

Metal–Organic Polymers Containing Discrete Single-Walled Nanotube as a Heterogeneous Catalyst for the Cycloaddition of Carbon Dioxide to Epoxides

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Supporting Information

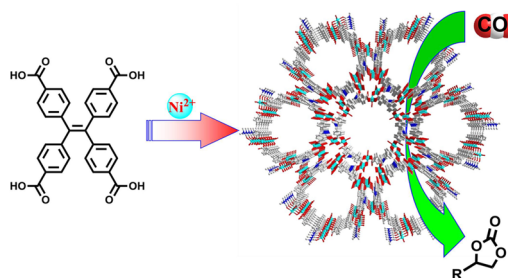
ABSTRACT: The cycloaddition of carbon dioxide to epoxides to produce cyclic carbonates is quite promising and does not result in any side products. A discrete single-walled metal–organic nanotube was synthesized by incorporating a tetraphenyl-ethylene moiety as the four-point connected node. The assembled complex has a large cross-section, with an exterior wall diameter of 3.6 nm and an interior channel diameter of 2.1 nm. It features excellent activity toward the cycloaddition of carbon dioxide, with a turnover number of 17,500 per mole of catalyst and an initial turnover frequency as high as 1000 per mole of catalyst per hour. Only minimal decreases in the catalytic activity were observed after 70 h under identical reaction conditions, and a total turnover number as high as 35,000 was achieved. A simple comparison of relative porous MOFs suggested that the cross-section of the channels is an important factor influencing the transport of the substrates and products through the channel.

Catalysts based on permanently porous or channel frameworks have the potential to unify the best features of homogeneous and heterogeneous catalysts.^{1–3} Considered to be promising analogues of carbon nanotubes, single-walled tubal metal–organic frameworks (MOFs) constructed by organic linkers and metal ions or clusters have attracted a great deal of attention because of their intriguing structural diversity and outstanding physical and chemical properties.^{4–6} Their modular nature and facile tunability makes these materials ideal heterogeneous catalysts because they possess active sites and accessible channels for the attraction and retention of substrates.^{7,8} However, from a synthetic point of view, the fabrication of well-defined single-walled metal–organic nanotube requires relatively extreme synthesis conditions, which leads to difficulties in the precise control of their size and shape.⁹ An ongoing challenge for the development of efficient metal–organic tubal catalysts includes the careful selection and incorporation of the catalytic sites within the original building blocks. Furthermore, strict control of the assembling processes is critical for the accurate positioning of these catalytic sites within the inner surface of the discrete nanotubal frameworks.¹⁰

In terms of catalysis, the efficient transformation of carbon dioxide into useful chemicals under mild conditions is very attractive both industrially and academically because it is an

inexpensive and abundant renewable C1 building block and is recognized to be environmentally benign.^{11,12} According to green chemistry and atomic economy, the cycloaddition of carbon dioxide to an epoxide to produce cyclic carbonates is quite promising, as the latter compounds are used widely in industry and the incorporation of carbon dioxide into these chemicals does not result in any side products.^{13–15} Inspired by advances in homogeneous catalysts with high activity and heterogeneous catalysts with excellent selectivity,^{16–18} we herein report the synthesis and catalytic properties of a single-walled metal–organic nanotube Ni–TCPE1 for the cycloaddition of carbon dioxide by the incorporation of the tetrakis(4-carboxyphenyl)ethylene (H₄TCPE) moiety as the four-point connected node (Scheme 1). We envisioned that the partially

Scheme 1. View of the Isolated Metal–Organic Nanotubes in the Crystals^a



^aConstitutive/constructional fragments are shown.

twisted ethyl core and multiple rotational phenyl rings would cause a nonplanar configuration of the ligand,¹⁹ benefiting the formation of highly connected frameworks. Relative to the phenyl rings, the weak π -stacking interactions are expected to stabilize hierarchical structures with loose molecular packing and good structural transformability, favoring the formation of diverse structures. Besides, a (4,4)-network Ni–TCPE2 was obtained under the similar synthetic conditions, demonstrating that strict control of the synthetic conditions is of great significance during the self-assembly.

The solvothermal reaction of Ni(NO₃)₂·6H₂O, H₄TCPE and L-proline (L-Pro) in a mixture of DMF and H₂O at 373 K for 3

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days gave the compound Ni–TCPE1 in 10% yield. Elemental and powder X-ray diffraction (XRD) analyses indicated that the bulk sample consisted of a pure, single phase (Figure S5). Single-crystal X-ray structural analysis revealed that Ni–TCPE1 crystallizes in the *P*-3 space group. L-Pro serves only as a template for the synthesis; it is not detected in the final, pure crystal products. Two carboxylate groups and one water molecule bridge two octahedral and independent nickel ions. The Ni₂ unit that connects to four carboxylate groups from four different ligands acts as a four-point connected node (Figure 1a).

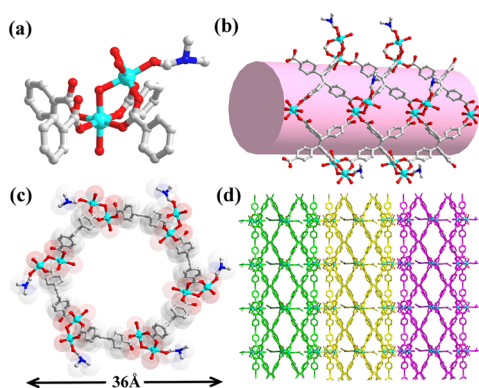


Figure 1. (a) Structure of Ni–TCPE1 showing the binuclear Ni₂ unit; (b) the side view of the 1D nanotube with the pink column representing the channel; (c) the top view of the nanotube; (d) the packing pattern between them along the *b* axis. Color code: Ni, cyan; O, red; N, blue; C, gray. The H atoms and lattice solvents are omitted for clarity.

Each of this deprotonated TCPE ligand connects to four Ni₂ units and also serves as a four-point connected node (Figure 1b). Accordingly, the skeleton of Ni–TCPE1 with this topology is considered to consist of equivalent linkers and four-point connected nodes; a large open-ended, single-walled metal–organic nanotube is formed. The top view of the nanotube indicates that it is an undulated hexanuclear metallamacrocycle with a large 90-membered ring consisting of six nickel atoms and six TCPE ligands with S₆ symmetry. Notably, Ni–TCPE1 has a large cross-section, with an exterior wall diameter of 3.6 nm and an interior channel diameter of 2.1 nm (Figure 1c). To the best of our knowledge, it represents the largest discrete single-walled metal–organic nanotube reported to date.

Ni–TCPE1 can be regarded as a nanotube folded from a (4,4)-topological sheet. Analogous to other types of single-walled carbon nanotubes, it is instructive to consider how the (4,4) square is rolled to create the nanotubes. The tube axis is along the *a* direction diagonal to the (4,4)-square layer. The large nanotubes are anchored together by hydrogen bonds involving the coordinated water molecules around the Ni(2) ions and the lattice water molecules. The nanotubes are closely packed in a hexagonal manner to form a three-dimensional (3D) structure. The PLATON program was used to calculate the void volume of Ni–TCPE1. A void volume of ~4600 Å³ per unit cell (~51% of the cell volume) was determined. For the structures, the contribution of heavily disordered solvent molecules was treated by the Squeeze procedure. The side view of the framework reveals other quadrangular openings with effective dimensions of 8.4 × 8.4 Å² along *a* and *b* axes.

From the structure analysis view, Ni(1) atom is positioned on the inner surface of the tube. Dye-uptake studies were performed by soaking Ni–TCPE1 in a methanol solution containing 2',7'-dichlorofluorescein. These experiments gave a quantum uptake

equivalent to 8.0% of the MOFs' weight (Figure S12a). Confocal laser scanning microscopy of the guest-adsorbed crystals gave a strong green fluorescence response²⁰ that can be assigned to fluorescein (Figure S12f). The uniform distribution of the dye molecules throughout the crystals suggests that the dyes penetrated deeply into the channels, rather than remaining on the external surface.²¹ The results demonstrate the ability of Ni–TCPE1 to adsorb organic substrates within its open channels. The tube-like structure with modified open metal sites provides adequate space for CO₂ uptake and promotes highly selective and efficient chemical transformations (Table 1).^{22–24} It was found that the CO₂ uptake of Ni–TCPE1 was as high as 47.8 cm³ g⁻¹ at 273 K and 32.8 cm³ g⁻¹ at 298 K (Figure 2c).

Table 1. Ni–TCPE-Catalyzed Coupling of Epoxides with CO₂

| Entry | Substrate | Ni-TCPE1 | | Ni-TCPE2 | |
|----------------|-----------|-----------|------|-----------|------|
| | | Yield (%) | TON | Yield (%) | TON |
| 1 ^a | | >99 | 2000 | 86.2 | 1720 |
| 2 ^a | | >99 | 2000 | 97.7 | 1950 |
| 3 ^a | | 95.7 | 1910 | 94.2 | 1890 |
| 4 ^b | | 93.7 | 1880 | 92.6 | 1850 |

^aReaction conditions: epoxide (20 mmol), catalyst (10 μmol, based on Ni), and TBABr (0.3 mmol) under carbon dioxide (1 MPa), 373 K and 12 h. The yields were determined by ¹H NMR analysis. ^bUnder common conditions, but without the epoxide (10 mmol).

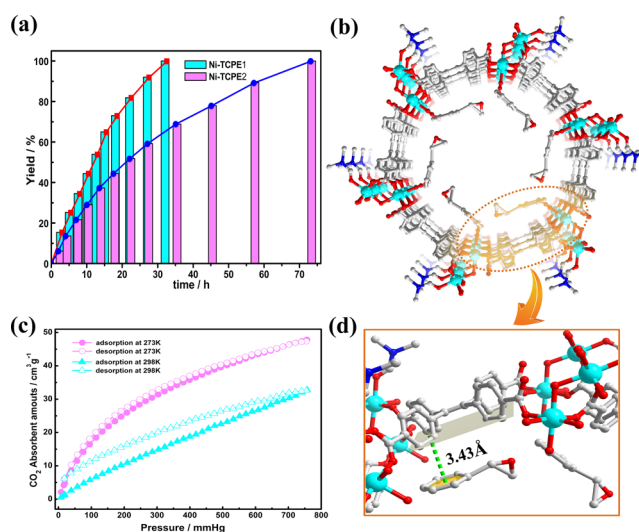


Figure 2. (a) Histogram of the yields of excessive styrene oxide using Ni–TCPE under standard conditions (CO₂ pressure was increased to 1 MPa when the pressure decreased to 0.4 MPa); (b) the structure of styrene-oxide-impregnated species Ni–TCPE1'; (c) CO₂ adsorption isotherms of Ni–TCPE1 measured at 273 and 298 K; and (d) enlarged view of the Ni–TCPE1' showing the positions of the substrate and the interactions between the tube and the substrate.

Our catalytic experiments were focused on the cycloaddition of carbon dioxide and epoxides. In a typical experiment, the reactions were conducted in an autoclave reactor using the epoxide (20 mmol) with carbon dioxide purged to 1 MPa under a solvent-free environment at 373 K. In the presence of 0.3 mmol of tetrabutylammonium bromide (TBABr), the loading of 0.5 mol% ratio of Ni–TCPE1 (based on Ni) afforded an almost complete conversion within 12 h. The TOF was \sim 165 per mole of catalyst per hour. No significant change in the conversion was observed when the phenyl group in styrene oxide was substituted for a phen-oxymethyl group. The introduction of oxiran-2-ylmethoxy or methoxy groups onto the phenyl ring gave \sim 96% and 94% of the respective products under the same reaction conditions. When the reactant was the enantiopure *R*- or *S*-styrene oxide, the reaction of carbon dioxide gave excellent enantioselectivity (with an ee value of \sim 92%) (Table S4). The retention of chirality demonstrated that the selective ring opening occurred preferentially at the methylene C–O bond of the terminal epoxides.^{25,26} The loading of excessive styrene oxide (87.5 mmol) with the unchanged quantity of Ni–TCPE1 (5 μ mol) gives an initial TOF up to 1000 per mole of catalyst per hour. To the best of our knowledge, this value is greater than any previously reported value for MOF-based catalysts for the cycloaddition of carbon dioxide to epoxides under the similar conditions,^{27,28} and Ni–TCPE1 also exhibited high efficiency even under atmospheric pressure of carbon dioxide, at room temperature (Table S7).^{29,30}

Recyclability is an essential feature of any catalyst considered for use in industrial applications. As for the small amount of catalyst in a reaction, the unavoidable loss of the catalyst would course inaccurate decrease of yields after each reaction (Table S3). In this regard, experiments were performed using a large excess of styrene oxide (87.5 mmol) and Ni–TCPE1 (5 μ mol) and by maintaining the pressure of the system (from 0.4 to 1.0 MPa) by adding carbon dioxide (Figure 2a). No other reaction conditions were altered. These time-course experiments gave a total TON value of 17,500 per mole of catalyst after 10 times of catalysis (32.5 h). Dye uptake studies on the recovered catalysts revealed that they exhibited 2',7'-dichlorofluorescein uptake ability (7.6%) almost identical to that of the original catalyst. Most important, only a slight decrease in the catalytic activity is observed after 70 h reaction, and a total TON value of 35,000 for Ni–TCPE1 was achieved after 20 times of repeating catalytic reaction. It should be noted that such a high value of TON ($>$ 20,000) reveals that Ni–TCPE1 has the broad prospects for the practical application in the chemical industry for the carbon dioxide cycloaddition to cyclic carbonates.

The quality of the styrene-oxide-impregnated crystals Ni–TCPE1 was sufficient for X-ray structural analysis (noted as Ni–TCPE1'). The same space group and almost identical cell dimensions between the impregnated crystals and the original crystals confirmed that the Ni–TCPE1 framework was maintained (Figure 2b). Multifold edge-to-face aromatic interactions were observed between the phenyl groups of the TCPE ligands and those of the substrates, with the shortest interatomic separation being 3.43 Å (Figure 2d). IR spectrum of Ni–TCPE1' revealed two epoxy vibration peaks at 982 and 871 cm^{-1} (Figure S10). ^1H NMR of the crystals Ni–TCPE1' in $\text{DMSO-}d_6/\text{DCl}$ exhibits the characteristic peaks of styrene oxide with significant downfield shifts of free styrene oxide (Figure S11). The obvious shifts of ^1H NMR and IR spectra compared with the free styrene oxide suggested the adsorption and the activation of the styrene oxide in the channels of the MOFs. The

cooperative weak interactions enforced the spatial proximity between the adsorbed substrates and the nickel ions. After the coordinating water molecules are removed, open Ni active sites in the pores of desolvated Ni–TCPE1 might be activated and can serve as Lewis acid catalytic sites to activate the epoxy ring through the oxygen atom of epoxide and also can serve as charge-dense binding sites that capture carbon dioxide because of its compatible quadrupole moment and polarizability.^{31,32} From a mechanistic point of view, the reaction is initiated by Br^- generated from TBABr, which attacks the less-hindered methylene carbon atom of the activated epoxide to open the epoxy ring.^{33,34} The activated epoxide intermediate reacts with activated carbon dioxide to yield a cyclic carbonate with high efficiency and selectivity.

Ni–TCPE2 was obtained with the similar synthetic procedures when the amount of *L*-Pro was increased, and it crystallized in chiral space group *C2*. This structure contains a disparate metal cluster of three Ni(II) ions with different coordination modes. The linear Ni_3 clusters are bridged by three μ_2 -oxygen atoms, one oxygen atom from *L*-Pro molecule, and six oxygen atoms that belong to four carboxylic groups of TCPE ligands (Figure 3a). The Ni atoms are coordinated in an

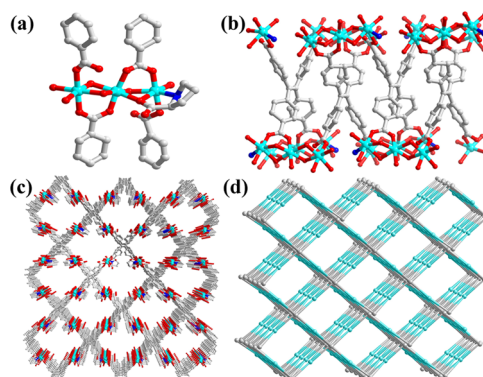


Figure 3. (a) The structure of the Ni_3 unit in Ni–TCPE2; (b) the side view of the channels displaying the environments of TCPE; (c and d) the truncated 3D structure and schematic representation of the PtS-type network. Color code: Ni, cyan; O, red; N, blue; C, gray. H atoms are omitted for clarity.

octahedral fashion; one of Ni atom from one side of cluster is coordinated to the N and O atoms within one *L*-Pro molecule and one lattice water molecule, while the other side of Ni atom is directly coordinated to two lattice water molecules. The Ni_3 clusters are cross-linked through carboxylic groups from TCPE to generate a 3D extended network with 1D quadrilateral channels of $17.9 \times 17.9 \text{ \AA}^2$ when viewed along the *c* direction (Figure 3c). In the absence of guest molecules, the effective free volume of Ni–TCPE2 was calculated using PLATON to be 46.4% of the crystal volume. The Ni_3 clusters are regarded as four-point-connected nodes, and the ligands are considered to be the linkers. The overall framework can be regarded as a PtS topology with the Schläfli symbol 4^28^4 . The CO_2 uptake of Ni–TCPE2 was declined to $44.7 \text{ cm}^3 \text{ g}^{-1}$ at 273 K and $29.9 \text{ cm}^3 \text{ g}^{-1}$ at 298 K (Figure S13).

Ni–TCPE2 exhibits efficient activity toward the cycloaddition of carbon dioxide to epoxides. The activity of Ni–TCPE2 is significantly lower than that of Ni–TCPE1, though the two catalysts contain the same amount of open metal sites. The recycling experiment was based on large excess of styrene oxide (87.5 mmol) and Ni–TCPE2 (5 μ mol). After 10 times of

reaction over a period of 72 h, a total TON value of 17,500 per mole of catalyst was achieved. This lower activity is partly attributed to the different weak interactions between the guest and pore-wall molecules³⁵ and to the potential pore blockage in Ni–TCPE2 by carbonaceous material formed during the reaction.^{36,37} These results manifest that the size of the channels is an important factor that controls the efficiency of the conversion by influencing the transport of the substrates and products through the channels.³⁸

In conclusion, a new material comprised discrete single-walled metal–organic nanotube was synthesized by incorporating the tetraphenylethylene moiety as the backbone and subsequently used as a heterogeneous catalyst for the cycloaddition of carbon dioxide to epoxides. This material represents the largest cross section of the reported single-walled metal–organic nanotubes. It features the strong stability and highest activity with a turnover number reach to 35,000 per mole of catalyst after 20 times (70 h) repeating reactions, further indicating the broad prospects of the nanotubes for the practical application in the chemical industry for the carbon dioxide cycloaddition to cyclic carbonates. Control experiments based on the 3D framework revealed the superiority of the large cross-section of the nanotubes. The excellent catalytic activity and better stability suggest that the new approach for the construction of metal–organic nanotubes as efficient heterogeneous catalysts is promising.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07925.

Experimental details and data (PDF)

Crystal data (CIF)

Crystal data (CIF)

Crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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