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Al(III) phthalocyanine catalysts for CO_2 addition to epoxides: Fine-tunable selectivity for cyclic carbonates versus polycarbonates

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ABSTRACT

A sustainable synthetic methodology to prepare bifunctional cationic imidazolyl and neutral *tert*-butylphenoxy Al(III)-phthalocyanine complexes is described, using ultrasound irradiation to synthesize the phthalonitrile precursors, followed by microwave-assisted cyclotetramerization. The metallophthalocyanine catalysts were applied in the coupling reaction of CO_2 with epoxides, where the structure of the phthalocyanine was shown to determine the reaction selectivity towards the formation of cyclic carbonates versus polycarbonates. The cationic imidazolyl phthalocyanines operate as efficient bifunctional catalysts to promote the CO_2 cycloaddition to terminal epoxides (styrene oxide, epichlorohydrin, propylene oxide and allyl glycidyl ether), leading to TONs up to 1414 and 100% selectivity for cyclic carbonates, without the need of using any co-catalyst. On the other hand, the neutral 4-*tert*-butylphenoxy Al(III) phthalocyanine catalyzed the copolymerization reaction between CO_2 and cyclohexene oxide, in the presence of PPNCl as co-catalyst, with TON = 814, providing the first example of a metallophthalocyanine catalyst with full selectivity for formation of polycarbonates.

1. Introduction

Carbon dioxide (CO_2) is an abundant greenhouse gas considered as one of the main causes of climate changes, which bring us serious social, health and economic burden in the present and near future. In this context, there has been a growing interest in the development of technologies that can reduce CO_2 emissions or, at least, mitigate its effects by means of its capture from atmosphere, storage and conversion into value-added products [1–9]. Indeed, the environmental urgency of reusing CO_2, combined with its high availability and low toxicity make it an attractive building block for chemical synthesis. However, its high thermodynamic and kinetic stability requires the use of efficient catalysts in order to turn CO_2 transformation into environmentally and economically viable processes [10–12]. To this effect, many strategies have been reported on CO_2 utilization for the synthesis of carboxylic acids and their derivatives, carbamates and carbonates, or as a precursor to carbon monoxide [13,14]. Among the most relevant transformations, the catalytic addition of CO_2 to epoxides, yielding cyclic carbonates [15–20] or polycarbonates [21–26] is especially useful, since these products play important roles as "green" organic solvents or as polymers for the plastics industry, respectively. These reactions have been mainly accomplished through the use of metallic catalysts, such as metal complexes of salens, [27–31] β-diiminates [32,33], aminotriphenolates [34–36] and porphyrins [37–43], as well as supported metal salts [44] and metal organic frameworks [45,46]. Another group of attractive but less explored metal complexes are metallophthalocyanines, which have been efficiently used as homogeneous [47–51] and heterogeneous catalysts [52–58] for CO_2 addition reactions to propylene oxide, styrene oxide, 1,2-epoxyhexane, epibromohydrin, epichlorohydrin, (2,3-epoxypropyl)benzene and glycidyl ethers as substrates. In general, cyclic carbonates are exclusively obtained as the main products for all types of substrates, while low conversions are observed for cyclohexene oxide.

Most of metal catalysts are known to act as Lewis acids for activating the epoxide [59]. In addition, a nucleophile is usually required as co-catalyst, to promote the epoxide ring opening upon its coordination with the metal center [60]. The co-catalyst can be an external agent added to the reaction (e.g. imidazole [47], DMAP [61,62], quaternary phosphonium [63,64] or ammonium salts [65–68]), or it can be part of the catalyst molecule, forming a bifunctional catalytic system (Fig. 1).

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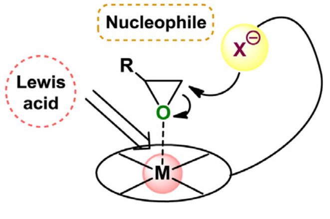
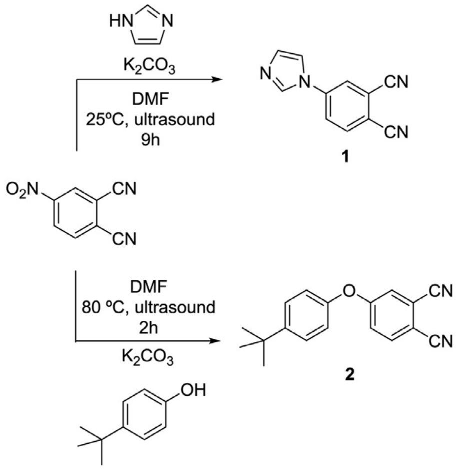


Fig. 1. Epoxide activation with a bifunctional catalyst.



Scheme 1. Synthesis of the phthalonitrile precursors.

Among the reported bifunctional catalysts, we highlight the use of salens [69–71], metalloporphyrins [72–75], triphenolates [76], hetero-scorpionates [77], tris(2-aminoethyl)amine-based complexes [78], as well as silanol [79] and heterogeneous Sn-SiO_2 imidazolium-based catalysts [80]. There is also a report of reusable bifunctional metallophthalocyanine-carbon nitride hybrid catalysts (metal = Cu or Co), which have been used in CO_2 cycloaddition to epoxides, in the absence of co-catalyst, and allowed to obtain the corresponding cyclic carbonates in yields ranging from 12 to 98% [81]. However, to the best of our knowledge, there are no reports of the application of bifunctional metallophthalocyanine homogeneous molecular catalysts in these reactions.

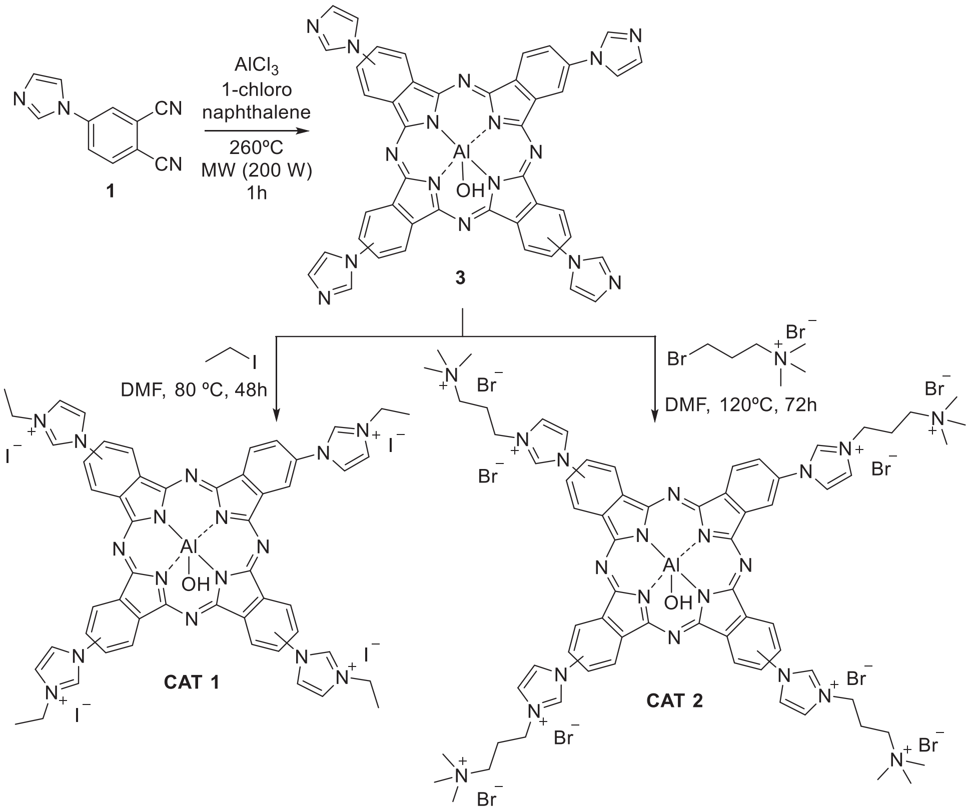
Recently, we have described the synthesis of monoterpene-based Zn (II) phthalocyanines [82] and their application as catalysts in CO_2 cycloaddition to styrene oxide [83], but the reactions required the use of a co-catalyst and moderate TONs (up to 900) were obtained.

As a part of our continuing research in this field, in this paper we describe an efficient and sustainable synthetic methodology to prepare bifunctional cationic imidazolyl-based Al(III) phthalocyanines and neutral *tert*-butylphenoxy Al(III) phthalocyanines. Furthermore, their application as selective catalysts in CO_2 addition reactions to epoxides is reported and the effect of the phthalocyanine structure in the catalytic activity and selectivity is described.

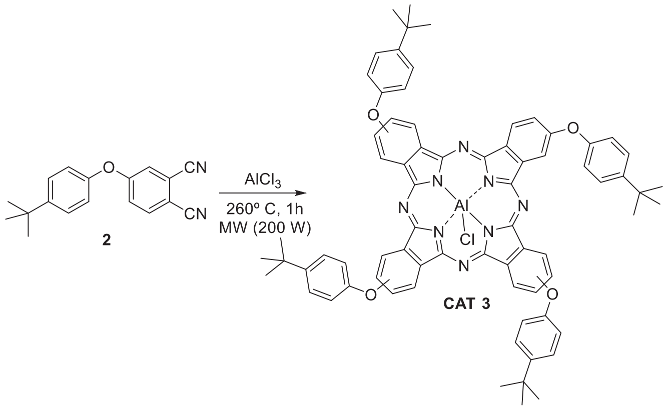
2. Results and discussion

2.1. Synthesis and characterization of Al(III) phthalocyanine catalysts

The Al(III)-phthalocyanine catalysts were prepared, through optimization of our recently developed sustainable synthetic methodology [82], which involves the synthesis of phthalonitrile precursors using ultrasound irradiation, followed by microwave-assisted cyclotetramerization reactions (Schemes 1–3). First, the 4-(1*H*-imidazol-1-yl) phthalonitrile 1 was synthesized by reacting commercially available 4-nitrophthalonitrile with imidazole in DMF, using K_2CO_3 as base, in an ultrasonic bath at 25 °C, over 9 h, under inert atmosphere. Similarly, phthalonitrile 2 was prepared by re-



Scheme 2. Synthetic pathway for cationic imidazole-based Al(III) phthalocyanine bifunctional catalysts.



Scheme 3. Microwave-assisted synthesis of *tert*-butylphenoxy Al(III) phthalocyanine.

action of 4-nitrophthalonitrile with 4-*tert*-butylphenol in an ultrasonic bath at 80 °C, for 2 h. Upon addition of water and ice, the desired phthalonitriles 1 and 2 were precipitated and isolated in 62% and 88% yields, respectively (Scheme 1). This synthetic strategy allowed to significantly diminish reaction times when compared to conventional synthesis and obtain the desired phthalonitrile precursors in higher yields than those previously reported in the literature [84,85].

Then, to overcome the difficulties associated with Al(III) phthalocyanine synthesis [86,87], the cyclotetramerization reaction of phthalonitrile 1 with Al(III) chloride was performed in 1-chloronaphthalene, a high boiling point solvent, at 260 ºC, under microwave irradiation (200 W), over 1 h (Scheme 2). After precipitation of the product from the reaction medium by addition of CH_2Cl_2 and purification by consecutive washing with acetone, water, acetone and dichloromethane (in this exact order), the corresponding tetra-imidazole β-substituted Al(III) phthalocyanine 3 was isolated in 60% yield. The HRMS (ESI) mass spectrum confirmed the formation of the Al(III)-phthalocyanine complex 3, bearing a hydroxyl group as axial ligand, which indicates that hydrolysis has occurred either during the synthesis or work-up procedure. The subsequent cationization was carried out, through reaction of 2 with iodoethane in DMF at 80 °C, over 48 h (Scheme 2). After direct precipitation from the reaction mixture by adding CH_2Cl_2, the tetra-cationic imidazolyl Al(III) phthalocyanine CAT 1 was isolated in 82% yield. Likewise, the octa-cationic imidazolyl Al(III) phthalocyanine CAT 2 was obtained by reaction of 2 with (3-bromopropyl)trimethylammonium bromide in DMF, at 120 °C, over 72 h. The crude product was precipitated from the reaction mixture with ethanol, followed by washing with ethanol, acetone and dichloromethane and isolated in 53% yield.

The structures of imidazole-based metallophthalocyanines CAT 1 and CAT 2 were elucidated by NMR spectroscopy and further confirmed by HRMS (ESI). The spectroscopic data of CAT 1 was in agreement with that previously reported [84]. The ^{1}H NMR spectrum of the new octa-cationic imidazolyl Al(III)-phthalocyanine CAT 2, in DMSO-d$_6$, is presented in Fig. 2. This spectrum shows broad signals, typical of cationic phthalocyanines, which may be attributed to aggregation. Additionally, since the metallophthalocyanine is composed by four different regioisomers, this translates into a more complex signal pattern, both in the aromatic and aliphatic regions. The aromatic signals range from 8.4 to 10.9 ppm, which is a consequence of the extensive π-conjugation of the macrocycle coupled with a strong electron-withdrawing effect caused by positively charged nitrogen atoms.

The synthesis of CAT 3 was accomplished through microwave-assisted cyclotetramerization of phthalonitrile 2 with Al(III) chloride, in 1-chloronaphthalene, at 260 °C for 1 h (Scheme 3). After cooling to room temperature, the metallophthalocyanine was precipitated by addition of a methanol/water (10:1) mixture, and further purified by column chromatography on silica gel using dichloromethane, followed by dichloromethane:methanol (95:5) as eluent, to afford CAT 3 with 70% isolated yield. This synthetic strategy allowed to obtain the desired Al(III) phthalocyanine in shorter time and higher yield than those achieved by previously reported conventional methods [88].

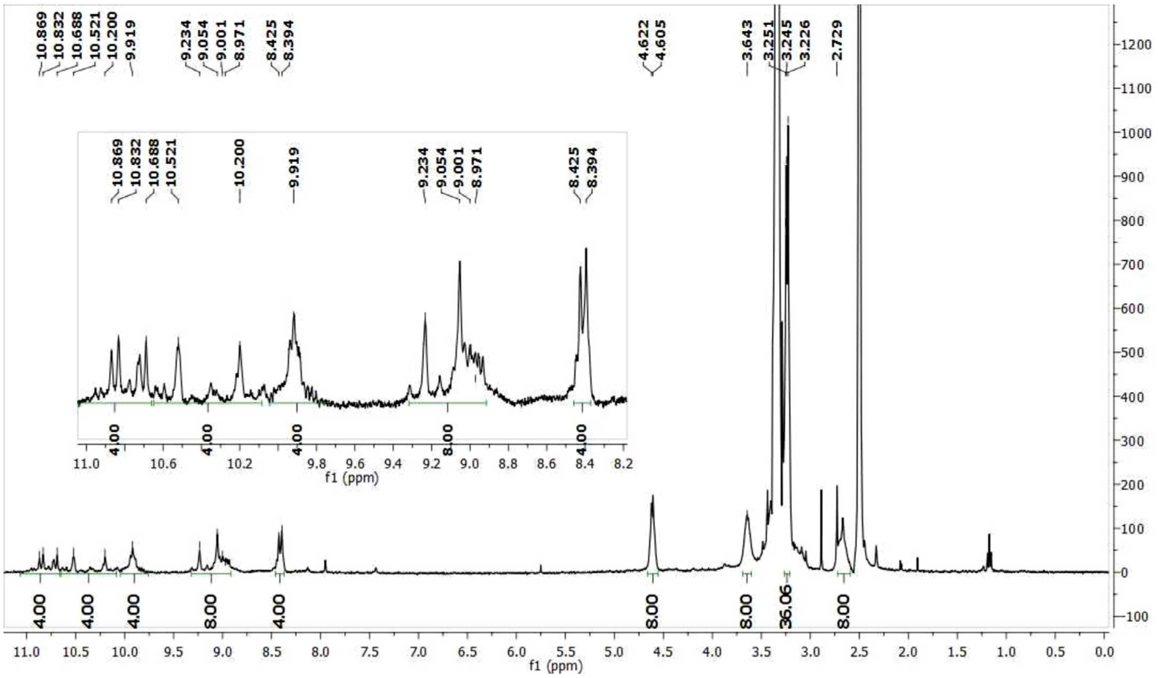
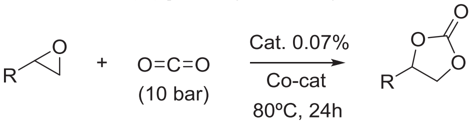
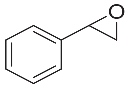
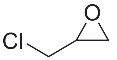
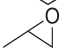
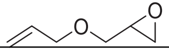


Fig. 2. ^{1}H NMR spectrum of CAT 2 in DMSO-d$_6$ (expansion of the region 8.2–11.0 ppm).

Table 1
Evaluation of Al(III)-phthalocyanine catalysts in CO_2 addition to terminal epoxides.[a]



Entry	Substrate	Catalyst	Co-cat	Solvent	Yield (%)[b]	TON[c]	TOF (h^{-1})[d]
1		CAT 1	–	–	71	1014	42
2		CAT 3	–	–	0	–	–
3		CAT 3	PPNCl	–	81	1157	48
4		CAT 1	–	CH_3OH	69	986	41
5		CAT 3	PPNCl	CH_3OH	38	543	23
6		CAT 1	–	CH_3CN	72	1029	43
7		CAT 2	–	CH_3CN	19	271	11
8		CAT 3	PPNCl	CH_3CN	80	1143	48
9[e]		CAT 1	–	–	94	1343	269
10[e]		CAT 1	–	–	99	1414	283
11		CAT 1	–	–	90	1286	53

[a] Reaction conditions: styrene oxide (35 mmol, 4 ml), catalyst: 0.07 mol%, co-catalyst (when indicated): PPNCl 0.07 mol%, solvent: 1 mL (when indicated), CO_2 (10 bar), 80 °C, 24 h.
[b] % Yield determined by ^1H NMR.
[c] Turnover number calculated as $mol_{(catalysis\ products)}/mol_{(catalyst)}$.
[d] Turnover frequency expressed as TON per hour.
[e] 5 h; Selectivity, determined by ^1H NMR, was 100% for cyclic carbonates in all cases.

2.2. CO_2 addition to epoxides

The bifunctional cationic imidazolyl Al(III)-phthalocyanines CAT 1-CAT 2, and the neutral 4–tert-butylphenoxy-based Al(III)-phthalocyanine CAT 3 were evaluated as catalysts in CO_2 addition reaction to epoxides. The catalysts were initially tested in the CO_2 cycloaddition reaction to styrene oxide. The reactions were performed under previously optimized conditions (0.07 mol% catalyst, 10 bar CO_2, 80 °C, 24 h) [39,83].

The cationic tetra-imidazolyl Al(III) phthalocyanine catalyst CAT 1 was first tested in the absence of solvent, without addition of any co-catalyst, leading to 71% yield of styrene carbonate (TON = 1014) (Table 1, entry 1). Under the same reaction conditions, the (4-*tert*-butylphenoxy) Al(III) phthalocyanine catalyst CAT 3 was inactive in the absence of a co-catalyst (Table 1, entry 2) while, in the presence PPNCl as co-catalyst, provided 81% yield of cyclic carbonates (Table 1, entry 3). When the reactions were carried out either in the presence of protic (methanol) or aprotic (acetonitrile) polar solvents, no significant differences were observed in the catalytic activity or selectivity of the bifunctional tetra-imidazolyl Al(III) phthalocyanine catalyst CAT 1 (Table 1, entries 4 and 6). On the other hand, the catalytic system CAT 3/PPNCl produced only 38% yield when the reaction was performed in methanol (Table 1, entry 5), while the use of acetonitrile as solvent had a negligible effect on the catalytic activity (Table 1, entry 8). The octa-cationic imidazolyl Al(III) phthalocyanine bifunctional catalyst CAT 2 was also tested in the reaction but this catalyst was only partially soluble in the epoxide, so acetonitrile (1 mL) was used as solvent. However, only 19% yield of styrene carbonate was obtained, which was attributed to a concentration decrease effect (Table 1, entry 7).

The promising results obtained with bifunctional catalyst CAT 1, in absence of solvent and co-catalyst, led us to select this catalyst for enlargement of the reaction's scope to other terminal epoxides. Remarkably, under the same reaction conditions, both CO_2 cycloaddition reactions to epichlorohydrin, and propylene oxide proceeded with practically full conversions in 5 h, leading to the formation of the corresponding cyclic carbonates in 94 and 99% yields, respectively (Table 1, entries 9–10). Moreover, CO_2 addition to allyl glycidyl ether led to full selectivity and 90% yield of cyclic carbonate products (Table 1, entry 11). Furthermore, the cationic tetra-imidazolyl catalyst CAT 1 was easily recovered from the reaction crude mixtures by precipitation with CH_2Cl_2, and reused in two consecutive runs without loss of activity or selectivity, producing similar yields of cyclic carbonates.

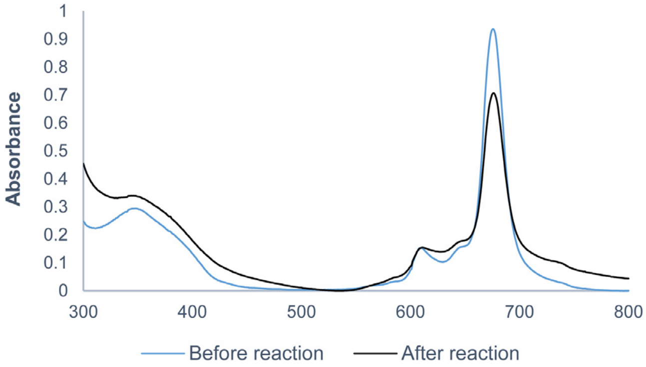


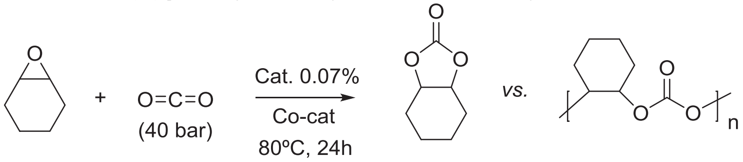
Fig. 3. UV–Vis spectra of CAT 1, in DMSO, before and after CO_2 addition to styrene oxide (Table 1, entry 1).

Catalyst stability studies were performed for CAT 1 by UV–Vis (Fig. 3), through analysis of aliquots taken from the initial mixture in styrene oxide and the final mixture after the catalytic CO_2 addition reaction (10 μL sample/8 mL DMSO). From analysis of Fig. 3, we concluded that ca. 80% of the catalyst remain intact, which demonstrate its stability.

In addition, the Al(III)-phthalocyanine catalysts were evaluated in the catalytic CO_2 addition to cyclohexene oxide, a more challenging disubstituted cyclic epoxide. Considering the lower reactivity of this substrate, the reactions were performed using a higher CO_2 pressure (40 bar), also at 80 °C and 0.07 mol% catalyst. The results are presented in Table 2.

The cationic tetra-imidazolyl Al(III)phthalocyanine complex CAT 1 was first evaluated in the absence of any co-catalyst and solvent, leading to only 5% conversion in 24 h, with 100% selectivity for the formation of cyclohexane cyclic carbonate (Table 2, entry 1). When the reaction was performed under the same condi-

Table 2
Evaluation of Al(III)-phthalocyanine catalysts in CO_2 addition to cyclohexene oxide.^{a}



Entry	Catalyst	Co-cat	Solvent	Conversion (%)^b	Product distribution^c		TON^d	TOF^e
					Cyclic Carbonates (%)	Polymers (%)		
1	CAT 1	–	–	5	100	0	71	3
2	CAT 1	PPNCl	–	20	100	0	286	12
3	CAT 1	PPNCl	CH_3CN	13	100	0	186	8
4	CAT 3	–	–	4	0	100	57	2
5	CAT 3	PPNCl	–	57	0	100	814	34

$^{a)}$Reaction conditions: cyclohexene oxide (40 mmol, 4 ml), catalyst: 0.07 mol%, co-catalyst (when indicated): PPNCl 0.07 mol%, solvent: 1 mL acetonitrile (when indicated), CO_2 (40 bar), 80 °C, 24 h.
$^{b)}$% Conversion determined by ^{1}H NMR.
$^{c)}$% Selectivity determined by ^{1}H NMR, through integral ratio of polycarbonate/cyclic carbonate peaks $^{d)}$ Turnover number calculated as $mol_{(catalysis\ products)}/mol_{(catalyst)}$.
$^{e)}$Turnover frequency expressed as TON per hour.

tions, but with addition of PPNCl as co-catalyst, 20% conversion was obtained in 24 h, also with full selectivity for cyclic carbonates (Table 2, entry 2). When acetonitrile was used as solvent, a lower conversion (13%) was observed (Table 2, entry 3), which was attributed to the lower substrate concentration in the initial reaction mixture. To appraise the effect of the phthalocyanine structure on the catalytic activity and selectivity, the studies proceeded with the evaluation of 4–*tert*-butylphenoxy Al(III) phthalocyanine (CAT 3) as catalyst in the CO_2 addition to cyclohexene oxide, under the above mentioned conditions. In the absence of co-catalyst, only 4% conversion was observed (Table 2, entry 4) but using PPNCl as co-catalyst, CAT 3 provided 57% conversion in 24 h, with a remarkable 100% selectivity for the formation of polymers (Table 2, entry 5). The polymer structure was analyzed by ^{1}H and ^{13}C NMR, which confirmed a high carbonate incorporation (96%). In addition, high performance size exclusion chromatography (HPSEC) (Fig. S7, SI) revealed a number-average molecular weight (M_n) of 1626 and a polydispersity (M_w/M_n) of 1.55.

These results clearly show that the developed Al(III) phthalocyanines are talented catalysts for CO_2 coupling reaction with epoxides. On one hand, the TONs and TOFs obtained with bifunctional catalyst CAT 1, without any co-catalyst, in CO_2 cycloaddition reactions to terminal epoxides (Table 1) were significantly higher than those obtained with Zn(II) phthalocyanines (TON = 900, TOF = 38 h^{-1}) [83], and have the same magnitude of those achieved with other metallophthalocyanine catalysts in the presence of a co-catalyst, such as copper-based (TOF = 502) [50], aluminum (TOF = 586 h^{-1}) [51], TOF = 188 h^{-1}) [55], iron (TOF = 900 h^{-1}) [53] and cobalt-based catalysts (TOF = 47 h^{-1}) [57], TOF = 12 h^{-1}) [81], under similar reaction conditions. Moreover, the activity of the catalytic system CAT 3/PPNCl in CO_2 addition to cyclohexene oxide (TON = 814, TOF = 34 h^{-1}) is superior to that achieved with other metallophthalocyanine-based catalysts [49,53,81], showing a markedly different selectivity for cyclohexane polycarbonate formation, from that reported with metallophthalocyanine catalysts.

We have previously observed that, with Mn(III) [38] and Cr(III) [39] porphyrin catalysts, the reaction selectivity is substrate-dependent, with cyclic carbonates being mainly formed when terminal epoxides are used as substrates, while polycarbonates are predominantly obtained with cyclohexene oxide, since the ring closure is less favored due to high geometric strain [89]. In the present study, the CO_2 addition reactions to terminal epoxides were also found to be substrate-dependent, giving exclusively cyclic carbonates, independently of the Al(III)-phthalocyanine catalyst used. However, when cyclohexene oxide is used as substrate, the cationic imidazolyl Al(III)-phthalocyanine bifunctional catalyst CAT 1 is highly selective for the formation of cyclic carbonates, while the *tert*–butylphenoxy Al(III)-phthalocyanine catalyst CAT 3, in the presence of PPNCl as co-catalyst, provides the polycarbonate product, which demonstrates that the catalyst structure has a crucial effect on the reaction selectivity.

As depicted in Fig. 4, both mechanisms involve the initial coordination of the epoxide to the metal center, followed by ring opening in the presence of a nucleophile, which may be included in the catalyst (i.e., the iodide anion in the case of cationic imidazolyl bifunctional catalyst CAT 1) or it can come from the co-catalyst (the chloride anion, in the case of CAT 3/PPNCl catalytic system). The subsequent CO_2 insertion into the alkoxo species (B) results in the formation of metal-carbonate (C), which may undergo back-biting reaction, leading to intramolecular cyclization or it may undergo chain-growing, upon consecutive epoxide and CO_2 insertions, leading to alternating copolymerization. In this case, when the cationic imidazolyl Al(III)-phthalocyanine bifunctional catalyst CAT 1 is used, the nucleophile (I^-) is a good leaving group, so it promotes ring closure and the subsequent formation of cyclic carbonates [90,91]. On the other hand, when CAT 3 is used, in the presence of PPNCl as co-catalyst, the poor leaving group ability of Cl^- possibly favors the growing of polymer chain and promotes the formation of the polycarbonate [90,91].

In sum, the cationic imidazolyl-based Al(III) phthalocyanines were shown to be active bifunctional catalysts for the CO_2 addition to terminal epoxides, without the need of using any co-catalyst. Furthermore, the *tert*–butylphenoxy Al(III)-phthalocyanine catalytic system CAT 3/PPNCl was active in CO_2 addition reactions to terminal epoxides, showing high selectivity for cyclic carbonates, and also in CO_2/cyclohexene oxide coupling, leading to an unprecedented selectivity for the formation of cyclohexane polycarbonate.

3. Conclusions

We have disclosed an efficient synthetic methodology to modulate the structure of Al(III) phthalocyanine complexes bearing cationic imidazolyl or *tert*–butylphenoxy moieties. It was demonstrated that the use of alternative energy sources, such as ultrasounds for the synthesis of the phthalonitrile precursors and microwave irradiation for the subsequent phthalonitrile cyclotetramerization with $AlCl_3$ allowed to obtain the desired Al(III) ph-

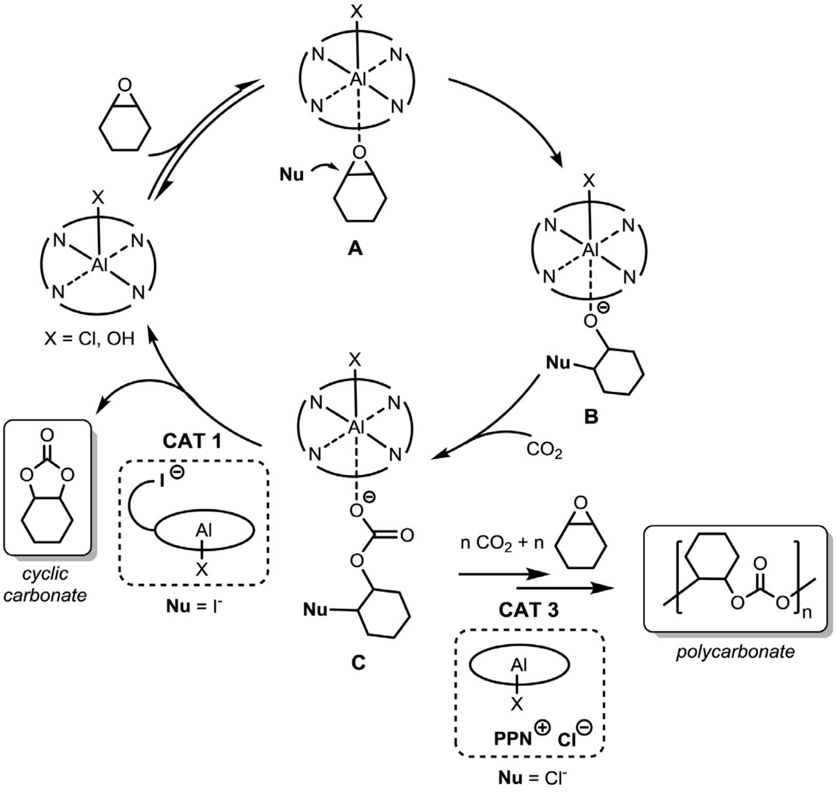


Fig. 4. Mechanistic pathways for the formation of cyclohexane cyclic carbonates, using CAT 1 versus polycarbonates using CAT 3/PPNCl.

thalocyanines in shorter times and higher yields, when compared with previous conventional methods. The Al(III) phthalocyanine complexes have efficiently catalyzed the coupling reaction between CO_2 and terminal epoxides (styrene oxide, epichlorohydrin, propylene oxide and allyl glycidyl ether), where the bifunctional cationic imidazolyl metallophthalocyanines were shown to be active (using only 0.07 mol%) and selective catalysts, to promote the cycloaddition for the formation of cyclic carbonates, even in the absence of any co-catalyst and recyclable, being recovered by simple precipitation from the reaction crude mixture and reused in two consecutive runs without loss of catalytic activity or selectivity. In addition, the use of *tert*–butylphenoxy Al(III)-phthalocyanine/PPNCl catalytic system in the CO_2 addition to cyclohexene oxide constitutes the first example ever reported of a metallophthalocyanine-based catalyst capable to promote CO_2/epoxide copolymerization.

Therefore, we can conclude that these Al(III) phthalocyanines are promising catalysts for CO_2 addition reactions to epoxides, and their structural modulation allows to selectively obtain cyclic carbonates versus polycarbonates. This work paves the way for the future development of highly active and selective catalysts through fine-tuning of the phthalocyanine structure.

4. Experimental

4.1. General

All reagents were purchased from Sigma-Aldrich, dried over alumina and stored under inert atmosphere. The solvents used in the synthesis reactions were, whenever necessary, purified or dried according to the methods described in the literature. Air and moisture sensitive reagents were manipulated using Schlenk techniques, under a nitrogen or argon atmosphere, in a vacuum system. All glass material was dried in an oven at 100 °C. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX 400 spectrometer, operating at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C. Chemical shifts for ^1H and ^{13}C are expressed in ppm, relatively to a TMS as internal standard, or relatively to residual peaks, present in the deuterated solvents used, $CDCl_3$ or DMSO–d_6. The MALDI-TOF and ESI mass spectra were acquired using an Autospec Micromass and Bruker Microtof, respectively. Microwave-assisted experiments were performed in an appropriate thick-walled glass vial (10 mL) under closed-vessel conditions, using a CEM Discover® SP Microwave System. The reactions carried out in a bath with ultrasound irradiation were conducted in a Bandelin Sonorex RK 100H device. High performance size exclusion chromatography (HPSEC) was performed for polycarbonate samples, using a Viscotek (ViscotekTDAmax) with a differential viscometer (DV), right-angle laser-light scattering (RALLS, Viscotek), and refractive index (RI) detectors. The column set was composed by a PL 10 mm guard column followed by one MIXED-E PLgel column and one MIXED-C PLgel column. Previously filtered THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. The samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2 mm pore before injection and the system was calibrated with narrow PS standards. The MnSEC and Đ of the synthesized polymers were determined by using a conventional calibration (OmniSEC software version: 5.0).

4.2. Synthesis and characterization of catalysts

4-(1′H-imidazol-1′-yl) phthalonitrile (1)

Imidazole (1.26 g, 18.5 mmol) was added to a solution of 4-nitrophthalonitrile (2.56 g, 14.8 mmol) and K_2CO_3 (10.2 g, 74 mmol) in DMF (38 ml) and the reaction mixture was stirred in an ultrasound bath, at 25 °C, for 9 h. At the end, the mixture was filtered to remove the K_2CO_3. Then, a mixture of water and ice (ca. 200 ml) was added to the reaction mixture until a precipitate was formed. The yellowish precipitate was then filtered under vacuum using a sintered plate glass funnel, and dried at 80 °C for 12 h. Then, the solid was recrystallized from methanol (50 ml), and the compound was filtered again under vacuum, using a sintered plate glass funnel and, finally, dried in vacuum at 80 °C for 4 h. Yield: 1.78 g (62%), obtained as a white solid. Spectroscopic data was in accordance with that previously reported [84].

4-(4–tert-butylphenoxy) phthalonitrile (2)

4–*tert*-Butylphenol (2.25 g, 15 mmol) was added to a solution of 4-nitrophthalonitrile (2.08 g, 12 mmol) and K_2CO_3 (9.8 g, 71 mmol) in DMF (40 ml). The reaction mixture stirred in an ultrasound bath, at 80 °C, for 2 h, under inert atmosphere. After cooling, ice water was added, and the precipitate formed was filtered. Yield 2.96 g (88%), obtained as a white solid. Spectroscopic data was in accordance with that previously reported [85].

2(3),9(10),16(17),23(24)-tetrakis(1′H-imidazol-1′-yl)phthalocyaninato hydroxyaluminium (III) (3)

4-(1′*H*-imidazol-1′-yl)phthalonitrile (1) (500 mg, 2.57 mmol) and $AlCl_3$ (171 mg, 1.28 mmol) were dissolved in 1-chloronaphthalene (5 ml), under inert atmosphere. Then, the mixture was heated, under microwave irradiation ($P = 200$ W), to 260 °C for 1 h. After cooling to room temperature, the product was precipitated by addition of dichloromethane and filtered-off. The green precipitate was washed with 20 ml of acetone, water, acetone and dichloromethane, in that order. Yield: 316 mg (60%) of a green solid. Spectroscopic data was in accordance with that previously reported [84].

2(3),9(10),16(17),23(24)-tetrakis(3′-ethyl-1′H-imidazol-1′-yl)phthalocyaninato hydroxy aluminium (III) iodide (CAT 1)

Phthalocyanine 3 (120 mg, 0.14 mmol) and iodoethane (1 ml, 12 mmol) were dissolved in DMF (2 ml). The reaction proceeded at 80 °C for 48 h under inert atmosphere and an additional 3 ml (36 mmol) of iodoethane were added during this period. The crude was precipitated with the addition of 20 ml dichloromethane and filtered. Yield: 165 mg (82%) of a green solid. Spectroscopic data was in accordance with that previously reported [84].

2(3),9(10),16(17),23(24)-tetrakis((3′-(3″-trimethylammonium)propyl)–1′H-imidazol-1′-yl)phthalocyaninato hydroxyaluminium (III) bromide (CAT 2)

The phthalocyanine 3 (85 mg, 0.11 mmol) and (3-bromopropyl)trimethylammonium bromide (261 mg, 1 mmol) were dissolved in DMF (5 ml). The reaction proceeded under inert atmosphere, at 120 °C, for 72 h. After cooling to room temperature, the product was precipitated with the addition of 40 ml ethanol and filtered-off. The green precipitate was washed with 20 ml of ethanol, acetone and dichloromethane, in that order. Yield: 95 mg (53%) of a green solid. UV–Vis (DMSO): ε_{abs}, nm ($M^{-1}cm^{-1}$): 346 (4.61×10^4), 611 (2.28×10^4), 678 (1.38×10^5). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.98–10.66 (m, 4H), 10.65–10.09 (m, 4H), 10.04–9.83 (m, 4H), 9.32–8.90 (m, 8H), 8.47–8.36 (m, 4H), 4.67–4.55 (m, 8H), 3.70–3.59 (m, 8H), 3.27–3.20 (m, 36H), 2.72–2.58 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm): 62.1 ($-\underline{C}H_2-N(CH_3)_3$), 52.8 ($-\underline{C}H_2-N_{Imid}$), 52.6 ($-\underline{C}H_3$), 23.0 ($-CH_2-\underline{C}H_2-CH_2-$) (aromatic C signals were not observed). HRMS (MALDI-TOF): obtained for $[M\text{-}8Br\text{-}4N(CH_3)_3]^+$ 988.3396; calcd. for $[C_{56}H_{49}AlN_{16}O]$ 988.4047.

2(3),9(10),16(17),23(24)-tetrakis(4–tert-butylphenoxi) phthalocyaninato chloride aluminium (III) (CAT 3)

The 4-(4–*tert*-butylphenoxy)phthalonitrile precursor (2) [85] (750 mg, 2.7 mmol) and $AlCl_3$ (103 mg, 0.77 mmol) were dissolved in 1-chloronaphthalene (1 ml). Then, the mixture was heated to 260 °C, under microwave irradiation ($P = 200$ W), for 1 h. After cooling to room temperature, the product was precipitated by addition of a solution of methanol/water (10:1) and it was left at 4 °C overnight. The blue precipitate was purified by column chromatography on silica gel using dichloromethane, followed by dichloromethane:methanol (95:5) as eluent. Yield: 555 mg (70%) of a blue solid. Spectroscopic data was in accordance with the literature [88].

4.3. General procedure of catalytic CO_2 addition reactions to epoxides

The catalytic reactions of CO_2 addition to epoxides were carried out in a stainless steel 120 mL autoclave. The catalyst (0.07 mol%) and co-catalyst (0.07 mol%) (when indicated) were placed in a glass beaker, inside the autoclave and it was left in vacuum for approximately 3 h, at 80 °C. Then, the epoxide substrate (4 ml), previously dried over alumina, was injected into the autoclave via cannula. The autoclave was then pressurized with CO_2 (10–40 bar) and the reaction proceeded at the desired temperature (80 °C). After 24 h, the autoclave was cooled and slowly depressurized. The % of conversion was determined by ^{1}H NMR of the crude mixture, using mesitylene as standard. Selectivity was calculated by integral ratio between polycarbonate and cyclic carbonate peaks. Product isolation and purification was carried out only when polymeric products were obtained (see below).

4.4. Isolation and characterization of poly(cyclohexanecarbonate)

The reaction crude was evaporated and the residue was dried in vacuum at 100 °C for 5 h. Then, the solid was washed with n-hexane, filtered and dried under vacuum at 100 °C for 12 h. The polymer was obtained in 50% yield (3.44 g), calculated from the mass of the isolated product relative to the weighted mass of epoxide and the CO_2wt of the catalyst and co-catalyst. The CO_2 content (%) was calculated from ^{1}H NMR data by the integral ratio between copolymer carbonate linkages (δ = 4.64 ppm) with respect to the ether linkage signals (δ = 3.57 ppm). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.65 (br s, 2H), 2.12 (br s, 2H), 1.71 (br s, 2H), 1.57–1.22 (br m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 153.8, 77.2, 29.7, 29.4, 23.1, 22.8.

Declaration of Competing Interest

The authors declare that they have no competing interests.

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