3-{9-hexadecanoyl-9H-dibenzo[*b,f*]pyrazino[2,3-*d*]azepine}porphyrazinatocopper(II) (**11**).** A mixture of dinitrile **9** (200 mg, 0.37 mmol) and anhydrous Cu(OAc)<sub>2</sub> (33 mg, 0.18 mmol) in freshly distilled 2-(dimethylamino)ethanol (DMAE) (5 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 mL) was irradiated in a 10-mL quartz vessel (equipped with a Teflon septum and a magnetic stir bar) by a microwave oven at 300W/175°C for 10 min. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and filtered off. The dark green product was purified by silica gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 19:1) to give **11** (138 mg, 67%) as green powder. mp >200 °C; UV-Vis (THF, c 1·10<sup>-5</sup> mol dm<sup>-3</sup>): λ<sub>max</sub> (ε) 378 (62300), 599 (13200), 660 (115600) nm (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); IR (KBr) cm<sup>-1</sup>: 1671, 1456, 1347, 1251, 1184, 1103, 948, 801, 749; MS (MALDI-TOF): *m/z* 2197.3; Anal. Calcd. for C<sub>136</sub>H<sub>156</sub>CuN<sub>20</sub>O<sub>4</sub>: C, 74.30; H, 7.15; N, 12.74. Found: C, 74.48; H, 7.26; N, 12.97.

**Tetrakis-2,3-{9-hexadecanoyl-9H-dibenzo[*b,f*]pyrazino[2,3-*d*]azepine}porphyrzinatocobalt(II) (**12**).** A mixture of dinitrile **9** (200 mg, 0.37 mmol) and anhydrous Co(OAc)<sub>2</sub> (33 mg, 0.19 mmol) in freshly distilled 2-(dimethylamino)ethanol (DMAE) (5 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 mL) was irradiated in a 10-mL quartz vessel (equipped with a Teflon septum and a magnetic stir bar) by a microwave oven at 300W/175°C for 10 min. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and filtered off. The dark green product was purified by silica gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 19:1) to give **12** (148 mg, 72%) as dark green powder. mp >200 °C; UV-Vis (THF, c 1·10<sup>-5</sup> mol dm<sup>-3</sup>): λ<sub>max</sub> (ε) 377 (63500), 597 (13600), 658 (118300) nm (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); IR (KBr) cm<sup>-1</sup>: 1670, 1455, 1350, 1253, 1183, 1099, 949, 802, 748; MS (MALDI-TOF): *m/z* 2193.4; Anal. Calcd. for C<sub>136</sub>H<sub>156</sub>CoN<sub>20</sub>O<sub>4</sub>: C, 74.46; H, 7.17; N, 12.77. Found: C, 74.39; H, 7.33; N, 13.06.

**X-ray Crystallographic Analysis.** Crystals of suitable quality of compound **8** (C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub>) were obtained by slow evaporation of an EtOH solution. Diffraction data were collected at r.t. on a Enraf Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ 0.71073 Å). Generator settings: 50 kV, 30 mA). Lorentz-polarization correction was applied. The structure was solved by direct methods (SIR92)<sup>36</sup> and expanded using Fourier techniques

(SHELX97).<sup>37</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the final model and freely refined. The final cycles of full-matrix least-squares refinements were based on  $F^2$ . All calculations were performed using the WINGX Crystallographic Software Suite.<sup>38</sup> CCDC deposition number 987293. An ORTEP drawing of the molecule of **8** is shown in Figure 1. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Crystal data for Compound **8**:  $C_{16}H_{11}NO_2$ , f.w. = 249.26  $g\ mol^{-1}$ , 293 K,  $\lambda = 0.71073\ \text{\AA}$ , monoclinic, space group  $P2_1/n$ ,  $a = 7.350(2)$ ,  $b = 20.834(3)$ ,  $c = 8.576(3)\ \text{\AA}$ ,  $\beta = 114.51(2)^\circ$ ,  $V = 1194.9(6)\ \text{\AA}^3$ ,  $Z = 4$ ,  $\rho_{calc} = 1.386\ g\ cm^{-3}$ ,  $\mu\ (Cu\ K\alpha) = 0.092\ mm^{-1}$ ,  $R1 = 0.0437$  for 1518 observed reflections with  $F_o > 4\sigma(F_o)$ ,  $wR2 = 0.1047$  for all 2165 reflections;  $Gof = 1.030$ ,  $2\theta$  range: 3-25.3°.

**General procedure for catalytic cyclopropanation.** A solution of ethyl diazoacetate (EDA) (5.0 mmol in 10 mL of  $CH_2Cl_2$ ) was added slowly under stirring to a refluxing  $CH_2Cl_2$  solution (0.2 M) consisting of alkene (12.5 mmol) and **11** or **12** (0.005 mmol). The reaction was halted when no trace of EDA [ $\nu_{N=N}\ 2110\ cm^{-1}$ ] was detected in the IR spectrum of the mixture. Yields and diastereomeric ratio were obtained by GC-MS and  $^1H$  NMR using examethylbenzene as internal standard.

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