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Supporting information

Self-Assembled Tetramethylcucurbit[6]uril-Polyoxometalate Nanocubes as Efficient and Recyclable Catalysts for Preparation of Propyl gallate

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Experimental Section

Materials: TMeQ[6] was prepared by procedures reported elsewhere[1]. Phosphomolybdic acid (PMA) was purchased from Sigma-Aldrich. Gallic acid and n-propanol were obtained from Beijing Chemical Reagent Company (Beijing, China). All reagents were used as received without further purification.

Preparation of TMeQ[6]-PMA NCs: TMeQ[6]-PMA NCs were synthesized via an facile one-step self-assembly reaction between TMeQ[6] and PMA in a solution system. For the typical preparation, 0.1 g TMeQ[6] and 0.347 g PMA were dissolved in 100 mL distilled water and then mixed in the solution with magnetic stirring for 2 h. Subsequently, the products were collected by centrifugation and washed several times with distilled water, and freezely dried. .

Characterization: The thermal properties of the conjugated microporous polymers were evaluated by thermogravimetric analysis (TGA) on a di□erential thermal analysis instrument (Q1000DSC +LNCS+FACS Q600SDT) over the temperature ranging from 30 to 800 °C with a heating rate of 10 °C min^{-1} under an N_2 atmosphere. The morphologies of the resulting samples were observed by field-emission scanning electron microscopy (FESEM, Hitachi SU8010). Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010 microscope operated at 200 kV. The crystallographic structure was measured by X-ray diffraction measurements (XRD, Rigaku, D/max-RB). The N_2 adsorption-desorption isotherms were performed using an automated gas sorption analyzer (Autosorb-iQ-2MP, Quantachrome, USA). Temperature-programmed desorption of NH_3 (NH_3-TPD) were conducted on the AutoChem II. 2920 instrument (Micromeritics, USA) equipped with a mass spectrum detector. The sample (100 mg) was reduced at 573 K for 2 h in H_2/Ar atmosphere, followed by purging with a high purity He flow for 2.0 h at 583 K. When the

temperature decreased to 323 K, NH_3 was introduced until saturation, followed by purging He for 90 min to remove physisorbed NH_3. Finally, the sample was heated from 323 K to 973 K at a rate of 10 K min^{-1}, and the released NH_3 was monitored by a mass spectrometer. Acid site type was analyzed on Nicolet 6700 spectrometer by using pyridine as the probe molecule (Py-FTIR). Before analysis, the as-prepared sample was activated at 200 °C within 5.33×10^{-2} Pa for 1 h.

Catalyst testing: Catalytic performance was evaluated by esterification of gallic acid and n-propanol to propyl gallate (PG). Typically, gallic acid and n-propanol were magnetically stirred in a 250 mL conical flask equipped with condenser. When the mixture was heated to designed temperature, catalyst was added and stirred for duration time. Afterwards, catalyst was separated via centrifugation and the isolated mixture was placed into separating funnel for 10 h. The catalytic activity was determined by the conversion of acid value reduction as depicted in Eq. (1) and acid value was measured by GB/T 1668-2008 standards [2].

$$\text{Conversion (\%)} = \frac{acid\ value\ (initial) - acid\ value\ (final)}{acid\ value\ (initial)} \times 100\% \quad (1)$$

The structure was identified by the infrared spectra and nuclear magnetic resonance spectra.

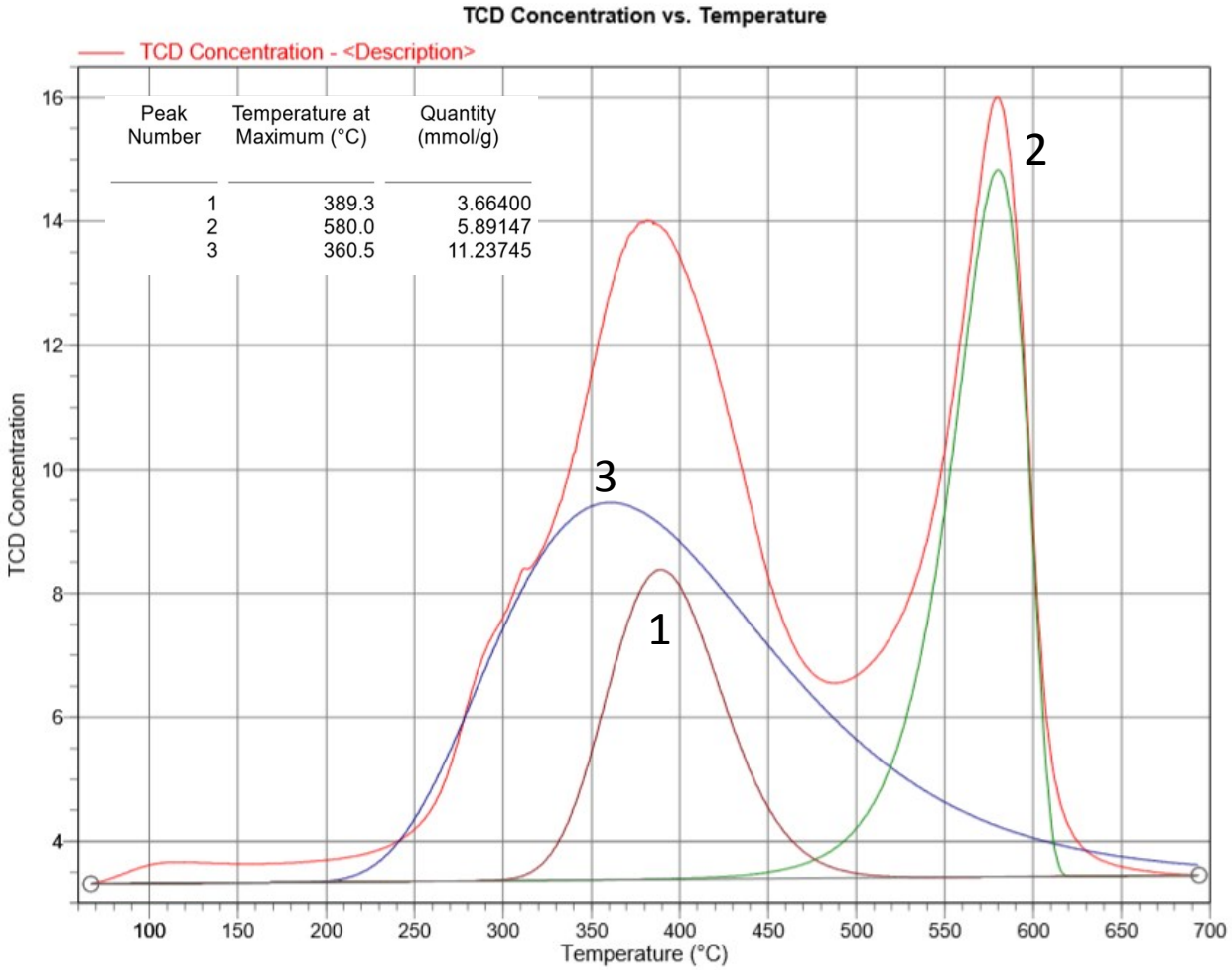

Figure S1. The desorption temperature profiles and the amounts of desorption ammonia of the TMeQ[6]-PMA NCs based on temperature programmed desorption experiments.

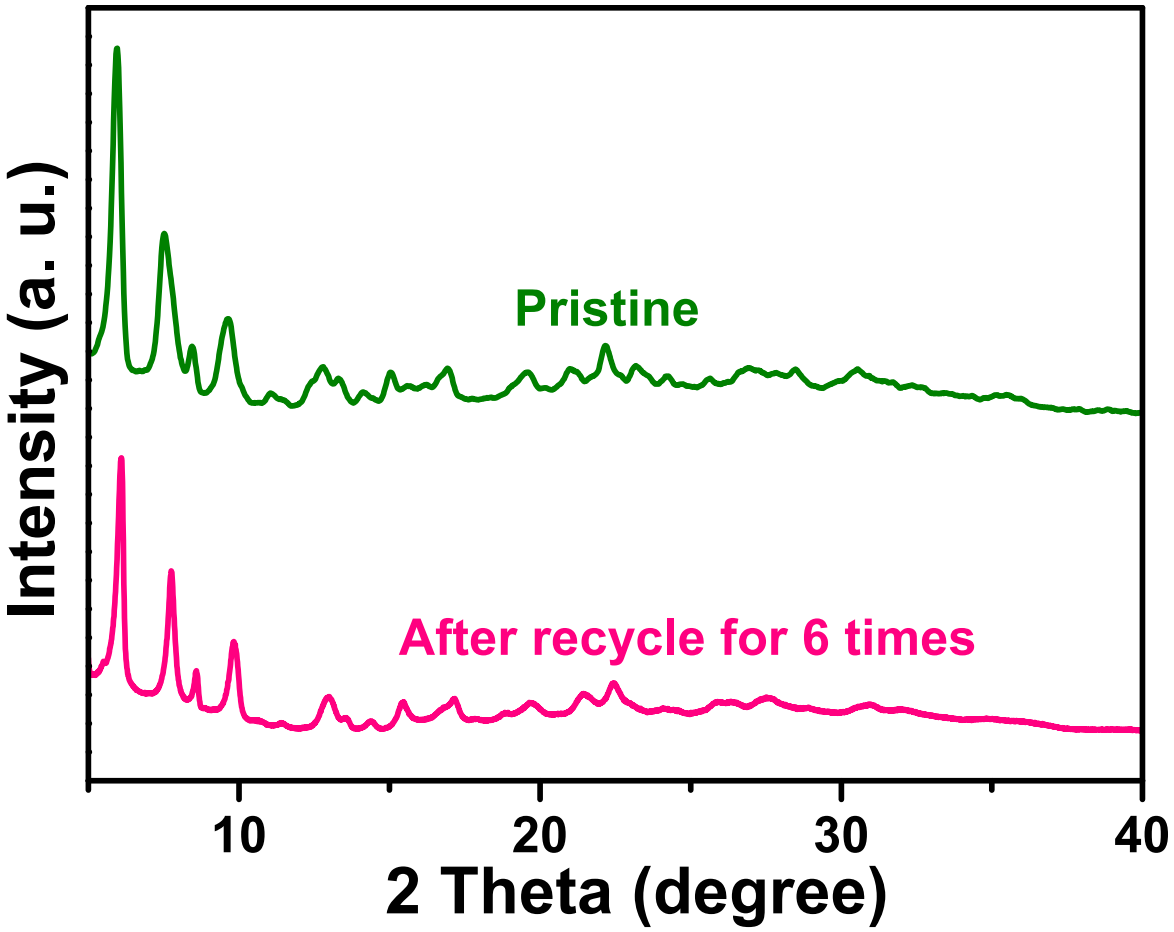

Figure S2. PXRD of TMeQ[6]-PMA NCs before and after recycle for six times.

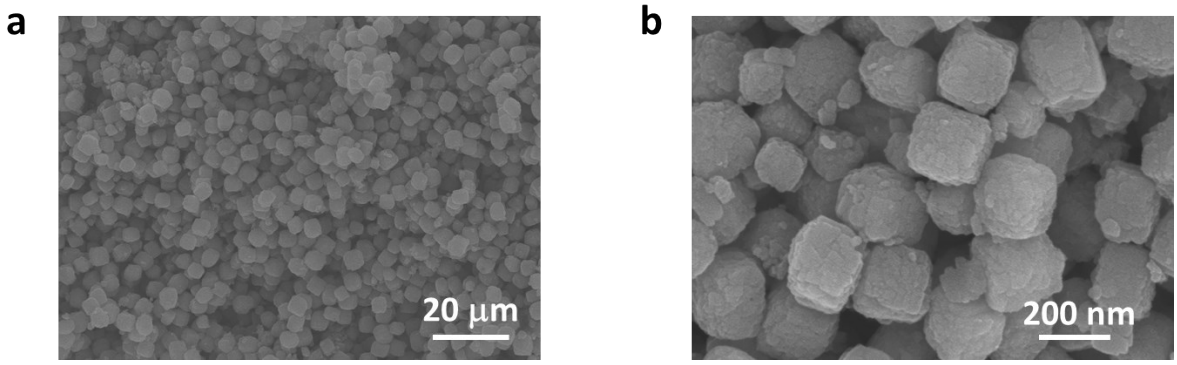

Figure S3. SEM of TMeQ[6]-PMA NCs after recycle for six times.

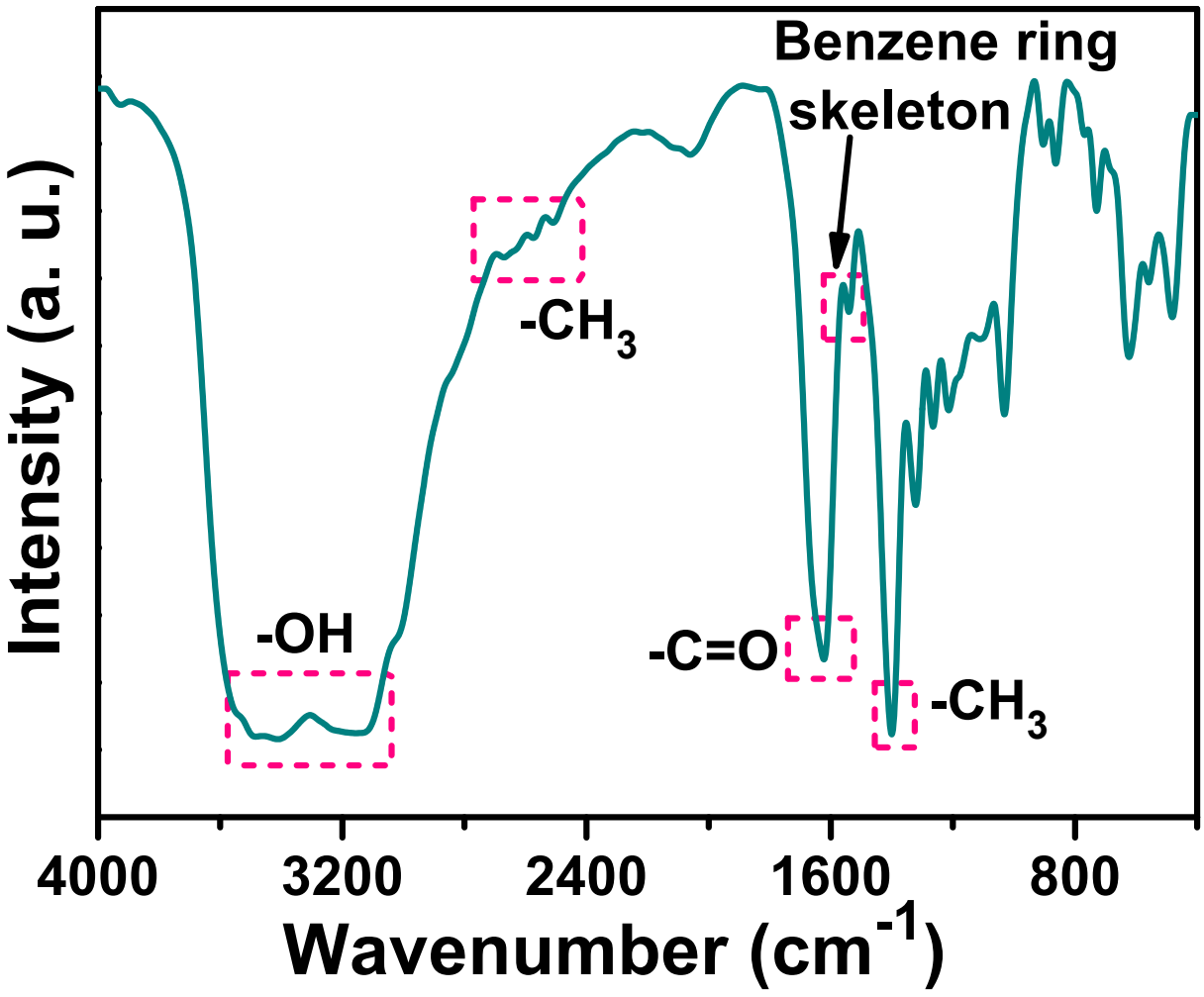

Figure S4. FTIR spectra of product.

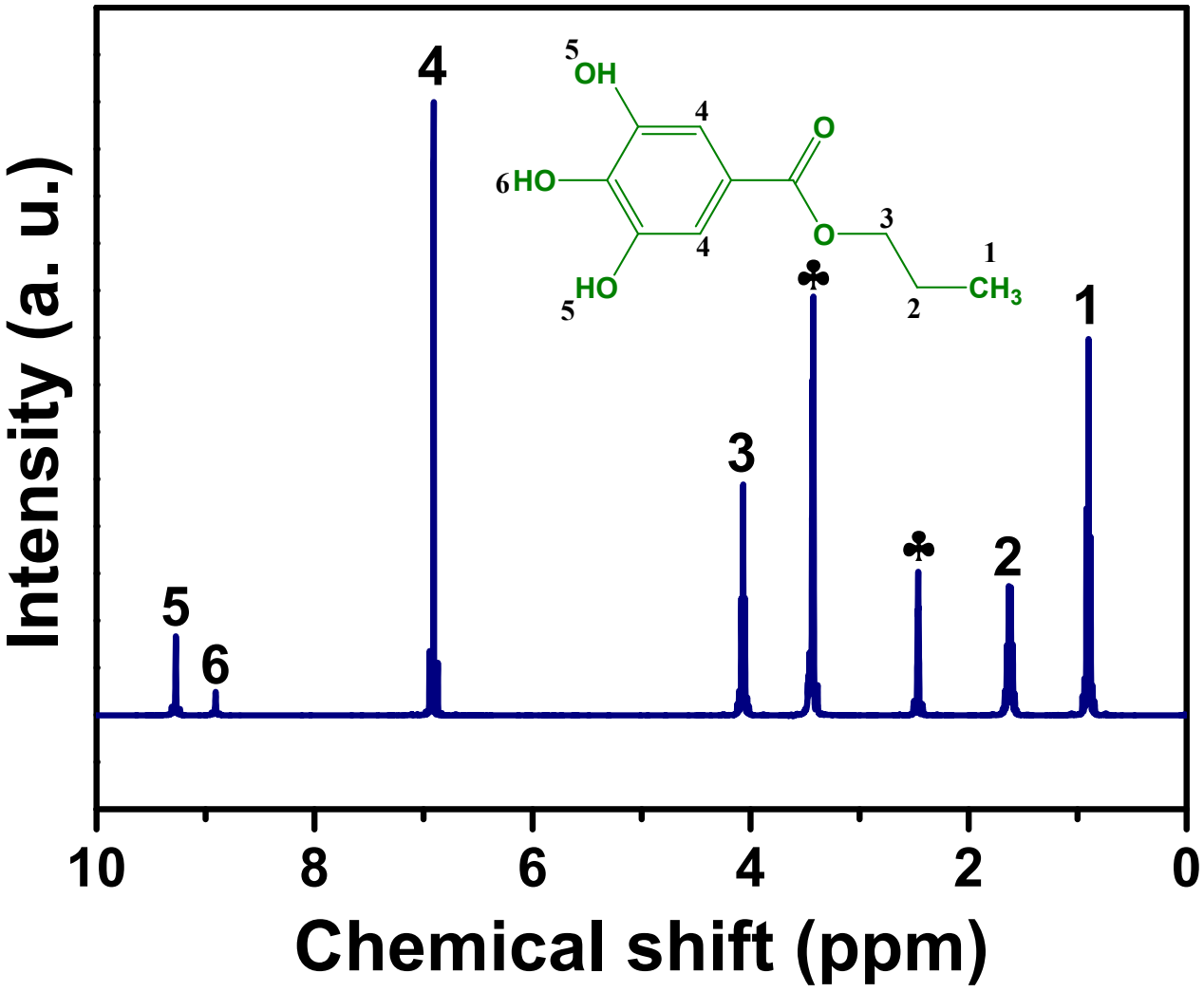

Figure S4. liquid-state 1H magnetic resonance (NMR) spectra of product.

Table S1. The elemental analysis of as-prepared TMeQ[6]-PMA NCs

Element	Atomic (%)
C	29.71
N	17.99
O	37.93
P	1.13
Mo	13.24
Total	100

Table S2. Comparison of PG Yield based on different catalysts in propyl gallate synthesis.

Catalysts	Yield of PG	References
H_2SO_4	56.5%	3
[Hnmp]HSO_4	84.3%	3
$MgFe_2O_4$ NPs	82%	4
L. plantarum	45%	5
Aspergillus niger	43%	6
Aspergillus oryzae	90%	7
Aspergillus niger	65%	8
TMeQ[6]-PMA NCs	95.6%	This work

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