Delocalized electron effect on single metal sites in ultrathin conjugated microporous polymer nanosheets for boosting CO$_2$ cycloaddition

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CO$_2$ cycloaddition with epoxides at low temperature and pressure has been broadly recognized as an ambitious but challenging goal, which requires the catalysts to have precisely controlled Lewis acid sites. Here, we demonstrate that both stereochemical environment and oxidation state of single cobalt active sites in cobalt tetraaminophthalocyanine [CoPc(NH$_2$)$_4$] are finely tuned via molecular engineering with 2,5-di-tert-butyl-1,4-benzoquinone (DTBBQ). Notably, DTBBQ incorporation not only enables formation of 5-nm-thick conjugated microporous polymer (CMP) nanosheets due to the steric hindrance effect of tert-butyl groups but also makes isolated cobalt sites with high oxidation state due to the presence of delocalized electron-withdrawing effect of alkene groups in DTBBQ via conjugated skeleton. Notably, when used as heterogeneous catalysts for CO$_2$ cycloaddition with different epoxides, single cobalt active sites on the ultrathin CMP nanosheets exhibit unprecedentedly high activity and excellent stability under mild reaction conditions.

INTRODUCTION

Catalysis of CO$_2$ and various epoxides into rich five-membered cyclic carbonates serves a twofold purpose: attenuation of anthropogenic greenhouse gas (1) and acquisition of high value-added products such as electrolytes in secondary batteries, monomers of polycarbonates and polyurethanes, aprotic polar solvents, and intermediates of fine chemicals (2–4). To date, production of numerous cyclic carbonates via CO$_2$ cycloaddition has been successfully industrialized based on homogeneous Lewis acid catalysts assisted with Lewis base co-catalysts (5–7); however, difficult separation of catalysts and products brings additional cost and time (8). To address the separation problem, Lewis acid–containing solids like metal oxides (9), metal-organic frameworks (MOFs) (3, 10, 11), and conjugated microporous polymers (CMPs) (12–16) have been tried as heterogeneous catalysts. Among those, we suppose that metal ion containing CMPs characteristic of permanent micropores, metal-macrocyle node, and π-conjugated skeleton will be the ideal catalysts owing to a couple of unique merits. Similarly to MOFs, well-dispersed single metal centers inside CMPs could maximize the catalytic performance. Furthermore, the coordination number of the metal centers inside CMPs is usually lower than that inside MOFs (e.g., 4-coordinated cobalt in Co-CMP versus 6-coordinated cobalt in MOF-74) (17, 18), likely facilitating coordination and activation of the substrate molecules. However, the activity of all the reported heterogeneous catalysts including CMPs is generally low, especially for CO$_2$ cycloaddition with large-sized epoxides. The reason why CMPs do not exhibit obvious advantage over metal oxides and MOFs originates from their three-dimensional (3D) amorphous nature, which makes control over the size, shape, and structure much more difficult when used as catalysts (19).

In this work, we demonstrate that simple design on bridging molecules could simultaneously regulate the morphology of CMPs and achieve the delocalized electron-withdrawing effect on inner single metal sites in the conjugated skeleton. Cobalt tetraaminophthalocyanine [CoPc(NH$_2$)$_4$], which is a neutralized unit characteristic of one Co$^{2+}$ and two N$^-$ with losing two hydrogen atoms (20) and is known as an efficient molecular catalyst in many homogeneous reactions including CO$_2$ cycloaddition (1), is selected as the basic building blocks, and 2,5-di-tert-butyl-1,4-benzoquinone (DTBBQ) is adopted as the bridging molecules because of the following reasons (Fig. 1). The di-carbonyl group in DTBBQ reacts with amino group in CoPc(NH$_2$)$_4$, giving rise to the formation of heterogeneous CMP catalysts (DTBBQ-CMP). Meanwhile, the tert-butyl group in DTBBQ possibly provides the steric hindrance and thus weakens the interlayer interactions, leading to facile production of 2D ultrathin DTBBQ-CMP nanosheets. There are rich and isolated cobalt active sites uniformly exposed on the nanosheet surfaces, which would promote CO$_2$ cycloaddition. The charge distribution of single cobalt sites in CoPc unit might be tuned by coordinating with DTBBQ via the conjugated skeleton. To verify this hypothesis, the commonly used 1,4-phthalaldehyde (BDA) also reacts with CoPc(NH$_2$)$_4$ to produce BDA-CMP aggregates (Fig. 1) (19, 21). Density functional theory (DFT) calculation reveals that the positive charge of single cobalt sites in DTBBQ-CMP nanosheets increases by 13% compared with BDA-CMP aggregates owing to the presence of delocalized electron-withdrawing effect of alkene groups in DTBBQ (fig. S1), which thus enhances the interaction with epoxides for substrate activation. It is noted that the delocalized electron effect on single cobalt sites in CMP nanosheets could be easily achieved via the conjugated skeleton, which is distinct from the metal oxides and MOFs.

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The measured specific surface area of nanosheets is only 16 m² g⁻¹, spectroscopy (ICP-OES) indicates ~6 weight % (wt %) cobalt inside. The distribution of cobalt is confirmed by energy-dispersive x-ray mapping of cobalt, carbon, and nitrogen elements are evenly distributed in the nanosheets (Fig. 2E), and the quantitative measurement by inductively coupled plasma–optical emission spectroscopy (XPS) survey. The Co 2p³/₂ binding energy in ultrathin DTBBQ-CMP nanosheets is 781.0 eV, higher than 780.7 eV for ultrathin DTBBQ-CMP aggregates, indicating a high oxidation state of Co (attributed to 1e⁻). The Co K-edge extended x-ray absorption fine structure (EXAFS) spectrum in R-position indicates ~6 weight % (wt %) cobalt inside. The measured specific surface area of nanosheets is only 16 m² g⁻¹, which is reasonable because the tert-butyl groups attached on the scaffolds likely block the pores inside nanosheets.

**RESULTS AND DISCUSSION**

**Synthesis and characterization of CMP nanosheets with single cobalt active sites**

In brief, DTBBQ-CMP is synthesized via Schiff-base polymerization between CoPc(NH₂)₄ and DTBBQ (Fig. 2A and figs. S2 to S4), which is proved by appearance of characteristic C=N stretching vibration peak at 1605 cm⁻¹ in Fourier transform infrared (FTIR) spectrum (Fig. S5) (19, 22). As-prepared DTBBQ-CMP products are flexible and ultrathin nanosheets (Fig. 2B and figs. S6 and S7), with a uniform thickness of ~5 nm (Fig. 2, C and D). The corresponding elemental mapping demonstrates that cobalt, carbon, and nitrogen elements are evenly distributed in the nanosheets (Fig. 2E), and the quantitative measurement by inductively coupled plasma–optical emission spectroscopy (ICP-OES) indicates ~6 weight % (wt %) cobalt inside. The measured specific surface area of nanosheets is only 16 m² g⁻¹, which is reasonable because the tert-butyl groups attached on the scaffolds likely block the pores inside nanosheets. Thermal gravimetric (TG) analysis shows that, at up to 200°C, only 0.58 wt % mass loss is observed, and the obvious weight loss occurs at the temperature around 560°C (Fig. S9), suggesting good thermal stability of DTBBQ-CMP nanosheets. The Co K-edge extended x-ray absorption fine structure (EXAFS) spectrum in R-position indicates the dominant peak at 1.47 Å (without phase correction), corresponding to the first coordination shell of cobalt atom in cobalt nitrogen bond (Co–N) (black curve in Fig. 2F). Fitting this peak denotes the bond distance of 1.90 Å (Fig. S10, A and C, and table S2). The 4-coordination mode of cobalt center with high D₄h symmetry in CoPc unit is further discerned by the pre-edge shoulder at 7709 eV (attributed to 1s–4p₂ transition) in Co K-edge x-ray absorption near edge structure (XANES) spectrum (black curve in Fig. 2G). Both EXAFS and XANES results highlight that the single cobalt active sites are well retained in ultrathin nanosheets.

Both experiment and calculation are carried out to elucidate the structure of ultrathin DTBBQ-CMP nanosheets. The layered feature of nanosheets is recognized by powder x-ray diffraction pattern, in which there are two distinct peaks at 2θ = 9.9° and 20.4° (Fig. S11). Note that the (001) peak at 2θ = 20.4° presents the perfect AA stacking is not the energetically most favorable and the most low-lying configuration exhibits slight mismatch of ~2 Å along the Y axis (red dot at the right bottom corner in Fig. 3C). The interlayer distance is 4.4 Å and the total thickness of nanosheets is 5 nm (Fig. 3E), one easily estimates that the ultrathin nanosheets contain 10 monolayers according to the equation (n + 1) * 0.44 ≈ 5, where n is the monolayer number (Fig. S12).

In addition, the contrast sample of CMP aggregates, which is prepared with BDA and CoPc(NH₂)₄ via formation of C=N bond (Fig. 1 and Fig. S13), is fully characterized. The obtained products are 3D amorphous aggregates in sizes of several hundred nanometers to several micrometers that are caused by strong π–π stacking between the adjacent units (Figs. S14 to S16). The specific surface area of BDA-CMP aggregates is 126 m² g⁻¹ (Fig. S17 and table S1), considerably larger than 16 m² g⁻¹ of ultrathin DTBBQ-CMP nanosheets. The coordination number of cobalt is also 4 in BDA-CMP aggregates (red curve in Fig. 2F, fig. S10, B and C, and table S2) (17, 25).

**Oxidation state of single cobalt active sites in CMP nanosheets**

Specially, XANES spectra manifest that the Co K-edge absorption of ultrathin DTBBQ-CMP nanosheets shifts to higher energy compared with BDA-CMP aggregates (black and red curves in Fig. 2G), indicating that single cobalt sites have less electrons in ultrathin DTBBQ-CMP nanosheets. This deduction is reinforced by x-ray photoelectron spectroscopy (XPS) survey. The Co 2p₃/₂ binding energy in ultrathin DTBBQ-CMP nanosheets is 781.0 eV, higher than 780.7 eV for BDA-CMP aggregates (Fig. S18), but no signal for trivalent cobalt ion is found. Both XANES and XPS data are in good agreement with the calculation result (Fig. S1), disclosing that the presence of electron-withdrawing alkene groups in the bridging molecule...
DTBBQ gives rise to higher oxidation state of single cobalt sites in DTBBQ-CMP.

**Catalytic CO₂ cycloaddition with propylene oxide**
Both ultrathin DTBBQ-CMP nanosheets and BDA-CMP aggregates are used as catalysts for coupling reaction of CO₂ and propylene oxide (PO; molecular size = 0.61 nm × 0.50 nm; fig. S19) with assistance of the co-catalyst tetrabutyl ammonium bromide (TBAB). Entries 1 to 5 in Table 1 summarize the test results. Without catalysts, the coupling reaction of CO₂ and PO might occur, but the yield of propylene carbonate (PC) is only 16.8% after a 48-hour reaction at room temperature (25°C) and atmospheric pressure (Table 1, entry 3). When BDA-CMP aggregates are used as catalysts, the yield of PC increases to 71.4% with a turnover number (TON) value of 2069 (Table 1,
entry 4); by increasing the BDA-CMP amount (5 versus 10 mg), the TBAB amount (0.06 versus 0.09 mmol), and the CO$_2$ pressure (0.1 versus 0.5 MPa), the yield of PC slightly enhances to 82.3% with a TON value of 2389 (Table 1, entry 5). Significantly, the ultrathin DTBBQ-CMP nanosheets exhibit an excellent catalytic activity, and the yield of PC reaches 99% with a TON value of 2903 at room temperature and atmospheric pressure (Table 1, entry 1, and fig. S20). We notice that without the co-catalyst TBAB, the yield is merely 10.4% with a low TON value of 301 for PC (Table 1, entry 2), suggesting that the synergistic effect between DTBBQ-CMP nanosheets and TBAB plays a crucial role in effective CO$_2$ cycloaddition. In addition, the reusability experiment indicates that the yield of target product PC remains almost unchanged for ultrathin DTBBQ-CMP nanosheets during five successive catalytic cycles regardless of whether the conversion ratio is set to 84.6 or 99% (figs. S21 and S22). This high stability is verified by transmission electron microscopy (TEM) observation, solid-state nuclear magnetic resonance (NMR), FTIR analysis, and x-ray diffraction (XRD) pattern (19), where no obvious structural and chemical difference between the fresh and used catalysts is distinguished (figs. S23 to S26). Moreover, the reaction solution is analyzed by ICP-OES and ultraviolet-visible (UV-vis) spectrum. The ICP-OES measurement indicates that the amount of cobalt element left in the solution after the catalytic reaction is only 2.8 parts per million (ppm), which is almost negligible. Furthermore, the UV-vis spectra show that CoPc(NH$_2$)$_4$ has two distinct characteristic absorption peaks at 323 and 709 cm$^{-1}$ (28), whereas no obvious signal of cobalt-phthalocyanine unit is found in the solution after the catalytic reaction (fig. S27). Both results demonstrate that CO$_2$ cycloaddition with PO is implemented by the heterogeneous DTBBQ-CMP nanosheets rather than the homogeneous cobalt counterparts.

**Interaction between substrates and active cobalt sites**

The introduction of the steric hindrance group of tert-butyl group could decrease π-π interaction and thereby likely increase the accessible active sites in DTBBQ-CMP nanosheets. The average pore size deduced by N$_2$ adsorption-desorption isotherms is about 1.4 and 1.5 nm for DTBBQ-CMP nanosheets and BDA-CMP aggregates (table S1), both of which are larger than the size of PO molecule (0.61 nm × 0.50 nm). Unfortunately, the average interplanar distance in DTBBQ-CMP nanosheets is only 4.4 Å (figs. S11 and S12), which is smaller than the size of PO molecule. This result indicates that PO molecules are too large to penetrate the interplanar spaces inside DTBBQ-CMP nanosheets. To further experimentally evidence whether all the cobalt sites are accessible in both CMPs, NMR technique is applied to measure the magnetic relaxation time of PO mixed with ultrathin DTBBQ-CMP nanosheets or BDA-CMP aggregates (table S3). The solvation relaxation NMR is known to be an effective method to study the interaction between suspended matter and solvent via probing the change in magnetic relaxation time of hydrogen-containing solvent molecules in both free and bound states. As for pure PO solution, the magnetic relaxation time is 4169 ms. When the catalyst is added, the magnetic relaxation time of PO solution slightly decreases to 3743 ms for ultrathin DTBBQ-CMP nanosheets or 3848 ms for BDA-CMP aggregates. Similar result is found with the larger-sized substrate 2-ethylhexyl glycidyl ether (1.16 nm × 0.86 nm). The magnetic relaxation time is 830 ms for pure solution, which decreases to 779 and 803 ms after addition of ultrathin DTBBQ-CMP nanosheets and BDA-CMP aggregates, respectively. The small decrease in magnetic relaxation time reveals that the substrates mainly absorb on the outside surface of catalysts and then react with CO$_2$ to form the cyclic carbonates. In addition, ultrathin DTBBQ-CMP
nanosheets have stronger interaction with the substrates compared with BDA-CMP aggregates, thus resulting in the higher substrate activation.

**Reaction mechanism elucidated by theoretical calculation**

In general, it is recognized that CO$_2$ cycloaddition with epoxide is initiated by coordination of the electron-deficient Lewis acidic cobalt center with the oxygen atom in epoxide, and this step would activate the epoxy ring. Afterward, the Br$^-$ ion generated from TBAB attacks the more hindered carbon atom of the coordinated epoxide, followed by the ring opening step. Subsequently, the oxygen anion of the opened epoxy ring interacts with CO$_2$ to form an alkyl carbonate anion, which is finally converted into the corresponding cyclic carbonate through the ring closing step. Meanwhile, the catalyst is regenerated (Fig. 4A) (13, 16). To quantitatively evaluate the activation energy of each step on single cobalt sites, DFT calculation was performed with the NWChem quantum chemistry program packages (see detailed calculation method in the Supplementary Materials) (29). As for the ultrathin DTBBQ-CMP nanosheets, the single CoPc complex is used as the simulation model. The reaction of PO with single cobalt sites is exothermic with an energy barrier ($\Delta$E) value of $-10.5$ kcal mol$^{-1}$. In other words, the active cobalt sites would

**Table 1. Catalytic CO$_2$ cycloaddition with different epoxides to produce cyclic carbonates.** Ultrathin DTBBQ-CMP nanosheets containing single cobalt sites exhibit an excellent catalytic performance with respect to BDA-CMP aggregates under mild reaction conditions. Reaction conditions: 1 ml of epoxide.

| Entry | Amount (mg) | TBAB (mmol) | CO$_2$ (MPa) | Temperature (°C) | Time (hours) | Yield* (%) | TON † |
|-------|-------------|-------------|--------------|------------------|--------------|------------|------|
| Substrate A: PO | | | | | | | |
| 1 | 5 | 0.06 | 0.1 | 25 | 48 | 99.0 | 2903 |
| 2 | 5 | 0.06 | 0.1 | 25 | 48 | 10.4 | 301 |
| 3 | – | – | 0.1 | 25 | 48 | 16.8 | – |
| 4 | 5 (BDA-CMP) | 0.06 | 0.1 | 25 | 48 | 71.4 | 2069 |
| 5 | 10 (BDA-CMP) | 0.09 | 0.5 | 25 | 48 | 82.3 | 2389 |
| Substrate B: 1,2-Epoxyethylbenzene | | | | | | | |
| 6 | 5 | 0.06 | 0.1 | 60 | 48 | 99.0 | 1714 |
| Substrate C: Glycidyl phenyl ether | | | | | | | |
| 7 | 5 | 0.06 | 0.1 | 50 | 48 | 99.0 | 1451 |
| 8 | 5 (BDA-CMP) | 0.06 | 0.1 | 50 | 48 | 86.7 | 1137 |
| Substrate D: 4-Tert-butylphenyl glycidyl ether | | | | | | | |
| 9 | 5 | 0.06 | 0.1 | 50 | 48 | 82.3 | 813 |
| 10 | 5 | 0.06 | 0.1 | 60 | 72 | 99.0 | 978 |
| 11 | 5 (BDA-CMP) | 0.06 | 0.1 | 60 | 72 | 91.0 | 805 |
| Substrate E: Butyl glycidyl ether | | | | | | | |
| 12 | 5 | 0.06 | 0.1 | 50 | 48 | 99.0 | 1375 |
| Substrate F: 2-Ethylhexyl glycidyl ether | | | | | | | |
| 13 | 5 | 0.06 | 0.1 | 60 | 48 | 81.7 | 862 |
| 14 | 5 | 0.06 | 0.1 | 65 | 72 | 99.0 | 929 |
| 15 | 5 (BDA-CMP) | 0.06 | 0.1 | 65 | 72 | 85.1 | 716 |

*Yield of the products is determined by gas chromatography. †The cobalt content is 6.0 wt % for ultrathin DTBBQ-CMP nanosheets and 6.7 wt % for BDA-CMP aggregates. TON = (mole of products)/(mole of active metal sites in catalyst).
spontaneously adsorb PO to form the relatively stable transition state. The subsequent attack of the nucleophile Br⁻ ion on PO is difficult and endothermic with a ΔE value of 19.3 kcal mol⁻¹. The insertion of CO₂ to form alkyl carbonate anion is a simple intramolecular process with a ΔE value of −8.0 kcal mol⁻¹, while desorption of the nucleophile Br⁻ to generate the target product PC is slightly endothermic with a ΔE value of 2.0 kcal mol⁻¹. Evidently, the attack of the nucleophile (Br⁻) on PO is a rate-determining step (Fig. 4B and calculation detail in the Supplementary Materials). As a comparison, a fractional charge of 0.1e is added into the CoPc model for BDA-CMP, and the higher energy for the rate-determining step is required for BDA-CMP (19.6 versus 19.3 kcal mol⁻¹), demonstrating that DTBBQ-CMP is more active for CO₂ cycloaddition than BDA-CMP (fig. S28). This calculation further confirms that the delocalized electron-withdrawing effect on single cobalt sites in CMP nanosheets does play an important role in promoting CO₂ cycloaddition.

Experimental evidences obtained by operando x-ray absorption spectra experiments

The maximum coordination number of cobalt center is known to be 6 [17, 25], so the 4-coordination cobalt sites in both ultrathin DTBBQ-CMP nanosheets and BDA-CMP aggregates could offer the additional coordination with the PO substrate. EXAFS spectra show that the dominant peaks of DTBBQ-CMP nanosheets and BDA-CMP aggregates both shift to a low R-position at 1.40 Å under operando conditions of PO reacting with CO₂ (without phase correction) (Fig. 5A and fig. S29) [30], denoting the coordination of first shell of cobalt sites with oxygen atom in PO. The simulation model was built from CoPc(NH₄)₂ by adding PO molecule coordinated to cobalt center and then the EXAFS spectra were fitted. Further quantitative analysis indicates that the average Co–N/O bond length is 2.2 Å, while the corresponding coordination number of cobalt centers is 4.6 for DTBBQ-CMP and 4.5 for BDA-CMP aggregates under operando conditions of PO reacting with CO₂ (without phase correction) (Fig. 5A and fig. S29) [30], denoting the coordination of first shell of cobalt sites with oxygen atom in PO.
conditions (fig. S30 and table S2). With respect to BDA-CMP aggregates, the higher coordination number of cobalt centers in DTBBQ-CMP nanosheets implies their stronger interaction with oxygen atom in PO to activate it (31). Meanwhile, XANES spectra display that the Co K-edge absorption of ultrathin DTBBQ-CMP nanosheets and BDA-CMP aggregates shifts to lower energy under operando conditions, and the peak shift of Co K-edge peak of ultrathin DTBBQ-CMP nanosheets is larger than that of BDA-CMP aggregates (inset in Fig. 5B and fig. S31). This result also suggests that single cobalt sites on the ultrathin DTBBQ-CMP nanosheets are more active for CO2 cycloaddition with the PO substrate.

Catalytic CO2 cycloaddition with other epoxides

To highlight the remarkable catalytic activity of single cobalt sites on ultrathin DTBBQ-CMP nanosheets, five typical large-sized epoxides including 1,2-epoxyethylbenzene (0.93 nm × 0.69 nm), glycidyl phenyl ether (1.05 nm × 0.70 nm), 4-tet-butylphenyl glycidyl ether (1.28 nm × 0.72 nm), butyl glycidyl ether (1.10 nm × 0.61 nm), and 2-ethylhexyl glycidyl ether (1.16 nm × 0.86 nm) are used as the substrates for CO2 cycloaddition (fig. S32). Significantly, the yields of all different carbonates could reach 99.0% when the ultrathin DTBBQ-CMP nanosheets are used as catalysts (Table 1, entries 6 to 15), and the corresponding TON values are 1714 for 1,2-epoxyethylbenzene (at 60°C), 1451 for glycidyl phenyl ether (at 50°C), 978 for 4-tet-butylphenyl glycidyl ether (at 60°C), 1375 for butyl glycidyl ether (at 50°C), and 929 for 2-ethylhexyl glycidyl ether (at 65°C) (figs. S33 to S37). As a comparison, the BDA-CMP aggregates exhibit the lower catalytic efficiency under the same reaction conditions, and the yields are 86.7% with a TON value of 1137 (at 50°C) for glycidyl phenyl ether, 91.0% with a TON value of 805 for 4-tet-butylphenyl glycidyl ether (at 60°C), and 85.1% with a TON of value 716 for 2-ethylhexyl glycidyl ether (at 65°C). It deserves to be stressed that the ultrathin DTBBQ-CMP nanosheets exhibit the superior performance for CO2 cycloaddition with different epoxides under mild reaction conditions compared to the state-of-art heterogeneous catalysts that usually suffer from high reaction temperature, big reaction pressure, low catalytic activity, and limited reactants (table S4).

Extending this strategy for synthesizing other ultrathin CMP nanosheets

To demonstrate the universality of the steric hindrance synthesis strategy, CuPc(NH2)₄ or ZnPc(NH2)₄ is tried to be polycondensed with DTBBQ. The uniform CMP nanosheets with an average thickness of 4.0 or 4.5 nm are obtained (figs. S38 to S40). In addition, when the MPc(NH2)₄ is replaced by tris(4-aminophenyl)amine or tris(4-aminophenyl)benzene, the ultrathin CMP nanosheets (4 nm thick) are also obtained (figs. S41 to S43). However, when BDA is used as the bridging molecules, only CMP aggregates are acquired regardless of using MPc(NH2)₄, tris(4-aminophenyl)amine, or tris(4-aminophenyl)benzene as the condensation precursor (figs. S44 to S48). Together, the steric hindrance of tert-butyl groups attached on CMP skeletons effectively weakens the π–π stacking between the adjacent units and hence promotes the formation of the ultrathin nanosheets (fig. S49).

CONCLUSIONS

In summary, the ultrathin DTBBQ-CMP nanosheets featuring single cobalt sites exhibit the extraordinary activity, stability, and reusability for catalytic CO2 cycloaddition with various epoxides at low reaction temperature and atmospheric pressure (table S4). Theoretical calculation and operando x-ray absorption experiment disclose that the electron-deficient single cobalt sites on the ultrathin nanosheets, which are modulated by the delocalized electron-withdrawing effect of alkene groups in DTBBQ on the conjugated skeleton, promote the interaction with the oxygen atoms in epoxides for efficient CO2 cycloaddition. In addition, by introducing the steric hindrance via tert-butyl group in DTBBQ, a series of ultrathin CMP nanosheets with weakened interlayer interactions are obtained, which provides a general toolbox to prepare the 2D counterparts. It can be anticipated that in the future, novel strategies to construct CMP nanosheets with fewer layers, or even single layer, will make more inside active sites accessible and therefore achieve further enhanced catalytic efficiency. Together, because of easy tuning of the charge of active centers by grafting different functional groups into the skeleton, the metal-containing conjugated systems will provide new insight into the design of high-performance single-site catalysts for many important reactions.

MATERIALS AND METHODS

Reagents

Analytical grade cobalt chloride hexahydrate (CoCl2·6H2O), zinc chloride (ZnCl2, 99%), and copper chloride dihydrate (CuCl2·2H2O) were all bought from Sigma-Aldrich. Mesitylene (98%), tris(4-aminophenyl)amine (98%), 1,3,5-tris(4-aminophenyl)benzene (97%), 4-nitrophthalimide (98%), urea (American Chemical Society reagent, 99%), ethanol (Analytical Reagent, 99.7%), terephthalaldehyde (98%), DTBBQ (99%), acetic acid (99%), 1,4-dioxane (98%), tetrabutylammonium bromide (TBAB), and PO were purchased from Aladdin. 1,2-Epoxyethylbenzene, 2-ethylhexyl glycidyl ether, 4-tet-butylphenyl glycidyl ether, glycidyl phenyl ether, and butyl glycidyl ether were bought from TCI. Ultrapure water (18 megohms) was supplied using a Millipore system (Millipore Q). All the chemicals were used without further purification.

Characterization

Scanning electron microscopy (SEM) measurement was performed on a Hitachi S8220 scanning electron microscope at 6.0 kV. TEM and high-resolution TEM imaging was carried out using Tecnai G2 F20 at 200 kV. Powder XRD patterns were recorded on D/MAX-TTRIII (Cross Beam Optics) with Cu Kα radiation (λ = 1.542 Å) operating at 40 kV and 200 mA. FTIR spectra were recorded on Spectrum One in the spectral range of 400 to 4000 cm⁻¹ using the KBr disc method. Specific surface area and pore size of catalysts were measured using a BET (Brunauer-Emmett-Teller) instrument (ASAP 2420-4, Micromeritics). The cobalt content in different samples was determined with an ICP–mass spectrometer (Thermo Fisher Scientific). Solid-state 13C cross-polarization magic angle spinning NMR (CP/MAS NMR) spectra were recorded at 400 MHz with an Advance III Bruker Corporation instrument (from Institute of Chemistry, Chinese Academy of Sciences). TG measurements were performed on a Mettler-Toledo model (Diamond TG/DTA) under N2 atmosphere (PerkinElmer).

Synthesis of tetratnitrometallophthalocyanine [MPc(NO2)₄; M = Co, Cu, or Zn]

A finely ground mixture of 4-nitrophthalimide (3.8 g, 19.7 mmol), MCl2 (1.2 g, M = Cu, Co, or Zn), urea (9.6 g, 160.0 mmol), and ammonium molybdate (50 mg) was reacted in solid state at 180°C for...
5 hours. The resulting crude product was ground and stirred in the aqueous HCl solution (1 M, 300 ml) and then in the aqueous NaOH solution (1 M, 300 ml) at 90°C for 1 hour. Last, the residue was filtered, washed with water, and dried under vacuum to obtain tetranitrometallophthalocyanine coordinated with copper, cobalt, or zinc, MPc(NO₂)₄ (M = Co, Cu, or Zn).

**Synthesis of tetraaminometallophthalocyanine [MPc(NH₂)₄, M = Co, Cu, or Zn]**

Crude tetranitrometallophthalocyanine [0.75 g; MPc(NO₂)₄] was reacted with Na₂S·9H₂O (3.0 g, 12.4 mmol) in N,N-dimethylformamide solution (15 ml) at 60°C for 4 hours. The solution was then poured into water (100 ml). Afterward, the obtained precipitate was collected by centrifugation and washed with water and dried under vacuum to obtain tetrani-

trometallophthalocyanine [0.75 g; MPc(NO₂)₄] was re-

tered, washed with water, and dried under vacuum to obtain tetrani-

terephthalaldehyde (36 mg, 0.26 mmol) were added into a mixed solution containing 5 ml of C₂H₅OH, 2 ml of mesitylene, and 0.2 ml of acetic acid (AcOH, 4 M) in a vessel. Subsequently, the mixture was sonicated for a while to get a homogeneous solution. After that, the tube was flash-frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump–thaw cycles and then was sealed off and heated at 120°C for 72 hours. Last, the precipitate was collected by filtration and washed with ethanol and dried at 50°C under vacuum for 12 hours to obtain the 3D polymers. Similarly, if 1,3,5-tris(4-aminophenyl)benzene (15.0 mg, 0.04 mmol) was replaced by tris(4-aminophenyl)amine (15.0 mg, 0.05 mmol) to react with terephthalaldehyde, then the corresponding CMP aggregates were obtained.

**Catalytic CO₂ cycloaddition with different epoxides**

The catalytic reaction was conducted in a 30-ml autoclave reactor purged with CO₂. The autoclave was set in an oil bath with frequent stirring for a period of time. At the end of the reaction, the reactor was placed in an ice bath for 20 min and then opened. The catalysts were separated by centrifugation, and a small aliquot of the supernatant reaction mixture was taken to be analyzed by gas chromatography (Shimadzu, GC-2014 Plus) to calculate the yield of the target product.

**XAFS curve fitting details**

Co K-edge x-ray absorption spectra (XAS) were acquired at beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF) at room temperature. The storage ring of BSRF was operated at 2.5 GeV with a maximum current of 250 mA in decay mode. The energy was calibrated using Co foil; the intensities of the incident and fluorescence XRD were monitored by using standard N₂-filled ion chamber and Ar-filled Lytle-type detector, respectively. The powder samples were uniformly mixed with boron nitride powder and pressed to a pellet for XAFS measurement. The XAFS raw data were background-subtracted, normalized, and Fourier-transformed by the standard procedures with the ATHENA program. EXAFS curve fitting was performed with Artemis software based on the EXAFS equation (32), which was expressed in terms of single and multiple-scattering expansion.

$$\chi(k) = \sum_{\Gamma} N_{\Gamma} \left| F_{\text{eff}}^\Gamma (\pi, k, R_{\Gamma}) \right|^2 \frac{\exp(-2R_{\Gamma}/\lambda(k) - 2k^2\sigma^2_{\Gamma})}{kR^2_{\Gamma}}$$

where $k = \sqrt{2m_{e}(E - E_0)}$ represented a scale conversion from the photo energy (E, eV) to the wave number ($k$, Å⁻¹) of the excited photoelectron as measured from absorption threshold $E_0$. The sums were over a series of equivalent scattering paths, $\Gamma$, which originated at the central absorption atoms, travelling to one or more of the neighboring atoms, and then back to the original central atoms. The equivalent scattering paths, with a degeneracy of $N_{\Gamma}$, were grouped according to the atomic number of the passed atoms and the total path length $R_{\Gamma}$ of the photoelectron. The dependence of the EXAFS oscillatory structure on path length and energy was reflected by the sin$(2kR_{\Gamma} + \phi_{\Gamma}(k) + 2\delta_{\Gamma}(k))$ term, where $\phi_{\Gamma}(k)$ was the effective scattering phase shift for path $\Gamma$. $F_{\text{eff}}^\Gamma(\pi, k, R_{\Gamma})$ denoted the effective scattering amplitude for path $\Gamma$. The amplitude decay due to inelastic scattering was captured by the exponential term $\exp(-2R_{\Gamma}/\lambda(k))$, where $\lambda(k)$ was the...
photonic free path. Additional broadening effect due to thermal and structural disorder in absorber-scatter \((s)\) path lengths was accounted for by the Debye-Waller term \(\exp \left(-2K^2\sigma_t^2\right)\). \(S_{\theta}^2\) was a many-body amplitude-reduction factor due to excitation in response to the creation of the core hole. In this work, while the scattering amplitudes and phase shifts for all paths as well as the photoelectron mean free path were theoretically calculated by ab initio code FEFF 6, the variable parameters that were determined by using the EXAFS equation to fit the experimental data were \(\bar{N}\), \(R^6\), and \(\sigma_t^2\). The \(S_{\theta}^2\) parameter was determined in the fit of \(CoPc(NH_2)_4\) standard and used as a fixed value in the rest of the EXAFS models. All fits were performed in the \(R\) space with \(k\)-weight of 3. The EXAFS \(R\)-factor \((R_i)\) that measured the percentage misfit of the theory to the data was used to evaluate the goodness of the fit. For the EXAFS curve fitting, an energy cutoff of 400 eV.

### Theoretical calculations

**Charge distribution of single cobalt sites in \(CoPc\)**

The DMol3 code was used for the DFT calculation and charge distribution analysis (calculated by Beijing Zijing Gaoke Technology Co. Ltd.). The electronic wave function was expanded with the double-nemonic polarized basis set. The Perdew-Burke-Ernzerhof (PBE) functional, which was based on the generalized gradient approximation (GGA), was used throughout to describe the electron-electron exchange and correlation interactions (33). A global orbital cutoff 4.5 \(\text{Å}\) was used as the maximum value from all the cutoffs specific to each element in this system. The Mulliken charge analysis was applied to obtain the charge distribution on each atom.

**Optimizing spatial configuration of one layer of \(DTBBQ-CMP\)**

The single layer was studied by the periodic DFT implemented in the Vienna Ab initio Simulation Package, and the PBE functional was chosen. To improve the description of the on-site coulomb interaction, the DFT + \(U\) method was adopted (34) and the \(U-J\) value was chosen as 3 eV for \(d\) electrons of the cobalt ion. Because the GGA had a weakness for describing the van der Waals interaction, the D3 dispersion correction by Grimme was used. Moreover, the electron-ion interaction was described with the projected augmented wave method. The electronic wave function was expanded by the plane-wave basis set with an energy cutoff of 400 eV. To achieve a good convergence to the relaxed structure, the residual force was less than 0.005 eV/\(\text{Å}\) on each atom after the geometry optimization. A Monkhorst-Pack \(k\)-point grid of \(3 \times 3 \times 1\) was adopted to sample the Brillouin zone. To avoid the interaction between the layer and its neighboring image in the periodic boundary conditions, a vacuum of 20 \(\text{Å}\) was fulfilled along the vertical axis.

**Scanning the potential energy profile of the two-layer model of \(DTBBQ-CMP\)**

The DFT was not feasible to investigate the sophisticated interlayer interaction in multilayer structures, because its computational effort was too heavy to carry out even for the double-layer structure. Then, an approximate form of the DFT, i.e., the SCC-DFTB method, was used with the DFTB+ (version 18.1) package. This method was based on the tight-binding approach, and the optimal minimal basis set and parametrized two-center approximation for Hamiltonian matrix were also applied to save computational efforts. The mio-0-1 and trans 3d-0-1 parameter sets were applied. The partial atomic charge was permitted to relax in a self-consistent manner (SCC). To include the dispersion interaction, the Lennard-Jones dispersion model was also included. The on-site coulomb interaction was also added with the DFTB + \(U\) method, and the \(U\) value was set to 3 eV.

**Simulation of catalytic \(CO_2\) cycloaddition by \(DTBBQ-CMP\)**

To investigate the reaction pathway, the DFT calculation was adopted with the NWChem (ver. 6.8) quantum chemistry package. The hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) functional was chosen, and the D3 dispersion correction by Grimme was also included. To save computational efforts, the moderate basis set 6-31G* was adopted for the geometry optimization and consecutive frequency analysis, and the larger basis set def2-TZVPP was chosen for the single point calculation of the optimized structure to improve the energetics. To include the solvation effect, the COSMO implicit solvation model was adopted and the dielectric constant of PO was 16.0.

**Simulation of catalytic \(CO_2\) cycloaddition by \(BDA-CMP\) with respect to \(DTBBQ-CMP\)**

To examine the adsorption behavior of charge state of cobalt center in \(CoPc(NH_2)_4\) molecule, the fractional occupation number method implemented in the NWChem quantum chemistry package was taken into account.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/6/17/eaaz4824/DC1

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Delocalized electron effect on single metal sites in ultrathin conjugated microporous polymer nanosheets for boosting CO2 cycloaddition

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