Homogeneous Catalysis

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Bifunctional Catalysts Based on *m*-Phenylene-Bridged Porphyrin Dimer and Trimer Platforms: Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides**

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Abstract: *Highly active bifunctional diporphyrin and triporphyrin catalysts were synthesized through Stille coupling reactions. As compared with a porphyrin monomer, both exhibited improved catalytic activities for the reaction of* CO_2 *with epoxides to form cyclic carbonates, because of the multiple catalytic sites which cooperatively activate the epoxide. Catalytic activities were carefully investigated by controlling temperature, reaction time, and catalyst loading, and very high turnover number and turnover frequency were obtained: 220 000 and 46 000* h^{-1}*, respectively, for the magnesium catalyst, and 310 000 and 40 000* h^{-1}*, respectively, for the zinc catalyst. Results obtained with a zinc/free-base hybrid diporphyrin catalyst demonstrated that the* Br^- *ions on the adjacent porphyrin moiety also function as nucleophiles.*

Over the last several decades, the chemical conversion of carbon dioxide (CO_2) into useful organic compounds has received considerable attention because CO_2 represents an abundant, inexpensive, and nontoxic C_1 source.[1,2] Although CO_2 is both kinetically and thermodynamically stable, recent progress in the catalytic conversion of CO_2 has been remarkable. The synthesis of cyclic carbonates from epoxides and CO_2 is promising because of high atom efficiency, and such carbonates have been widely used as raw materials for the production of polycarbonates, as well as electrolytes for lithium-ion secondary batteries, aprotic polar solvents, and fuel additives. Various catalysts have been developed to allow the efficient synthesis of cyclic carbonates from epoxides and CO_2, including salen-type complexes and metalloporphyrins.[3–6] Our group has reported the highly active bifunctional metalloporphyrin catalyst **1′**, in which the metal center and Br^- ion act as a Lewis acid and nucleophile, respectively (Figure 1 a,b and Scheme 1).[7] The reaction catalyzed by **1′** is initiated through nucleophilic attack by the Br^- ion on the less hindered side of the epoxide, along with simultaneous activation of the epoxide by coordination to the magnesium(II) center. Multiple cooperative interactions are the effective strategy frequently used in organocatalysis.[8] Following our previous work, we also developed a reusable organic-inorganic hybrid zinc(II) porphyrin catalyst immobilized on biogenous iron oxide.[7b] The zinc(II) complex was more effective than its magnesium(II) counterpart because of the stability of the former, and the zinc(II) complex could be

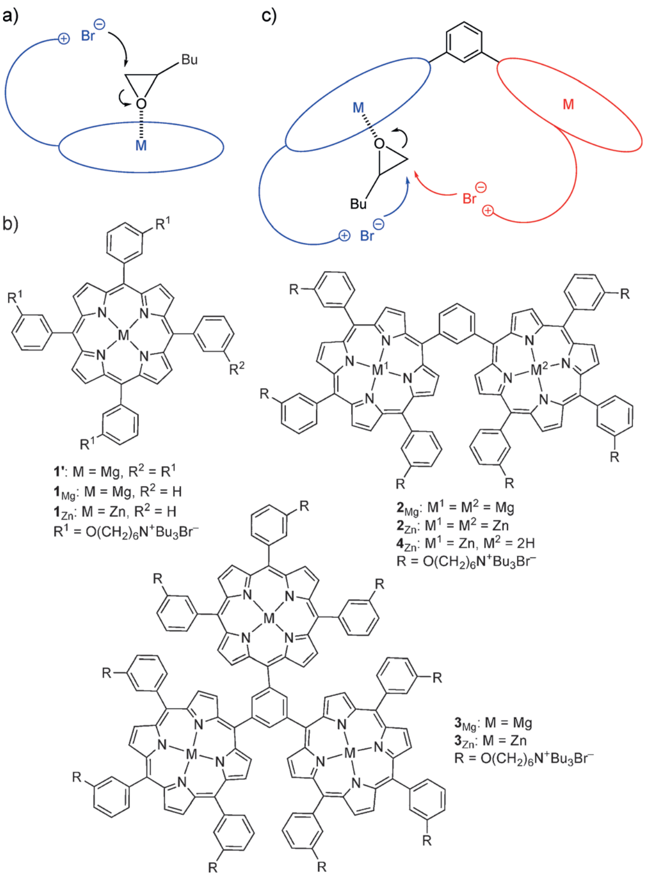
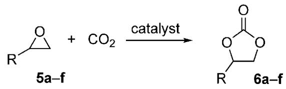


Figure 1. a) Cooperative activation of an epoxide with a bifunctional catalyst **1**. b) Structures of the bifunctional catalysts **1**–**4**. c) Two modes of activation of epoxide by bifunctional catalysts **2**–**4**.



5a: R = Bu **5d**: R = Ph
5b: R = C_8H_{17} **5e**: R = CH_2OPh
5c: R = $C_{12}H_{25}$ **5f**: R = CH_2Cl

Scheme 1. Synthesis of the cyclic carbonates **6a–f** from CO_2 and epoxides **5a–f**.

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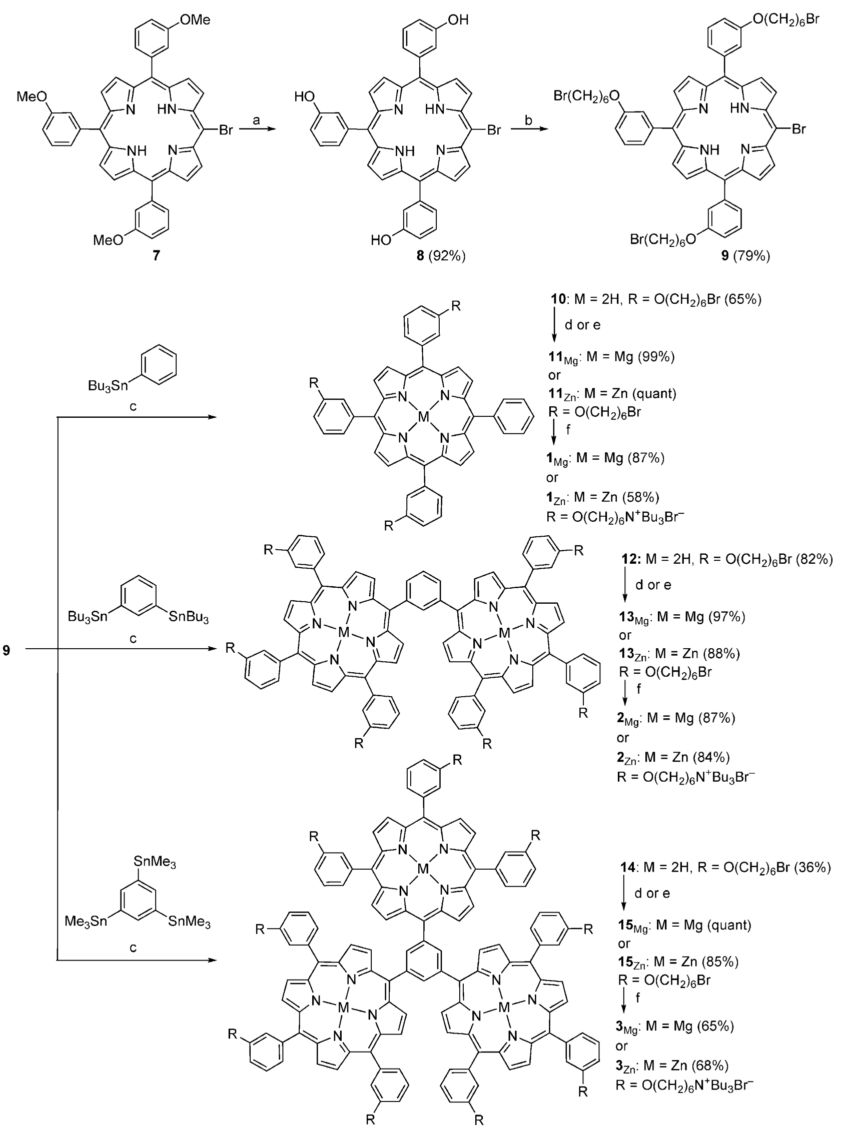
reused up to ten times without any loss of catalytic activity. Herein, we designed bifunctional metalloporphyrin dimers (**2**) and trimers (**3**; Figure 1 b). These porphyrin catalysts contain more active sites, in the form of multiple coordination sites with six or nine nucleophiles. We selected the *m*-phenylene-bridged platform because Br^- ions on the adjacent porphyrin moieties may function as better nucleophiles (Figure 1 c), which was strongly supported by a comparison of the catalytic activities of $\mathbf{1}_{Zn}$ and $\mathbf{4}_{Zn}$. Another motivation to construct the *m*-phenylene-bridged porphyrin dimers **2** and trimers **3** is to mimic the strategy of several enzymes which have evolved by dimerization or oligomerization to form and tune up a proficient catalytic site in a molecular cleft.[9] Herein we report that the bifunctional catalysts **2** and **3** are capable of showing very high turnover numbers (TONs) and turnover frequencies (TOFs) for the CO_2 fixation reaction.

The syntheses of the multiporphyrin catalysts are presented in Scheme 2. Magnesium(II) and zinc(II) ions, both of which showed good performance previously,[7] were employed as the metal centers. Treatment of 5-bromo-10,15,20-tris(3-methoxyphenyl)porphyrin (**7**)[10] with BBr_3 provided the trihydroxy-appended porphyrin **8**, and the subsequent alkylation of **8** with an excess amount of 1,6-dibromohexane produced 5-bromo-10,15,20-tris[3-(6-bromohexyloxy)phenyl]porphyrin (**9**). The Stille coupling reaction of **9** with 1,3,5-tris(trimethylstannyl)benzene provided the triporphyrin **14** in 36% yield.[11] Magnesium(II) metalation of **14** and reaction of $\mathbf{15}_{Mg}$ with tributylamine provided the triporphyrin catalyst $\mathbf{3}_{Mg}$. By applying the same Stille coupling strategy, $\mathbf{2}_{Mg}$ and the reference compound $\mathbf{1}_{Mg}$ were also readily obtained from **9** by using the corresponding tin-based reagents. In addition, the zinc(II) porphyrins $\mathbf{1}_{Zn}$, $\mathbf{2}_{Zn}$, and $\mathbf{3}_{Zn}$ were prepared by zinc(II) metalation of the free-base porphyrins **10**, **12**, and **14**, respectively, and subsequent reaction with tributylamine. The high-resolution electrospray ionization mass spectrum of $\mathbf{3}_{Zn}$ exhibited a parent ion peak at *m*/*z* 1639.1876 ($C_{282}H_{414}N_{21}O_9Br_6Zn_3$ $[M-3\,Br]^{3+}$ = 1639.1844).



Scheme 2. Synthesis of **1**–**3**. Reaction conditions: a) 1. BBr_3, CH_2Cl_2, −78 °C, 2. H_2O, RT; b) 1,6-dibromohexane, K_2CO_3, acetone, reflux; c) $[Pd(PPh_3)_4]$, CsF, toluene, reflux; d) $MgBr_2$, Et_3N, CH_2Cl_2, RT; e) $Zn(OAc)_2$, $CHCl_3$, MeOH, reflux; f) Bu_3N, $CHCl_3$, CH_3CN, reflux.

We initially examined the catalytic activities of $\mathbf{1}_{Mg}$–$\mathbf{3}_{Mg}$. The use of 0.003 mol% of $\mathbf{1}_{Mg}$ resulted in 80% conversion of 1,2-epoxyhexane (**5 a**) into the cyclic carbonate **6 a** after 3 hours, whereas using either $\mathbf{2}_{Mg}$ or $\mathbf{3}_{Mg}$ led to almost quantitative conversion within 3 hours (Table 1, entries 1–3). These results indicate that both $\mathbf{2}_{Mg}$ and $\mathbf{3}_{Mg}$ were more active than $\mathbf{1}_{Mg}$. When the catalyst loading was reduced, $\mathbf{2}_{Mg}$ showed twice the activity of that of $\mathbf{1}_{Mg}$, while the activity of $\mathbf{3}_{Mg}$ was comparable to that of $\mathbf{2}_{Mg}$, even though $\mathbf{3}_{Mg}$ has more active

Table 1: Synthesis of the cyclic carbonate **6 a** from CO_2 and epoxide **5 a** with bifunctional catalysts (see Scheme 1 for structures).[a]

Entry	Catalyst	Loading (mol%)	*t* [h]	Yield [%][b]
1	$\mathbf{1}_{Mg}$	0.003	3	80
2	$\mathbf{2}_{Mg}$	0.003	3	>99
3	$\mathbf{3}_{Mg}$	0.003	3	>99
4	$\mathbf{1}_{Mg}$	0.002	1	25
5	$\mathbf{2}_{Mg}$	0.002	1	49
6	$\mathbf{3}_{Mg}$	0.002	1	44
7	$\mathbf{1}_{Mg}$	0.0003	24	18
8	$\mathbf{2}_{Mg}$	0.0003	24	37
9	$\mathbf{3}_{Mg}$	0.0003	24	47
10	$\mathbf{3}_{Mg}$	0.001	6	96
11	$\mathbf{3}_{Zn}$	0.001	6	76
12	$\mathbf{3}_{Zn}$	0.0003	24	47

[a] Reaction conditions: **5 a** (1.0 g, 10 mmol), catalyst (quantity indicated above), CO_2 (initial pressure 1.7 MPa), 120 °C, in a 30 mL autoclave. [b] Determined by ^1H NMR spectroscopy using 2-methoxynaphthalene as an internal standard.

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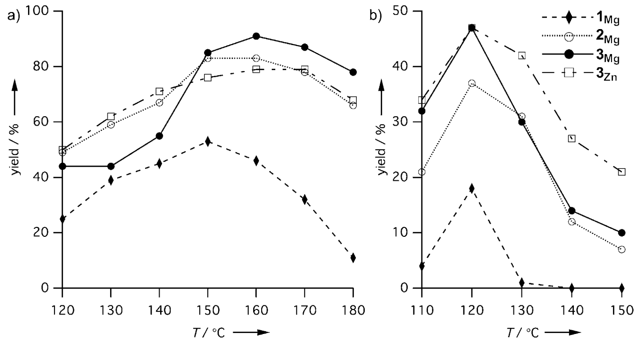

Figure 2. Effect of temperature on the synthesis of the cyclic carbonate **6a**. a) Reaction conditions: **5a** (1.0 g, 10 mmol), catalyst (0.002 mol%), CO_2 (1.7 MPa), 1 h; b) Reaction conditions: **5a** (1.0 g, 10 mmol), catalyst (0.0003 mol%), CO_2 (1.7 MPa), 24 h.

sites (entries 4–9). This result was attributed to the poor solubility of $\mathbf{3}_{Mg}$ (entry 6), so the effects of temperature and reaction time were also investigated. When the catalyst loading and reaction time were fixed at 0.002 mol% and 1 hour, respectively, the yield of **6a** increased with increasing temperature from 120 to 160 °C (Figure 2a and see Table S1 in the Supporting Information). Notably, $\mathbf{3}_{Mg}$ showed higher activity than $\mathbf{2}_{Mg}$ at temperatures above 150 °C, and its TOF reached 46000 h^{-1} at 160 °C. The yields decreased with a further increase in temperature above 160 °C, probably because the catalyst was decomposed at such high temperatures. At a reaction time of 24 hours, the maximum yield was observed with $\mathbf{3}_{Mg}$ at 120 °C, with a TON of 160000 (Figure 2b and see Table S2). These results indicate that both the solubility and the stability of the catalysts are significant.

The catalytic activities of the zinc(II) porphyrins were subsequently investigated. Although the zinc(II) porphyrin was slightly less active than the magnesium(II) porphyrin, the former was more stable, which increased its durability and reusability.[7b] Similar to the magnesium porphyrins, both $\mathbf{2}_{Zn}$ and $\mathbf{3}_{Zn}$ showed much higher catalytic activities than $\mathbf{1}_{Zn}$ (see Table S3). Importantly, although $\mathbf{3}_{Zn}$ was less active than $\mathbf{3}_{Mg}$ over a shorter period of time, cyclic carbonate was produced in greater yields by using $\mathbf{3}_{Zn}$ over a longer period of time (Table 1, entries 9–12, and Figure 3). The temperature dependencies of $\mathbf{3}_{Zn}$ and $\mathbf{3}_{Mg}$ demonstrated that $\mathbf{3}_{Zn}$ was more stable than $\mathbf{3}_{Mg}$ and that 120 °C was the optimum reaction temperature in both cases. In addition, the yield of the cyclic carbonate increased with reaction time, and this effect was most pronounced for $\mathbf{3}_{Zn}$. Notably, $\mathbf{3}_{Zn}$ showed higher activities than $\mathbf{1}_{Zn}$ at the same concentration, with respect to the metal center, and $\mathbf{3}_{Zn}$ (0.0003 mol%) retained its activity even after five days, thus achieving a TON of 310000 (Figure 3, and see Table S4).

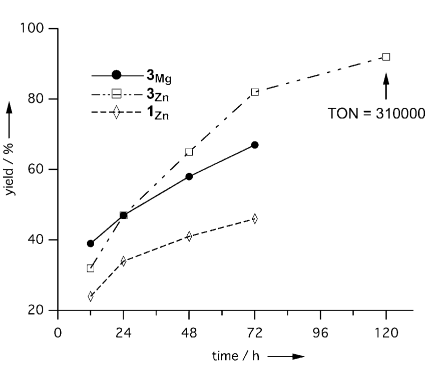

Figure 3. Time course for the production of the cyclic carbonate **6a**. Reaction conditions: **5a** (1.0 g, 10 mmol), $\mathbf{3}_{Mg}$ or $\mathbf{3}_{Zn}$ (0.0003 mol%) or $\mathbf{1}_{Zn}$ (0.0009 mol%), CO_2 (1.7 MPa), 120 °C.

We investigated the substrate scope of the highly active and stable catalyst $\mathbf{3}_{Zn}$. By using 0.002 mol% $\mathbf{3}_{Zn}$, various epoxides were efficiently converted into the corresponding cyclic carbonates, whereas more bulky substrate **5c** showed somewhat lower conversion (Table 2, entries 1–6). Even when 100 mmol of **5a** was used (tenfold scale), **6a** was isolated in 92% yield, which indicates that this reaction can be scaled up easily (entry 7). Although the yield of cyclic carbonate decreased when the CO_2 pressure was reduced, the reaction was found to take place under atmospheric CO_2 pressure (balloon), and **6a** was produced in acceptable yield by using 0.02 mol% (tenfold) of $\mathbf{3}_{Zn}$ (entries 8 and 9).

Table 2: Synthesis of the cyclic carbonate **6** from CO_2 and epoxide **5** with bifunctional catalysts (see Scheme 1 for structures).[a]

Entry	5	R	*t* [h]	Yield [%][b]
1	**5a**	Bu	12	99(94)[c]
2	**5b**	C_8H_{17}	12	96(95)[c]
3	**5c**	$C_{12}H_{25}$	12	70(67)[c]
4	**5d**	Ph	9	96(93)[c]
5	**5e**	CH_2OPh	12	93(91)[c]
6	**5f**	CH_2Cl	12	97(94)[c]
7[d]	**5a**	Bu	12	95(92)[c]
8[e]	**5a**	Bu	12	15
9[e,f]	**5a**	Bu	12	84

[a] Reaction conditions: **5** (10 mmol), catalyst $\mathbf{3}_{Zn}$ (0.002 mol%), CO_2 (1.7 MPa), 120 °C, in a 30 mL autoclave. [b] Determined by ^1H NMR spectroscopy using 2-methoxynaphthalene as an internal standard. [c] Yield of isolated product. [d] Reaction conditions: **5a** (100 mmol), $\mathbf{3}_{Zn}$ (0.002 mol%), CO_2 (2.5 MPa), 120 °C, in a 200 mL autoclave. [e] Under 0.1 MPa CO_2 atmosphere (balloon). [f] 0.02 mol% of $\mathbf{3}_{Zn}$ was used.

Finally, we attempted to further substantiate the validity of the molecular design (Figure 1c). To assess the effect of neighboring Br^- ions, we prepared the zinc(II)/free-base hybrid dimer $\mathbf{4}_{Zn}$ (Scheme 3). The Stille coupling reaction of **9** with 2.2 equivalents of bis(tributylstannyl)benzene provided **16** in 60% yield. Zinc(II) metalation of **16** followed by the Stille coupling reaction of the zinc(II) porphyrin **17** with free-base porphyrin **9** afforded the zinc(II)/free-base hybrid diporphyrin **18** in 64% yield. Finally, the reaction of **18** with tributylamine provided $\mathbf{4}_{Zn}$. Under the same reaction conditions, $\mathbf{4}_{Zn}$ produced **6a** to a greater extent than $\mathbf{1}_{Zn}$, which indicates that the Br^- ions on the free-base porphyrin moiety in $\mathbf{4}_{Zn}$ also act as nucleophiles (Table 3, entries 1 and 2). This result suggests that the Br^- ions on the neighboring porphyrins in **2** and **3** contribute to the enhancement of the catalytic activities. Certainly, when the catalyst loading was equal, $\mathbf{2}_{Zn}$ and $\mathbf{3}_{Zn}$ showed higher catalytic activities than that of either $\mathbf{1}_{Zn}$ or $\mathbf{4}_{Zn}$ (entries 3 and 4).

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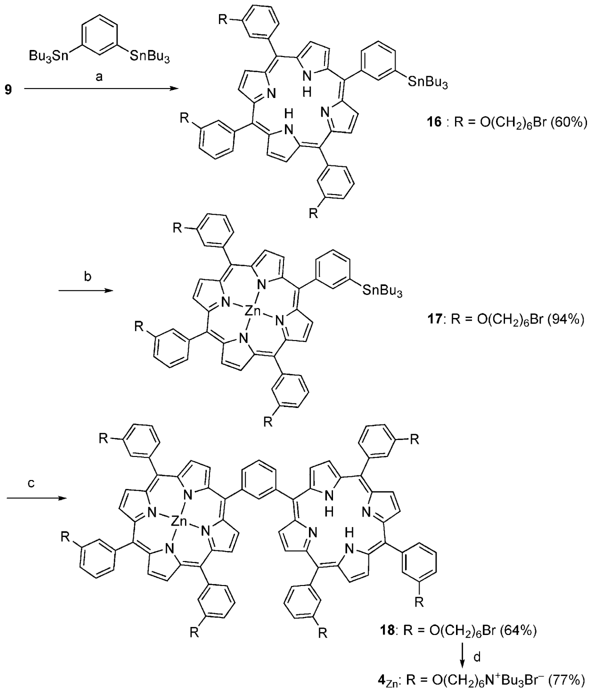

Scheme 3. Synthesis of $\mathbf{4}_{Zn}$. Reaction conditions: a) [Pd(PPh$_3$)$_4$], CsF, toluene, reflux; b) Zn(OAc)$_2$, CHCl$_3$, MeOH, reflux; c) **9**, [Pd(PPh$_3$)$_4$], CsF, toluene, reflux; d) Bu$_3$N, CHCl$_3$, CH$_3$CN, reflux.

Table 3: Synthesis of **6a** from CO$_2$ and **5a** with bifunctional catalysts.[a]

Entry	Catalyst	Loading (mol%)	t [h]	Yield [%][b]
1	$\mathbf{1}_{Zn}$	0.003	3	51
2	$\mathbf{4}_{Zn}$	0.003	3	77
3	$\mathbf{2}_{Zn}$	0.003	3	82
4	$\mathbf{3}_{Zn}$	0.003	3	92

[a] Reaction conditions: **5a** (1.0 g, 10 mmol), catalyst (0.003 mol%), CO$_2$ (1.7 MPa), 120 °C, in a 30 mL autoclave. [b] Determined by ^{1}H NMR spectroscopy using 2-methoxynaphthalene as an internal standard.

In summary, we successfully synthesized bifunctional multiporphyrin catalysts **2** and **3** through Stille coupling reactions. These compounds efficiently catalyzed the reactions of epoxides with CO$_2$ to form cyclic carbonates under solvent-free conditions. Despite the six and nine ion pairs in **2** and **3**, respectively, which might decrease the solubility in epoxide, the catalytic activities of **2** and **3** were much higher than that of **1**. The maximum TON and TOF were 220 000 and 46 000 h^{-1}, respectively, for $\mathbf{3}_{Mg}$ and 310 000 and 40 000 h^{-1}, respectively, for $\mathbf{3}_{Zn}$. To the best of our knowledge, they are the highest values reported thus far for the synthesis of cyclic carbonates from epoxides and CO$_2$. The TOF value of 46 000 h^{-1} is equal to 13 s^{-1}, which is close to the lowest limit of the k_{cat} values (10^2–10^6 s^{-1}) for enzymatic reactions in water at ambient temperature.[12] These data clearly demonstrate that proficient catalytic sites are formed in the molecular cleft of *m*-phenylene-bridged porphyrin dimers **2** and trimers **3**.

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