Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Activation of CO_2 by *t*BuZnOH species: Efficient routes to novel nanomaterials based on zinc carbonates

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Supporting Information

Experimental Section

All manipulations with alkilzinc compounds were conducted under a nitrogen atmosphere by using standard Schlenk techniques. Di-*tert*-butylzinc[1] and *tert*-butylzinc hydroxide[2] were prepared as described previously. All other reagents were purchased from commercial vendors. Solvents were dried and distilled prior to use. Liquid-state NMR spectra were acquired on Varian Mercury 400MHz and Varian Inova 500MHz spectrometers. Solid-state NMR spectra were acquired on Bruker Avance II 500 MHz spectrometer. The infrared spectra were recorded on a FT-IR Perkin-Elmer System 2000 spectrometer.

BET Surface Analysis

Approximately 300-500 mg of the corresponding solid product were evacuated under vacuum overnight at room temperature. The sample was transferred to a preweighed sample tube and degassed at room temperature approximately 24 h on an Micromeritics ASAP 2020 or until the outgas rate was < 5 μmHg. The sample tube was reweighed to obtain a consistent mass for the degassed modified product. BET surface area (m^2g^{-1}) measurements were collected at 77 K by dinitrogen on an ASAP 2020.

SEM measurements

Samples investgated under microscope were instilled from THF solution and evaporated on SEM standard table (Agar Scientific). Samples were not coated by any means. Prepared samples were examined by scanning electron microscope (SEM Zeiss ULTRA Plus) with field emission gun. A wide variety of magnifications (from x1000 up to x250000), working distances (from 1.9mm up to 3.0mm) and accelerating voltage (from 0.9kV up to 2kV) were used to match ideal imaging conditions for different samples.

TEM measurements

Microscopic samples were prepared by droplet coating of THF suspensions on Cu grids (QUANTIFOIL R2/2 Carbon Film, 300 mesh) and examined using a Cs corrected scanning transmission electron microscope (STEM HITACHI HD2700) at nominal magnifications between x1300000 and x5000000. The electron optical parameters were C S = 0.6 mm, C C = 1.2 mm, electron energy spread = 1.5 eV. From these images, first indications of particle structure were obtained. Particle size distributions were calculated by counting the diameters of 100 particles in the lower magnification images, defining size intervals of 0.25 nm between $d_{min} \leq d \leq d_{max}$ and counting the number of particles falling into these intervals.

Synthesis of 2: The freshly dissolved **1** (0.200 g, 1.43 mmol) in THF (10.0 mL) was exposed to CO_2 atmosphere at ambient temperature in a Schlenk flask without stirring. The gelation of the post-reaction mixture was observed after 24h. Then the resulting white gel **2** were aged for two weeks under ambient conditions and yields a suspension of a solid, which were separated by decantation. Isolated yield 0.171g (95%). Elemental analysis (%) calcd for $ZnCO_3$ (125.42 g mol^{-1}): C 9.58, Zn 52.15; found: C 9.49, Zn 52.03; IR: ν = 2958s, 2909s, 2845s, 1521w, 1376s, 1256s, 1093m, 797s cm^{-1}.

Synthesis of 3: To a freshly dissolved **1** (0.252 g, 0.30 mmol) in toluene (4.0 mL) a solution of tBu$_2$Zn (0.324 g, 1.80 mmol) in toluene (3.0 mL) was added. The resultant solution was allowed to warm to room temperature and exposed to CO_2 atmosphere at ambient temperature in a Schlenk flask without stirring. Compound **3** was obtained as colourless rhomboid crystals after crystallization from the parent mixture at room temperature after ca. 1 day. Isolated yield 0.330g (91%). Elemental analysis (%) calcd for $C_{54}H_{108}O_{18}Zn_{12}$ (1830.08 g mol^{-1}): C 35.41, H 5.90; found: C 35.51, H 5.98; ^{1}H NMR ([D$_8$]-THF, 400.10 MHz, 298 K): δ = 1.06 (m, br, 9H, ZnC(CH_3)$_3$) ppm; CP-MAS ^{13}C NMR: δ = 165.27 (CO_3^{2-}), 33.04, 33.38 (ZnC(CH_3)$_3$), 24.29, 27.54 (ZnC(CH$_3$)$_3$) ppm; IR (Nujol): ν = 2961s, 2920s, 2855s, 1846w, 1806w, 1510s, 1377s, 1364s, 1169s, 1092w, 1012s, 937w, 885w, 837m, 825s, 814s, 753m, 721m cm^{-1}.

X-Ray Crystallography

Data were collected using the ‘oil drop technique’ to mount crystals on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **3**, $C_{54}H_{108}O_{18}Zn_{12}$: M = 1830.08, crystal dimensions 0.46 × 0.32 × 0.24 mm^3, trigonal, space group R -3 (no. 148), a = 20.4631(2) Å, b = 20.4631(2) Å, c = 16.2871(11) Å, U = 5906.3(5) $Å^3$, Z = 3, $F(000)$ = 2808, D_c = 1.544 g m^3, T = 100(2)K, μ(Mo-Kα) = 3.636 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 27.45 °, 2996 unique reflections. The structure was solved by direct methods using the SHELXS97 [3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.0515, $wR2$ = 0.0827 for all data and 133 parameters ($R1$ = 0.0391, $wR2$ = 0.0786 for 2532 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.086. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.76 /- 0.53 $eÅ^{-3}$. CCDC- 866665.

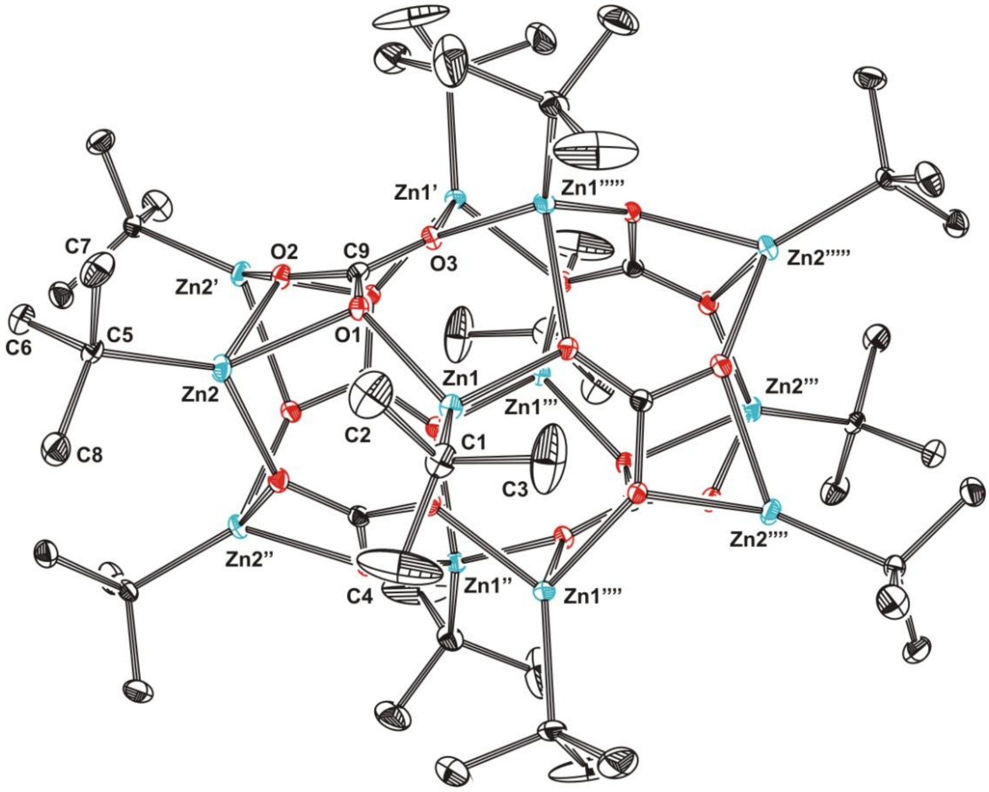

Figure S1. ORTEP diagram of molecular structure of **3** with thermal ellipsoids set at 30% probability; hydrogen atoms have been omitted for clarity.

Table S1. Selected Bond Lengths (Å) and Angles (deg) for **3**.

Zn1 – C1	1.973(4)
Zn1 – O1	2.067(2)
Zn2 – O1	2.102(2)
Zn2 – O2	2.218(2)
C9 – O1	1.295(4)
C9 – O2	1.279(4)
C9 – O3	1.279(4)

O1 – C9 – O2	116.4(3)
O1 – C9 – O3	120.8(3)
O2 – C9 – O3	122.8(3)
Zn1 – O1 – Zn2	109.7(1)
C9 – O1 – Zn1	132.2(2)
C9 – O1 – Zn2	93.4(2)

Symmetry transformations used to generate equivalent atoms denoted by prime, double prime, triple prime, quadruple prime and quintuple prime (*x*-*y*, *x*, -*z*), (-*x*, -*y*, -*z*), (*y*, -*x* + *y*, -*z*), (-*x* + *y*, -*x*, *z*), (-*y*, *x*-*y*, *z*), respectively.

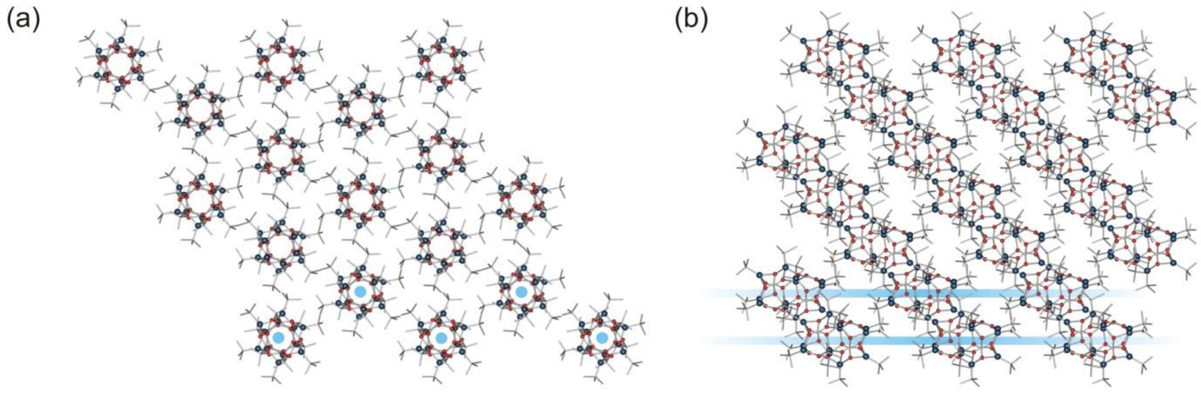

Figure S2. The crystal structure of the barrel like **3**; (a) the crystal structure is formed by linear ordered molecules along the *c* axis and (b) a view along *a* axis.

Gas sorption measurements

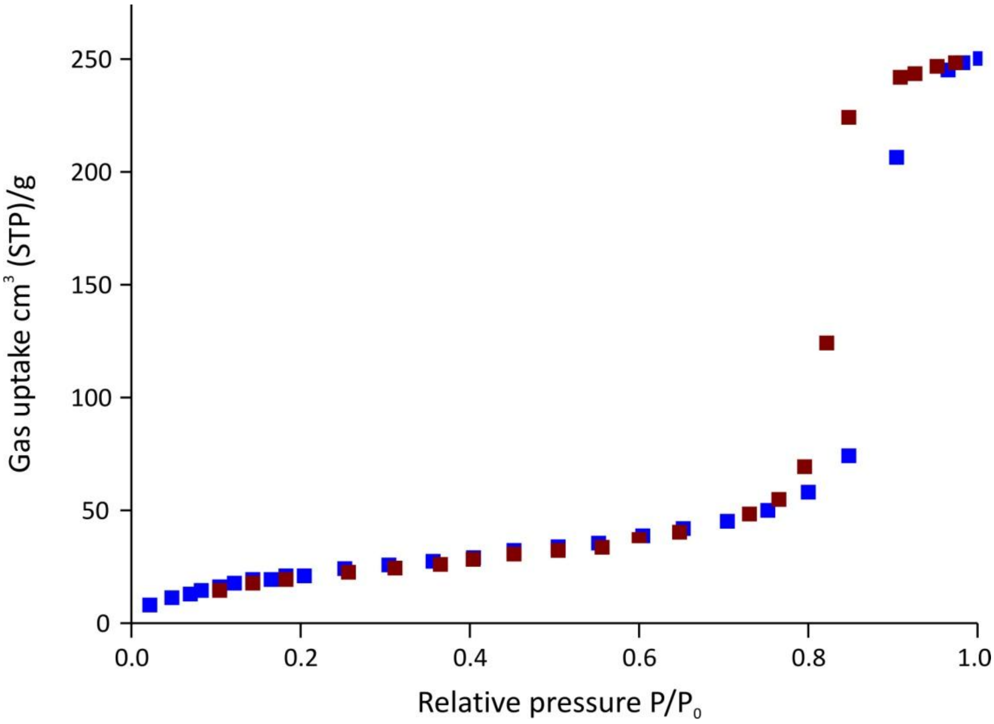

Figure S3. N_2 adsorption (blue) and desorption (red) isotherms for **2** at 77K.

CP-MAS ^{13}C NMR analysis

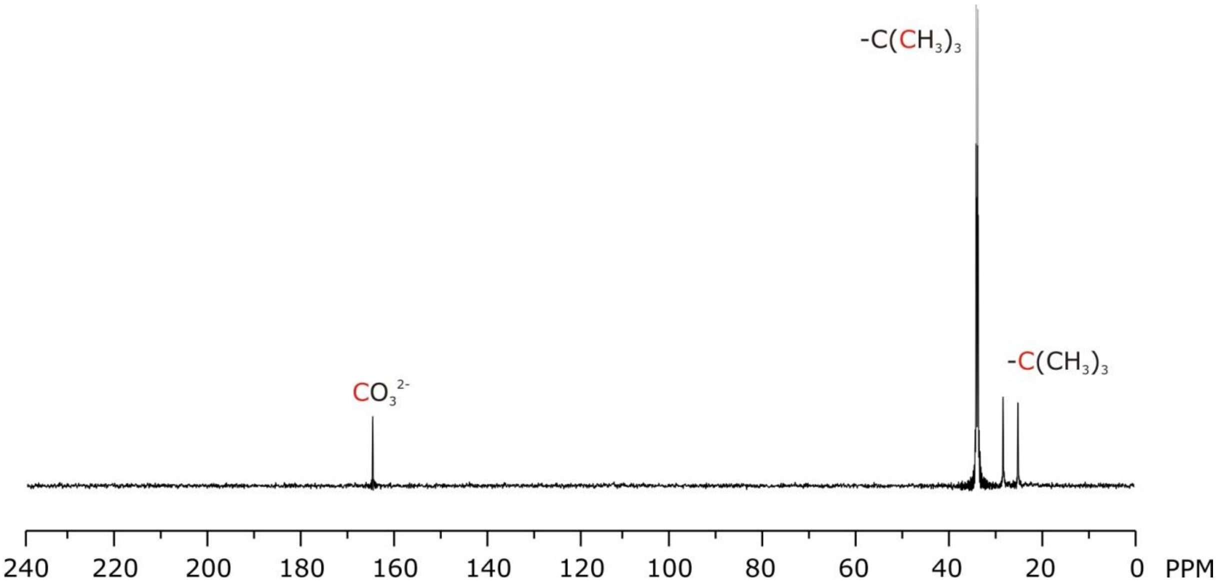

Figure S4. Solid-state ^{13}C NMR spectrum for **2**.

FT-IR analysis

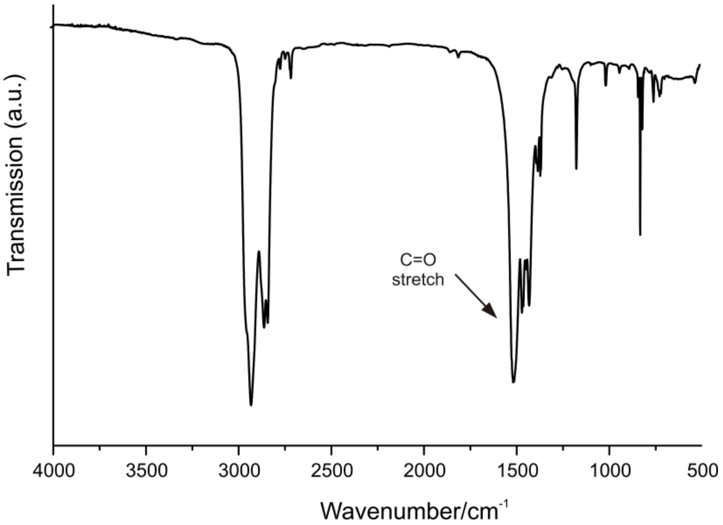

Figure S5. FT-IR spectrum of **3**.

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[1] W. Bury, E. Krajewska, M. Dutkiewicz, K. Sokołowski, I. Justyniak, Z. Kaszkur, K. J. Kurzydłowski, T. Płociński, J. Lewiński, *Chem. Commun.* **2011**, *47*, 5467–5469.

[2] J. Lewiński, M. Dranka, W. Bury, W. Śliwiński, I. Justyniak, J. Lipkowski, *J. Am. Chem. Soc.* **2007**, *129*, 3096-3098.

[3] SHELXS-97, Program for Structure Solution”: Sheldrick, G. M. *Acta Crystallogr*. Sect. A **1990**, *46*, 467.

[4] Sheldrick, G. M. SHELXL-97, Program for Structure Refinement, Universität Göttingen, 1997.