Imidazolium bromide substituted magnesium phthalocyanine polymers: New promising materials for CO_2 conversion

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ABSTRACT

The conversion of CO_2 with epoxides into the corresponding cyclic carbonates represents a green approach to transform a waste into value-added products. To promote this conversion, a catalyst in needed. This study presents the synthesis of two cross-linked materials composed of magnesium phthalocyanine and imidazolium bromide moieties: MgPc-BIBI-Br and MgPc-SIBI-Br. Magnesium phthalocyanines are cost-effective and versatile catalysts, synthesized in high yield from low-cost precursors and can be easily modified for specific needs. Imidazolium bromide groups play a crucial role as well, acting as a nucleophile source essential to promote the ring-opening process of the epoxide. The materials have been extensively characterized through analytical and spectroscopic techniques and tested as catalysts in the conversion of epichlorohydrin into 4-chloromethyl-1,3-dioxalan-2-one. They both achieved excellent catalytic performance (maximal TON values of 3070 for MgPc-SIBI-Br and 1903 for MgPc-BIBI-Br) and recyclability (both recyclable at least for 4 cycles). The reported results represent an improvement if compared to similar materials already reported in the literature in which the addition of external nucleophilic species (e.g. TBAB, BMIM-Br, etc.) is needed. To the best of our knowledge, this work is the first example in which imidazolium bromide and magnesium phthalocyanine moieties are combined in bifunctional polymeric materials that convert CO_2 into cyclic carbonates via heterogeneous catalysis.

1. Introduction

In the current global energy landscape, one of the most pressing priorities is the utilization of alternative energy sources capable of matching with the energy output traditionally provided by fossil fuels. The key challenge is to do this without generating environmentally harmful waste byproducts, including greenhouse gases that contribute to global warming and broader atmospheric pollution [1–4]. Notably, carbon dioxide (CO_2) represents the most prolific waste generated from the utilization of fossil fuels and is the primary driver of global climatic alterations. In this scenario, both the temporal factor and the provision of conducive living conditions assume paramount significance in the endeavor to realize the aforementioned goals. Thus, an additional and likewise important objective involves the limitation and, where feasible, the remediation of damages stemming from the remaining utilization of

fossil fuel resources. A greener and sustainable perspective allows to consider CO_2 not only as waste, but rather as a low-priced, abundant, and sustainable C_1 resource for the production of value-added chemical products such as solvents or additives [5–8]. Among them, cyclic carbonates may find application as precursors in polymer production, additives in fuel formulations, constituents of electrolytes in batteries, and serve as aprotic high-boiling point solvents [9–11]. One established route for cyclic carbonate synthesis involves the cycloaddition of CO_2 with epoxides [12–23]. It is noteworthy that the conversion of CO_2 into cyclic carbonates aligns closely with several foundational principles of green chemistry, including waste-to-resource conversion, the attainment of 100 % atom economy, the feasibility of solvent-free conditions, and the utilization of catalysts [24]. However, due to the intrinsically stable and unreactive nature of CO_2, this transformation necessitates the use of efficient nucleophilic catalysts. Both heterogeneous and

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homogeneous catalysts have demonstrated the capacity to promote CO_2 conversion under mild conditions [25–31]. Yet, for sustainable applications, a preference emerges for heterogeneous ones, particularly those employing readily available, earth-abundant, and cost-effective metal co-catalytic species [32]. These nucleophiles facilitate the ring-opening process of epoxides, particularly when they possess a high degree of mobility within the reaction solvent, thereby enhancing their propensity to interact with the epoxydic substrate [33–36]. In light of this evidence, the utilization of nucleophilic catalytic species in a homogeneous phase may appear the most convenient alternative; however, this choice would involve more complexity in the product purification process, causing not only a higher consumption of resources, but also making very difficult to recycle the nucleophilic catalyst [27]. Therefore, a more convenient and sustainable [24] alternative entails the adoption of heterogeneous bifunctional catalysts, wherein both the metal center and nucleophilic species coexist within the same material framework [35–39]. This approach would facilitate its separation from the reaction mixture thus favoring the isolation of the final product. In our previous works [35,36, 39,40] we have extensively discussed the utilization of porphyrins for crafting such catalysts. An equally promising alternative involves the use of phthalocyanines: this bioinspired class of compounds shares a structural resemblance with porphyrins, yet their merit in catalytic applications extends beyond mere structural affinity. Metal-Phthalocyanine complexes (**M-Pc**) are notable for their accessibility in terms of precursor cost, facile large-scale synthesis, and robust chemical and thermal stability, also resulting in minimal metal leaching [41–51]. These features render **M-Pc** highly suitable candidates for the design of heterogeneous bifunctional materials which find many applications in different catalytic contexts, such as thermocatalytic,

photocatalytic or electrocatalytic ones [40,52–54], aligning with the objectives outlined above. The purpose of this study is to demonstrate the efficacy of amorphous highly cross-linked copolymers which incorporate magnesium-phthalocyanine (**MgPc**) and imidazolium bromide (**ImiBr**) components as constituents for the development of bifunctional catalysts employed in the conversion of CO_2 into cyclic carbonates. We chose a phthalocyanine tetrasubstituted with imidazole moieties with magnesium as metal center (**MgPc-Im$_4$**), since this metal is inexpensive, nontoxic, and easily available. The decision to incorporate **ImiBr** moieties into the molecular-level catalyst design arises from our research background [55–59] underscoring the crucial role of bromide ions of an imidazolium salt system in expediting CO_2 conversion: these bromide counterions, serve as excellent functional promoters, facilitating the opening of epoxide rings and, subsequently, the insertion of CO_2. Starting from **MgPc-Im$_4$** as the common building block, preliminary catalysts for the conversion of CO_2 into cyclic carbonates have been synthesized both in a homogeneous version (**MgPc-(Imi-Bu)$_4$Br$_4$**) and in a heterogeneous counterpart (**Poly-MgPc-(Imi-Bu)$_4$Br$_4$**), (Fig. 1). In light of the first catalytic dataset results obtained, we decided to improve the morphology of these bifunctional materials, so as to have more efficient catalysts. The new design process was aimed to maximize the ratio between the nucleophilic catalyst (Br⁻) and the Lewis acid metallic active site (Mg) within each individual monomer unit, resulting in the development of two novel materials, **MgPc-BIBI-Br** and **MgPc-SIBI-Br** (Fig. 1).

Following their characterization, a comprehensive evaluation of their catalytic performance ensued, covering key aspects like recyclability, versatility, and turnover numbers has been carried out. The outcomes were promising, demonstrating robust conversion values and
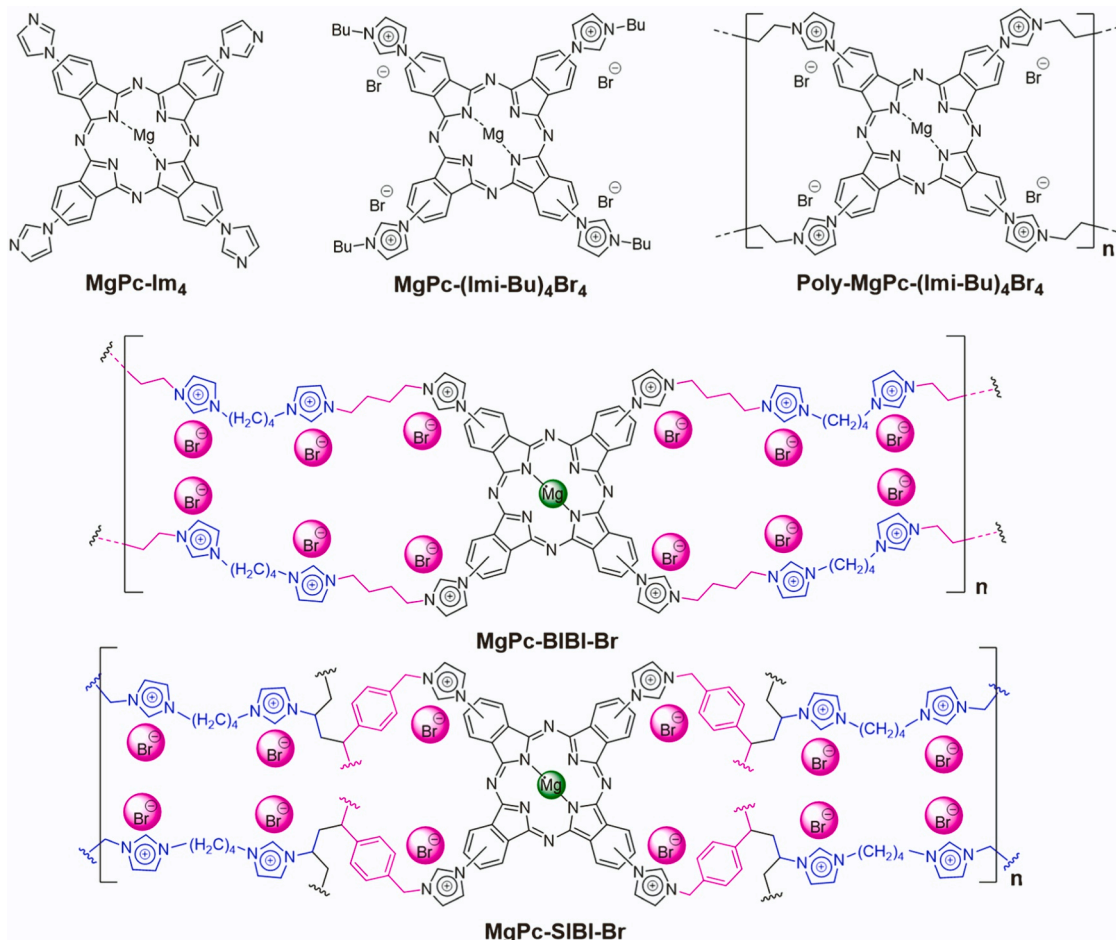

Fig. 1. Proposed base units for **MgPc-Im$_4$**, **MgPc-(Imi-Bu)$_4$Br$_4$**, **Poly-MgPc-(Imi-Bu)$_4$Br$_4$**, **MgPc-BIBI-Br** and **MgPc-SIBI-Br**.

notable selectivity for cyclic carbonates. Notably, these reactions were conducted in a batch reactor, affording operation under both CO_2 pressures, and temperatures applied in the industrial context, so making easier a hypothetical scale up of the studied process.

2. Materials and methods

Chemicals and solvents were purchased from commercial suppliers and were used without further purification. The syntheses of 1,1′-(butane-1,4-diyl)bis(3-vinyl-1*H*-imidazol-3-ium) bromide, 1,4-di(1*H*-imidazol-1-yl)butane, 1-(bromomethyl)-4-vinylbenzene and Homopolymer (**13**) are reported in the Supporting Information section (Exp. 1–4; Figures S1-S3). Transmission electron microscopy/energy-dispersive X-ray spectroscopy (TEM/EDX) images were obtained using a Philips Tecnai 10 microscope operating at 80 kV. The samples were prepared by dispersion of a small quantity of the material in absolute ethanol and deposited into a copper grid. Analyses of X-ray photoelectron spectroscopy (XPS) were conducted using a ThermoFisher ESCALAB 250Xi instrument equipped with a monochromatic Al Kα X-ray source (1486.6 eV) and a hemispherical deflector analyzer (SDA) operating at constant pass energy (CAE). The experiments utilized a 200 μm diameter X-ray spot. Sample charge neutralization was achieved using a flood gun with low energy electrons and argon ions. The analysis chamber pressure was maintained at approximately 10^{-8} Torr during data collection. Survey spectra were recorded with a pass energy of 200 eV, while high-resolution spectra were collected at 50 eV pass energy. Peak analyses were performed using Thermo Avantage software, employing a non-linear least squares fitting program with a weighted sum of Lorentzian and Gaussian components. Background subtraction followed the methods of Shirley and Sherwood. Inductively coupled plasma optical emission spectroscopy (ICP-OES) were performed in an Optima 8000 ICP-OES spectrometer. Thermogravimetric analysis was performed under nitrogen flow from 25 to 900 ºC with a heating rate of 10 ºC/min in a Mettler Toledo TGA STAR system. Chemical combustion analysis was performed on a Perkin-Elmer 2400 Serie 2 analyzer. ^{1}H- and ^{13}C NMR liquid-state spectra were recorded at room temperature on a JEOL ECX 400 MHz spectrometer, operating at 9.4 T and equipped with a broadband 5 mm probe. Solid state ^{13}C NMR spectra were recorded at room temperature on a JEOL ECZ-R 600 MHz spectrometer operating at 14.1 T, using a 3.2 mm AUTOMAS probe and spinning frequencies of 10 kHz. SS ^{13}C CP-MAS NMR spectra showed in this work were processed using Mestrenova software: apodization with a line broadening of 60 Hz, phase and baseline correction.

2.1. Synthesis of 4-(1 H-imidazol-1-yl)phthalonitrile (2)

4-Nitrophthalonitrile (14.8 g, 85.6 mmol, 1 eq), imidazole (7.3 g, 107.2 mmol, 1.25 eq) and anhydrous K_2CO_3 (59.2 g, 428 mmol, 5 eq) were solubilized in 225 mL of anhydrous DMF under argon atmosphere, and the so obtained suspension was sonicated overnight. Thereafter, once the reaction mixture has been cooled down to room temperature, the excess of K_2CO_3 was filtered off, and the filtrate was diluted with 2.25 L of cold water. The resulting mixture was left at room temperature for 1 h, then the precipitate was filtered, washed with water and recrystallized by refluxing in EtOH (250 mL) until complete dissolution of the solid. As soon this dissolution has been achieved, the solution was left to slowly cool down at room temperature, avoiding excessive agitation. After one night, 7.49 g of 4-(1 H-imidazol-1-yl)phthalonitrile (**2**) were obtained as light brown needles. The filtrate of crystallization was evaporated, and the resulting solid was recrystallized in the minimum amount of EtOH to afford 5.8 g more of compound **2**, then giving 13.3 g of a light brown thin crystals (80 % yield)

^{1}H NMR (400 MHz, DMSO-D6) δ 8.11 (ddd, J = 8.6, 2.2, 0.8 Hz, 2H), 7.81 (dq, J = 8.6, 1.4 Hz, 2H), 7.53 (t, J = 1.4 Hz, 1H), 6.71 (dd, J = 1.5, 0.8 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-D6) δ 140.82, 136.60, 136.30, 131.51, 125.03, 124.62, 118.20, 117.05, 116.21, 115.98, 112.29.

2.2. Synthesis of MgPc-Im₄ (3)

Compound **2** (1.62 g, 8.35 mmol, 1 eq), Mg in turnings (97 mg, 4.17 mmol, 0.5 eq) and I_2 (54 mg, 209 μmol, 2.5 mol%) were suspended in dry *n*-pentanol (16 mL) under argon atmosphere in a flame-dried 100 mL test tube, and the mixture was stirred at 135°C for 36 h. Then the mixture was cooled to room temperature, diluted with acetone (200 mL), and the resulting precipitate was filtered, washed three times with acetone, and stirred overnight at room temperature in 300 mL of water in order to remove the excess of metallic Mg eventually present in the precipitate. The solid suspension has been filtered, washed with water followed by acetone, and finally washed overnight with EtOH in a Soxhlet apparatus. Thereafter, the powder was dried at 60°C overnight to afford 1.39 g of pure magnesium tetra(imidazole-1-yl)phthalocyanine (**MgPcIm₄**) (mixture of isomers, Figure S4) as a blue/purple powder with 83 % yield

^{1}H NMR (400 MHz, DMSO-D6) δ 9.36 – 8.56 (m, 12H), 8.25 (m, 8H), 7.40 (m, 4H).

^{13}C NMR (100 MHz, DMSO-D6) δ 151.84, 139.29, 137.94, 136.86, 136.00, 130.92, 123.67, 121.74, 119.32, 113.58.

2.3. Synthesis of MgPc-(Imi-Bu)₄Br₄ (4)

To a solution of **MgPcIm₄** (200 mg) in anhydrous DMF (2.5 mL) was added 1-bromobutane (5.0 eq) and the mixture was stirred at 110°C overnight. After cooling the mixture to room temperature, it was diluted with acetone (30 mL) and the resulting precipitate was sonicated, filtered and washed with acetone to afford the desired quaternarized magnesium tetra(3-butylimidazolium-1-yl)phthalocyanine

^{1}H NMR (500 MHz,) δ 10.50 – 10.33 (m, 4H), 9.89 (m, 4H), 9.80 – 9.53 (m, 4H), 8.97 – 8.78 (m, 4H), 8.78 – 8.62 (m, 4H), 8.35 – 8.24 (m, 4H), 4.55 – 4.31 (m, 8H), 2.04 (m, 8H), 1.57 – 1.32 (m, 8H), 1.08 – 0.96 (m, 12H).

2.4. Synthesis of Poly-MgPc-(Imi-Bu)₄Br₄ (5)

To a suspension of **MgPcIm₄** (200 mg) in anhydrous DMF (2.5 mL) was added 1,4-dibromobutane (2.0 eq) and the mixture was stirred at 110°C overnight. After cooling the mixture to room temperature, it was diluted with acetone (30 mL) and the resulting precipitate was sonicated, centrifuged, and the solvent was removed. This washing procedure was repeated one time with acetone and one time with methanol to afford the desired cross-linked magnesium tetra(Imidazole-1-yl) phthalocyanine (**Poly-MgPc-(Imi-Bu)₄Br)₄**)

2.5. Synthesis of MgPc-BIBI-Br (8)

MgPcIm₄ (0.3 g, 0.374 mmol) and 1,4-di(1*H*-imidazol-1-yl)butane (0.31 g, 1.65 mmol) were added under argon atmosphere into a flame-dried 100 mL test tube and then solubilized in 12.5 mL of anhydrous DMF. Subsequently, 1,4-dibromobutane (0.81 g, 3.74 mmol) was added dropwise to the solution so as to obtain a reaction mixture which was left to stir at 110°C overnight. Once this mixture has cooled down to room temperature, the presence of a dark blue solid has been observed; this solid was filtered, washed twice with hot water, twice with hot methanol, three times with acetone, and finally dried at 60°C overnight to obtain 1.3 g of **MgPc-Imi₄(But-Bis Imi)₄** as a spongy solid.

2.6. Synthesis of MgPc(Imi-Stiryl)₄Br₄ (11)

4-Vinyl benzyl bromide (0.59 g, 3 mmol) and **MgPcIm₄** (0.5 g, 0.62 mmol) were added together in a 50 mL round bottom flask under Ar atmosphere, and then solubilized in 30 mL of anhydrous DMF. The resulting reaction mixture was left to stir overnight at 70°C. Subsequently, the solution was cool down to room temperature and then filtered to collect a peacock blue-colored precipitate which has been washed two times with DMF and five times with acetone. After a drying time of 8 h at 60°C, 0.96 g of pure **MgPc(Imi-Stiryl)₄Br₄** (mixture of isomers) were obtained, with 96 % yield.

^{1}H NMR (400 MHz, DMSO) δ 10.77 – 10.53 (m, 4H), 9.96 – 9.48 (m, 8H), 8.97 – 8.70 (m, 8H), 8.31 (s, 4H), 7.81 – 7.48 (m, 16H), 6.81 (ddd, J = 17.3, 11.0, 6.2 Hz, 4H), 5.94 (dd, J = 17.3, 7.0 Hz, 4H), 5.73 (d, J = 3.7 Hz, 8H), 5.36 (dd,17.3 Hz, 7.0 Hz, 4H).

2.7. Synthesis of MgPc-SIBI-Br (12)

MgPc(Imi-Stiryl)₄Br₄ (0.2 g, 0.13 mmol) and 1,1′-(butane-1,4-diyl) bis(3-vinyl-1*H*-imidazol-3-ium) bromide (0.23 g, 0.55 mmol) were added under Ar atmosphere into a 25 mL double-necked round bottom flask and then solubilized with 5 mL of anhydrous DMF. The so obtained solution was sonicated and purged with argon for 20 min in order to maximize this solubilization process. Thereafter, freshly recrystallized AIBN (0.02 g, 0.13 mmol) was added into the flask, and the resulting reaction mixture was left to stir at 110°C overnight. Once this mixture has cooled down to room temperature, the presence of a cerulean blue colored solid has been observed; this solid was filtered, washed twice with hot water, twice with hot methanol, three times with acetone, and finally dried at 60°C overnight to obtain 0.4 g of **MgPc-Imi₄(Stiryl-But-Bis Imi)₄** with a 90 % ca. yield in weight.

3. Catalytic experiments

Catalytic experiments were performed in a Cambridge Design Bullfrog batch reactor with temperature control and mechanical stirring (see Figure S5). In this reactor, also pressure can be monitored. Before each experiment, the material was dried overnight in a vacuum oven at 60 ºC. In each test, the catalyst was added to 24 mL of epoxide in a Teflon vial under solvent free conditions. After closing the reactor, the mixture was stirred at 500 rpm. The system was then purged for 10 min with N_2 before the addition of 25 bar of CO_2. After this, the system was heated to the required temperature with a rate of 5 ºC/min. The reaction mixture was kept to the required temperature during the reaction time. When needed a refill of CO_2 was performed during the experiment to preserve the amount of reactant required for the reaction. In any case the pressure of CO_2 added overpasses the initial pressure reached at the temperature of the experiment. After this time, the reactor was cooled down to room temperature and then it was depressurized. The catalyst was separated from the reaction mixture *via* Millipore (0.45 μm pore size) filtration, and the filtrate was analyzed by ^{1}H NMR in $(CD_3)_2SO$.
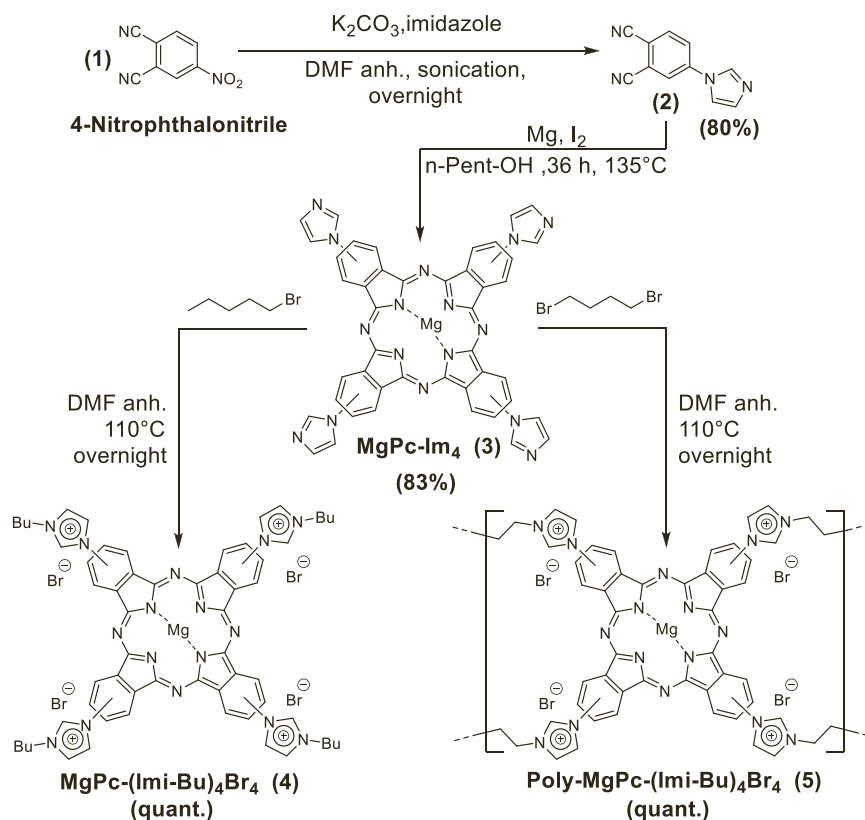
4. Recycling tests

Recycling tests were carried out in the reaction of epichlorohydrin with CO_2. At the end of the reaction, the material was recovered *via* Millipore (0.45 μm pore size) filtration and washed three times with 50 mL of toluene, three times with 50 mL of ethanol and one time with diethyl ether. Then, before the next cycle, the catalyst was dried overnight in a vacuum oven at 60 ºC. After drying, the catalyst was reused for the next cycle taking care of maintaining the same ratio between moles of catalyst and moles of epoxides for each cycle.

5. Results and discussion

Our initial goal entailed the synthesis of a magnesium phthalocyanine complex endowed with four imidazolium moieties which was used as the main building block for the preparation of the materials developed in this work. The synthesis of the magnesium phthalocyanine monomer (**MgPc-Im₄**) was carried out following a commonly used synthetic pathway for substituted metal phthalocyanines (Scheme 1) [54]. The first step involved the introduction of the imidazole moiety on the commercially available 4-nitrophthalonitrile **1** under overnight sonication to obtain the 4-(1*H*-imidazol-1-yl)phthalonitrile **2** in good purity and yield as demonstrated by spectroscopic results shown in ^{1}H NMR (Figure S6) and ^{13}C NMR (Figure S7) spectra. The formation of the phthalocyanine moiety was performed reacting **2** in presence of solid magnesium and a catalytic amount of iodine giving the desired magnesium phthalocyanine **3** as a mixture of isomers in both a very good purity and yield (83 %, see Scheme 1) [60], as shown by ^{1}H NMR (Figure S8) and ^{13}C NMR (Figure S9) spectra. Then the quaternarization of the four imidazole moieties was performed with 1-bromobutane or 1, 4-dibromobutane to afford, respectively, the phthalocyanine **MgPc-(Imi-Bu)₄Br₄ (4)** and the material **Poly-MgPc-(Imi-Bu)₄Br₄ (5)**, in quantitative yield and optimal purity as illustrated in the corresponding spectra: ^{1}H NMR (Figure S10), and ss^{13}C-CP-MAS NMR (Figure S11) for **Poly-MgPc-(Imi-Bu)₄Br₄ (5)**

Once characterized (Figures S12, S13, Tables S1, S2), both **MgPc-(Imi-Bu)₄Br₄** and **Poly-MgPc-(Imi-Bu)₄Br₄** were tested as bifunctional catalysts for the conversion of CO_2 into cyclic carbonates using epichlorohydrin as epoxide. The catalytic efficiency was expressed in terms of turnover numbers (TONs, moles of product obtained divided by moles of active sites – Mg or Br⁻), and turnover frequencies (TOFs, TON/ reaction time in hours). The experimental results (Table 1) revealed that, as expected, the homogeneous catalyst, **MgPc-(Imi-Bu)₄Br₄**, exhibits a superior catalytic activity compared to its reticulated heterogeneous version **Poly-MgPc-(Imi-Bu)₄Br₄** (entries 1 and 2); however, all the advantages related to heterogeneous catalysis should not be underestimated. Furthermore, a dedicated test was conducted wherein the sole catalytic species employed was 1-butyl-3-methylimidazolium bromide (**BMIM-Br**) (entry 3), the phthalocyanine **MgPc-Im₄ (3)** (entry 4), and also an entire homogeneous combination of these last two components (entry 7). The high conversions achieved with this last catalytic test underlines the importance of the presence of both catalyst and co-catalyst in the reaction mixture [33–36]. However, the catalytic performances of both **MgPc-(Imi-Bu)₄Br₄** and **Poly-MgPc-(Imi-Bu)₄Br₄** was not excellent if compared with other bifunctional materials [36]. A possible explanation of the minor catalytic activity could be related to the low Br⁻/Mg ratio (Table 1).

To confirm this hypothesis, two additional catalytic tests with a bicomponent system were performed (entries 5 and 6): catalysts were employed in tandem with the addition of **BMIM-Br** in homogeneous phase. This addition was intended to augment the nucleophile/Lewis acid (Br⁻/Mg) ratio up to a value of 10.5 within the catalytic system. This higher value is comparable with the Br⁻/Mg ratio used in other similar studies [59]. The main intent was to investigate the correlation between the Br⁻/Mg ratio and the catalytic performances (Table 1). As clearly indicated in Table 1, when the Br⁻/Mg ratio was increased to 10.5 a significant enhancement was observed in the conversion of epichlorohydrin into its corresponding cyclic carbonate. This dataset, suggests that, under the same conditions, a catalytic system with a higher Br⁻/Mg ratio yields enhanced conversion than a system where the mentioned ratio is lower. Moreover, it is evident that, when the Lewis acid (magnesium) and the nucleophile (bromide) operate in synergy in the reaction mixture, higher conversions are obtained. These results indicate that the two components cooperate in the synergistic way described in Fig. 2. The mechanism leading to the synthesis of cyclic carbonates from epoxides and CO_2 has been extensively reported. Moreover, the importance of the proximity between Lewis acid centers and nucleophiles has

K_2CO_3, imidazole

DMF anh., sonication, overnight

4-Nitrophthalonitrile (1)

(2) (80%)

Mg, I_2

n-Pent-OH, 36 h, 135°C

MgPc-Im_4 (3)
(83%)

DMF anh.
110°C
overnight

DMF anh.
110°C
overnight

MgPc-(Imi-Bu)_4Br_4 (4)
(quant.)

Poly-MgPc-(Imi-Bu)_4Br_4 (5)
(quant.)

Scheme 1. Synthetic procedure for the preparation of MgPc-Im_4 (3), MgPc-(Imi-Bu)_4Br_4 (4) and Poly-MgPc-(Imi-Bu)_4Br_4 (5).

Table 1

Synthesis of 4-chloromethyl-1,3-dioxalan-2-one catalyzed by **3–5** and their combination with **BMIm-Br**.

CO_2 (25 bar)
cat.

100°C, 3h
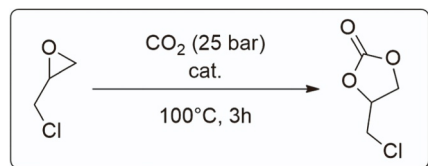
Entry	Catalyst	Br⁻/Mg ratio[a,b,c]	Conv. (%)	Selectivity[g] (%)	TON (Mg)	TON (Br)	TOF (Mg)	TOF (Br)
1	4[a,b]	4	29	>99	1966	492	655	164
2	5[a,b]	4	19	>99	1195	299	398	97
3	**BMIM-Br**[c]	-	10	>99	-	153	-	51
4	3[a]	-	3	>99	184	-	61	-
5	4[a,b]+**BMIM-Br**[d]	10.5	80	>99	5520	525	1840	175
6	5[a,b]+**BMIM-Br**[d]	10.5	68	>99	4330	410	1440	140
7	3[a,b,f]+**BMIM-Br**[e]	10.5	71	>99	4940	470	1650	160

Reaction conditions: epichlorohydrin 306 mmol, 60 mg cat.
[a] Mg content (calculated via ICP-OES analysis, Table S1).
[b] Br⁻ content already present in the catalyst.
[c] 43 mg of BMIM-Br.
[d] 63 mg of BMIM-Br.
[e] 102 mg of BMIM-Br.
[f] 36 mg of catalyst. Conversion values have been estimated via ^{1}H NMR (Figures S14-S20).
[g] Selectivity towards the 4-chloromethyl-1,3-dioxalan-2-one product.

already been widely demonstrated in the literature, including via computational investigations conducted by us in a recent work [35,36, 59]: the epoxide coordinates on the magnesium atom, making itself more available to nucleophilic attack by the bromide ion. A first intermediate is thus formed which reacts with CO_2 to give a second intermediate whose closure leads to the formation of the cyclic carbonate and the release of the bromide ion (Fig. 2).

Based on these premises, we decided to design two heterogeneous bifunctional catalysts using monomeric units wherein each magnesium center was accompanied by the maximum number possible of bromide ions, with the specific objective of increasing the Br⁻/Mg ratio. Two different materials, **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)** were prepared (Scheme 2). In both cases **MgPcIm_4 (3)** was employed as the starting molecule of choice: **MgPc-BIBI-Br (8)** has been obtained
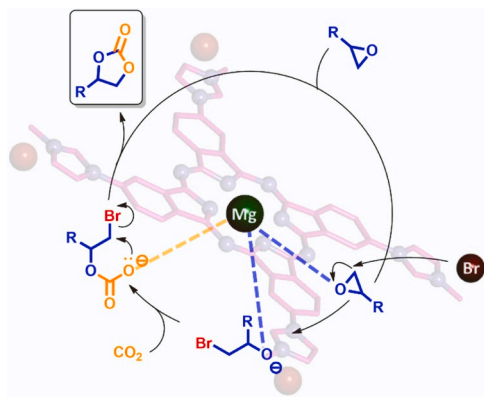
Fig. 2. Representation of the synergy between the Lewis acid magnesium phthalocyanine and the imidazolium bromide in the synthesis of cyclic carbonates in bifunctional systems containing **Mg-Pc** and **Imi-Br**.

through a random poly-nucleophilic substitution involving **MgPcIm₄ (3)**, **6** and **7**; while for the synthesis of **MgPc-SIBI-Br (12)**, the building block **MgPcIm₄ (3)** was pre-functionalized with **9** to obtain **MgPc-(Imi Stiryl)₄Br₄ (11)** in both good yield and purity as demonstrated by ^{1}H NMR (Figure S21). **11**, subsequently, underwent a random radical polymerization in combination with **10** to give **12**.

TEM micrographs evidenced that both **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)** display an amorphous nanometric-scale arrangement (Fig. 3) as a consequence of the densely branched molecular structure. Moreover, EDX analysis performed via TEM, showed that these materials exhibit a homogeneous distribution of their elementary components and therefore a homogeneous distribution of their active sites (Figures S22, S23).

Solid state cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (CP-MAS ^{13}C NMR) spectroscopy gave information

regarding the structure of **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)**: distinctive signals were observed, corresponding to the resonance of carbon atoms within the core structure of phthalocyanine and the imidazolium moieties, all detectable within the 115–150 ppm range. Additionally, signals attributed to aliphatic carbon atoms were spotted in the upfield region of the spectra, ranging from 20 to 60 ppm (Fig. 4). In the case of **MgPc-SIBI-Br (12)**, to remark the success of the polymerization process, it is noteworthy that there are no significant signals observed in the 100–115 ppm range, which is where carbon atoms from the vinyl groups typically resonate.

Thermogravimetric analysis (TGA) conducted on **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)** under air flow was employed to evaluate their thermal stability (Fig. 5): initial weight losses observed around 272°C for **MgPc-BIBI-Br (8)** and 265°C for **MgPc-SIBI-Br (12)** are attributed to the degradation of imidazolium fractions. On the other hand, the weight losses corresponding to the degradation of the phthalocyanine core are observed at approximately 466°C for **MgPc-BIBI-Br (8)** and at 442°C for **MgPc-SIBI-Br (12)**. Such conclusions are consistent with the results obtained from the TGA analyses of **MgPc-(Imi-Bu)₄Br₄ (4)** and **Homopolymer (13)** (Figure S12) which have been synthesized as described in Scheme 2. Notably, the main weight loss recorded for this homopolymer occurs around 330°C, corresponding to the degradation of imidazolium moieties. In the case of **MgPc-(Imi-Bu)₄Br₄ (4)**, this degradation takes place at an inflection point of 288°C, while the degradation of the phthalocyanine core occurs at 471°C (Figure S12).

Mg content for materials **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)** has been determined *via* inductively coupled plasma - optical emission spectrometry (ICP-OES, Table S1). According to CHN analysis, for the sample of **MgPc-BIBI-Br (8)**, a total nitrogen content of 15.1 % was detected, while for the sample of **MgPc-SIBI-Br (12)** was found to be 12.5 % (Table S2). Both XPS survey spectra acquired for **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)** (Figure S24) confirmed the presence of Mg and Br arising from the phthalocyanine core and imidazolium moieties, respectively. The high-resolution XPS spectra of the N1s region of **MgPc-**
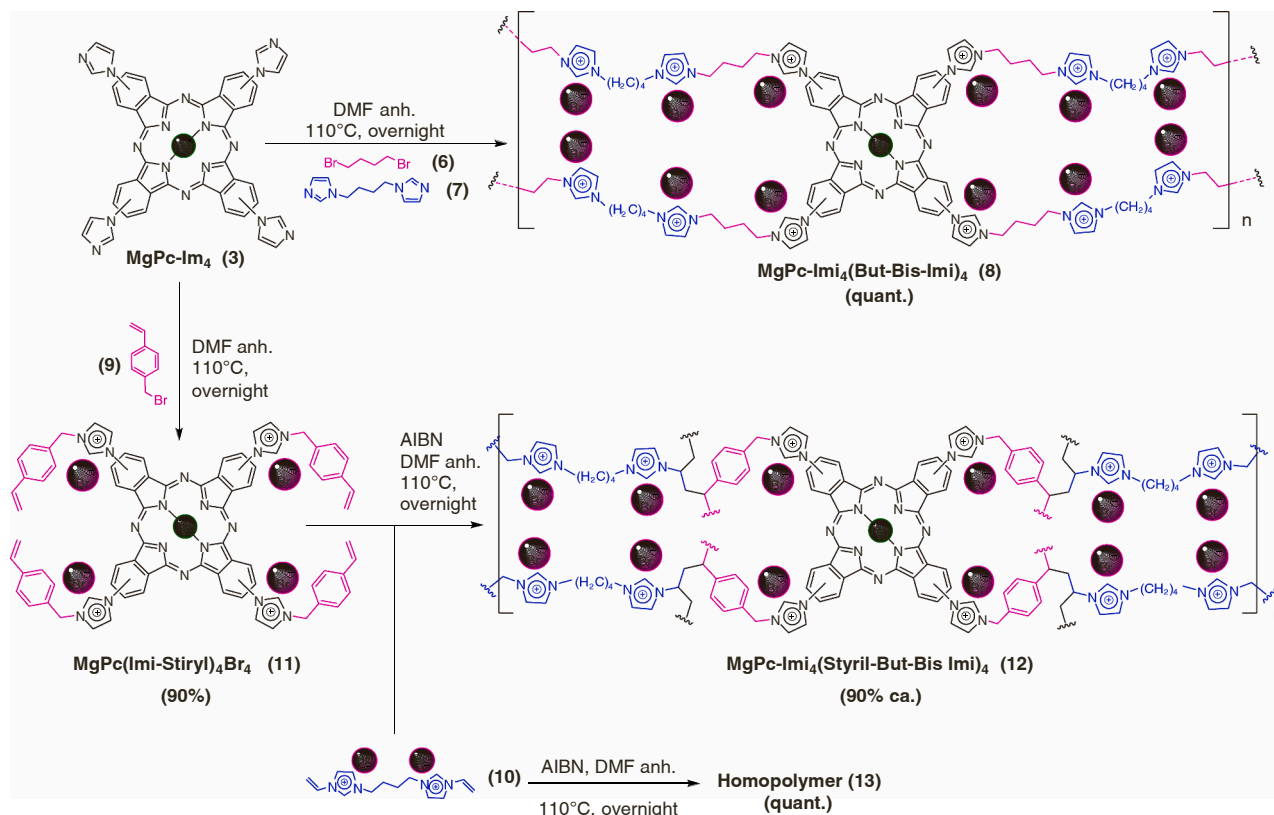
Scheme 2. synthetic procedure for the preparation of **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)**.
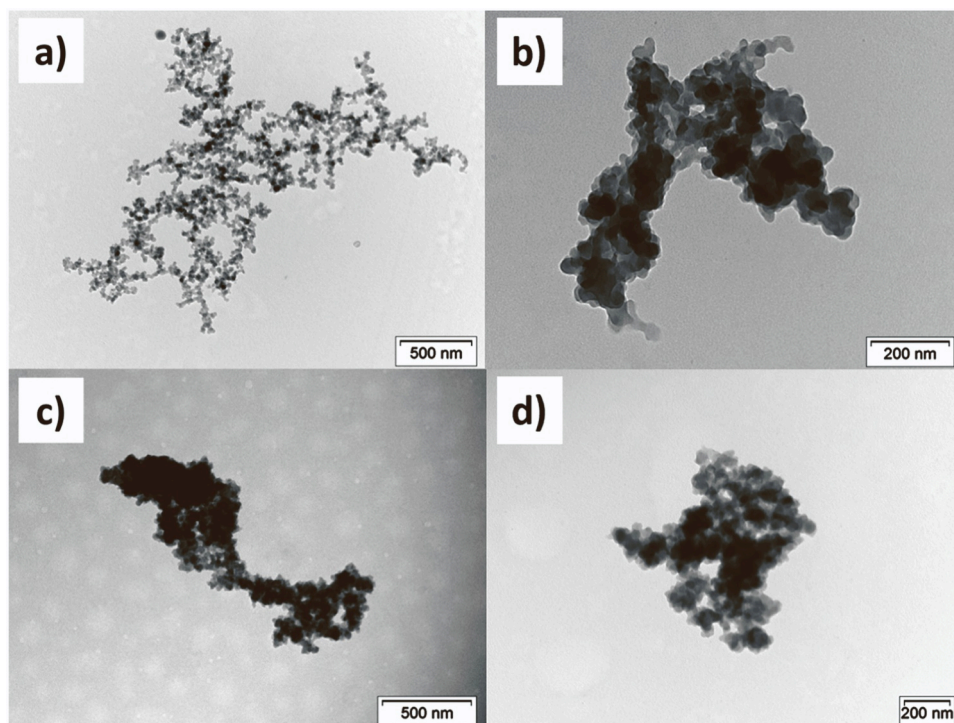
Fig. 3. TEM micrographs of a-b) **MgPc-BIBI-Br (8),** and c-d) **MgPc-SIBI-Br (12).**
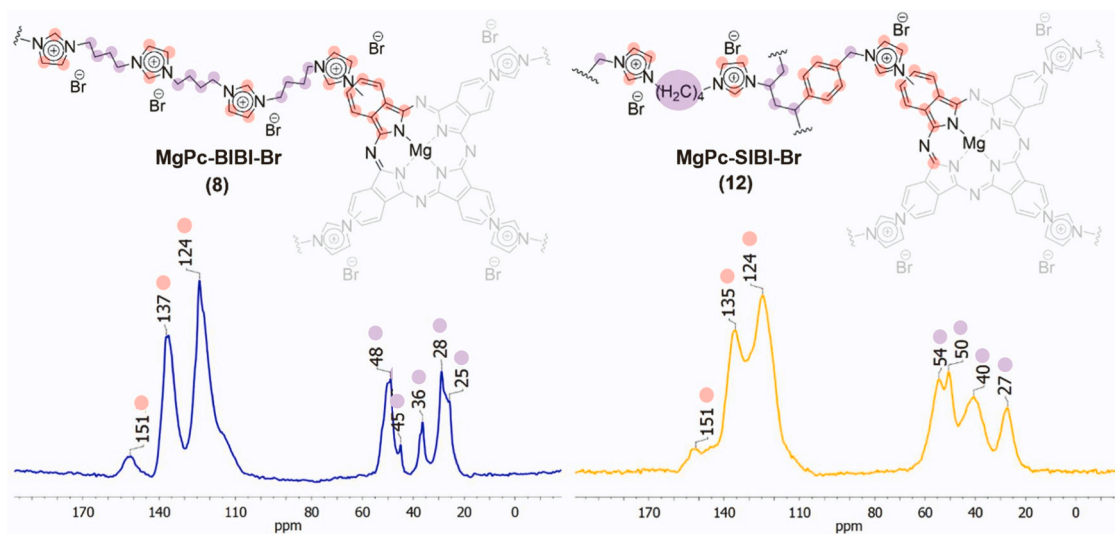

Fig. 4. ss ^{13}C CP-MAS NMR of **MgPc-BIBI-Br (8)** (blue line) and **MgPc-SIBI-Br (12)** (yellow line).

BIBI-Br (8) (Fig. 6a) has been deconvoluted into two peaks at 398 eV (18 % A.U.C.) and 401 eV (82 % A.U.C.). Such peaks correspond to nitrogen atoms of the phthalocyanine ring coordinated with magnesium (Mg–N) and the nitrogen atoms of the imidazolium rings (Imidazolium-N), respectively. Meanwhile, the same kind of peaks relating to **MgPc-SIBI-Br (12)** (Fig. 6b) have been detected at 399 eV (26 % A.U.C.) and 401 eV (74 A.U.C.) for Mg–N and Imidazolium-N nitrogen atoms, respectively.

Once characterized, we investigated the catalytic activity and recyclability of both **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)** for the conversion of epichlorohydrin into the corresponding cyclic carbonate under solvent free conditions and without the addition of any external nucleophilic entities like tetrabutylammonium bromide or **BMIM-Br**. In this regard, it is crucial to emphasize that all the key chemical species in

our materials that promote the epichlorohydrin conversion operate exclusively within a heterogeneous phase in the reaction mixture. The assessment of the catalytic efficiencies was conducted by considering TONs and TOFs values for both our materials (Fig. 7).

It is noteworthy that both materials exhibit a good trend of recyclability along with an interesting behavior of their catalytic activity: indeed, initially, there is an increase in activity between the first and second cycles, followed by a stabilization in the third and fourth ones. As we have already observed and described in some of our previous works [55,58], this behavior can be ascribed to alterations in the polymeric network due to the pressure, temperature and stirring conditions employed for each catalytic test. However, **MgPc-SIBI-Br (12)** seems to possess a better catalytic activity compared to the one of **MgPc-BIBI-Br (8)** (Fig. 7). Therefore, in order to evaluate and quantify the potential
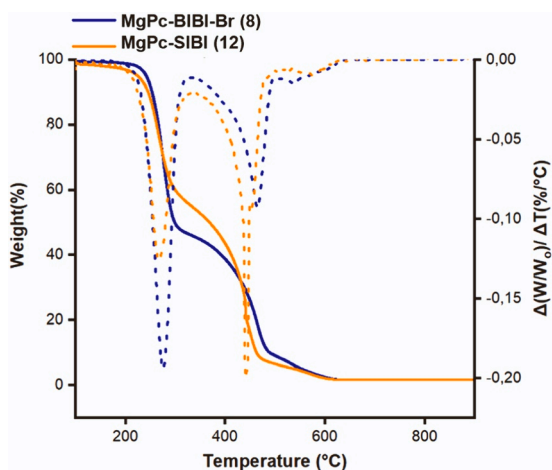
Fig. 5. TGA (solid lines) under Air flow and DTG (dotted lines) of) **MgPc-BIBI-Br (8)** (blue line), and **MgPcSIBI-Br (12)** (orange line).

versatility of this catalyst towards CO_2 valorization, **MgPc-SIBI-Br (12)** was tested in the conversion of various epoxides under different conditions. (Scheme S4).

Although very captivating catalytic data regarding the conversion of CO_2 already exist in the literature, our findings are equally compelling (see Table S3 for comparison with other reported systems): initially, we developed the bifunctional heterogeneous material **Poly-MgPc-(Imi-Bu)$_4$Br$_4$ (5)**, which evolved into a significantly more effective version

MgPc-SIBI-Br (12). The latter achieved notably higher TON values (3070 vs. 1195, Table 1, Fig. 7). This, coupled with its recyclability, the entirely heterogeneous nature of its catalytic components, and its versatility in converting efficiently other substrates (Table 2), marks an exceptional result that sets the stage for further investigations and experimental work.

6. Conclusions

Magnesium tetra(imidazol-1-yl)phthalocyanine (MgPc-Im$_4$) units were successfully polymerized in various methods, in conjunction with other compounds containing imidazole moieties, resulting in the creation of porous organic polymers denoted as **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)**. Extensive characterizations were conducted for both these materials and their precursor, employing a range of analytical techniques including liquid state and solid-state NMR spectroscopy, XPS, TEM, FT-IR, CHN, ICP-OES, TGA, and EDX. The combination of outcoming data highlighted the heterogeneous nature of **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br (12)**, and therefore the heterogeneous nature of their specific chemical constituents responsible for the conversion of CO_2 into cyclic carbonates (Fig. 1). In this regard, our research underscores the noteworthy relationship between an elevated Br$^-$/Mg ratio and heightened conversion levels towards such conversion. Notably, we have engineered recyclable systems, where these constituents synergistically (Scheme S3) operate within an exclusively heterogeneous phase. This approach is particularly advantageous for several reasons. Firstly, there are only a few examples in the literature of metal-phthalocyanines being used for the synthesis of cyclic carbonates.
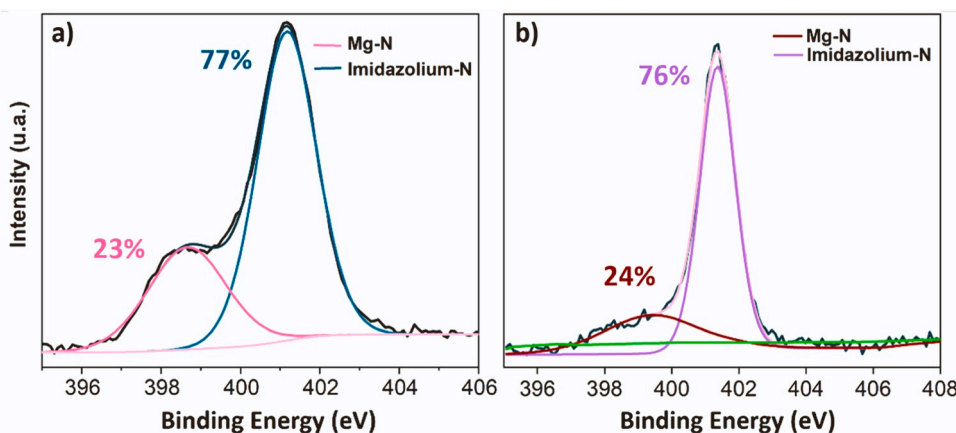

Fig. 6. a) XPS spectrum of a) high-resolution N1s region of **MgPc-BIBI-Br (8)** and b) N1s region of **MgPc-SIBI-Br (12)**.
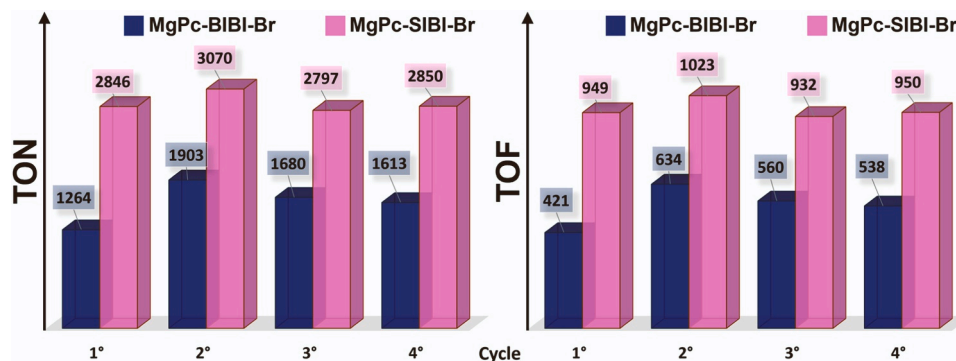

Fig. 7. TON and TOF values of Mg for recycling tests catalyzed by **MgPc-BIBI-Br (8)** and **MgPc-SIBI-Br.** Reaction conditions: 24 mL epichlorohydrin (306 mmol), 160 mg cat. (50 μmol of Mg for **MgPc-BIBI-Br**; 43 μmol of Mg for **MgPc-SIBI-Br**, both calculated via ICP-OES, see Table S1) CO_2 (25 bar), 100°C, 3 h. Each test has been set up respecting the initial stoichiometric ratios between epichlorohydrin and catalyst based on the amount of catalyst recovered after each test. Conversion values have been estimated via ^{1}H NMR (Figs. S25-S32).

Table 2

Cyclic carbonates synthesis catalyzed by **MgPc-SIBI-Br (12)**.

Substrate	Entry	T(°C)	t(h)	Conv.(%)	Selectivity[b](%)	TON[c]	TOF[c]
(epoxide structure) OH 360 mmol	**1**	80	24	83	>99	18950	790
(epoxide structure) Cl 306 mmol	**2[a]**	100	3	42	>99	3070	1020
	3[a]	100	8	83	>99	5950	740
(epoxide structure) 210 mmol	**4**	125	24	71	>99	13125	550
(structure) 131 mmol	**5**	125	24	50	>99	8200	340

Reaction conditions: 24 mL of epoxide, 60 mg cat. (16 μmol of Mg estimated by ICP-OES analysis), 25 bar of CO_2, 500 r.p.m.

[a] 160 mg of catalyst employed (43 μmol);

[b] selectivity towards the corresponding cyclic carbonate.

[c] values calculated towards the amount of Mg in the catalyst. Conversion values have been estimated via ^1H NMR (Figures from S33 to S37)

More importantly, unlike these examples, we avoid using external nucleophilic agents like TBAB or BMIM-Br. This not only simplifies the nature of the reaction mixture, but, according to experimental results (Fig. 7, Table 2), brings to slightly better performances compared to the ones obtained from analogous systems present in the literature [50, 61–64]. Such evidences strengthen the credibility of employing metal phthalocyanine complexes in the context of CO_2 valorization. Moreover, certain intermediates derived from MgPc-Im$_4$ that have been synthesized in this study, offer excellent prospects for diverse functionalization methodologies and can be seamlessly integrated into various inorganic matrices (carbon nanotubes, silica, titania, etc.), potentially giving rise to a novel class of materials. The combination of these factors, along with the flexibility to select different metals for complexation and the variation of anions associated with imidazolium salt fractions, positions phthalocyanine metal complexes as a promising and substantial avenue in the field of CO_2 conversion. This represents a compelling working hypothesis that certainly warrants further thorough investigation and exploration.

CRediT authorship contribution statement

Francesco Giacalone: Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Michelangelo Gruttadauria:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition. **Vittorio Marsala:** Investigation, Formal analysis. **Remy Jouclas:** Supervision, Investigation, Data curation, Conceptualization. **Benedetto Taormina:** Visualization, Validation, Investigation, Formal analysis, Data curation. **Carmela Aprile:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Carmela Aprile reports article publishing charges was provided by University of Namur. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2024.102875.

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