Electronic Supplementary Information

Thiacalix[4]arene-supported Tetradecanuclear Cobalt Nanocage Cluster as Precursor to Synthesize CoO/Co_9S_8@CN Composite for Supercapacitor Application

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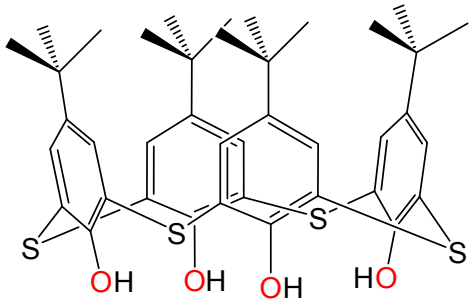

Scheme S1 *p-tert*-Butylthiacalix[4]arene(H_4TC4A).

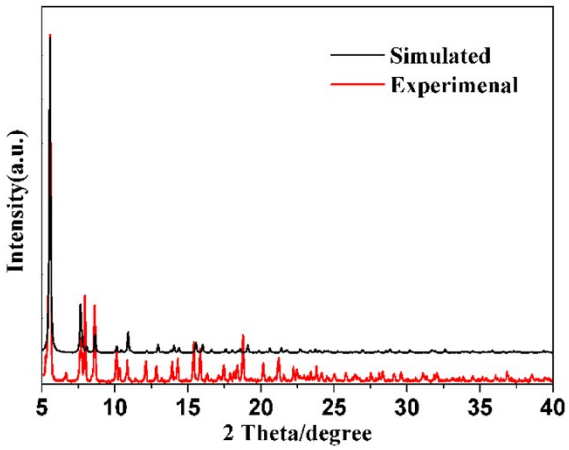

Fig. S1 PXRD of complex **1**.

Comparison of XRD patterns for compound **1** (black line as experimented) is accordant with the simulated one (red one) derived from the single crystal X-ray data, confirming the pure phase of the samples of Co_{14} clusters.

Magnetic measurements

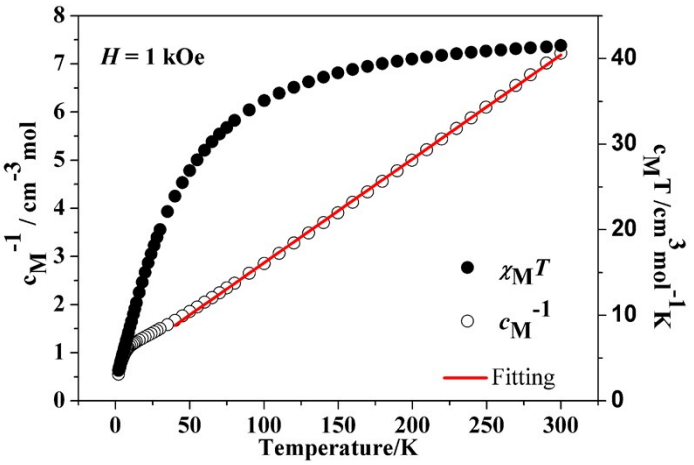

Fig. S2 Plots of $\chi_m T$ vs. T and χ_m^{-1}vs. T for compound **1** in a 1 kOe field.

Magnetic susceptibility measurements were carried out on fresh samples of compound at 2-300 K with a 1000 Oe applied field. The plots of $\chi_m T$ vs. T and χ_m^{-1} vs. T showed that the $\chi_m T$ value decreases gradually from 41.53 cm^3 mol^{-1} K at 300 K to 3.55 cm^3 mol^{-1} K at 2 K. The magnetic property of this compound can be attributed to fourteen octahedrally coordinated Co^{II} cations. For each Co^{II} center, the experimental $\chi_m T$ value at room temperature is 2.97 cm^3 mol^{-1} K, which is accord with the typical value of the Co^{II} ion (for Co^{II}, the $\chi_m T$ value normally ranges from 2.7 to 3.4 cm^3 mol^{-1} K). For this complex, fitting the experimental data in the range of 50~300 K to the Curie–Weiss law $1/\chi_m = (T - \theta)/C$ gives Curie constants (C) of 46.27 cm^3 mol^{-1} K and Weiss constants (θ) of -34.29 K. The negative Weiss constants (θ) suggest antiferromagnetic interactions between the cobalt (II) centers.

TGA-DSC analyses of compound 1

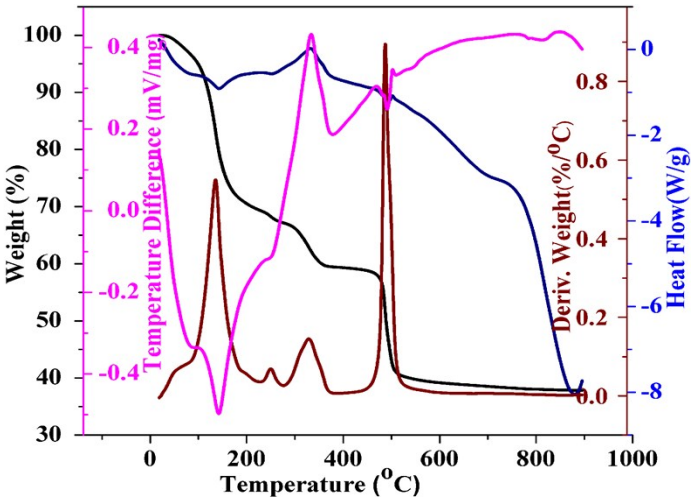

Fig. S3 TGA/DSC curves of compound **1** (in N_2).

TGA analysis on compound **1** indicates that the onset of the solvent loss is at the beginning of recording and the weight decreases sharply to 180 °C which can be ascribed to the release of the solvent molecules and coordinated H_2O. The observed weight loss of 27.2% is close to the calculated value (27.4%). Further weight loss takes place without showing any distinct plateau before 370 °C and then the compound began to decompose completely, reaching a relative stable weight at high temperature.

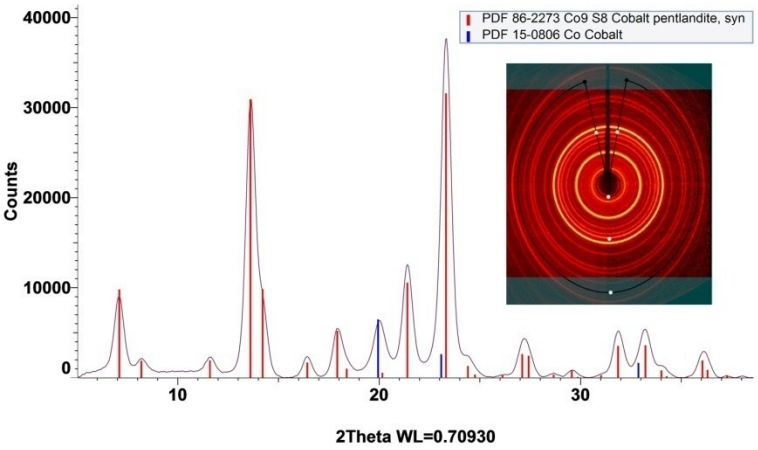

Fig. S4 The XRD of the final decomposition of TGA.

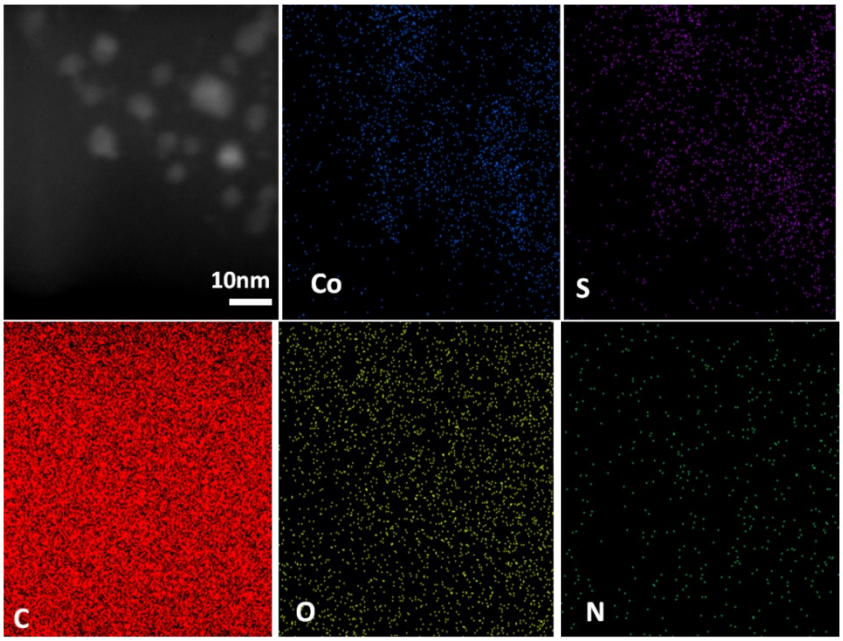

Fig. S5 The EDS element mapping of the nanocomposites

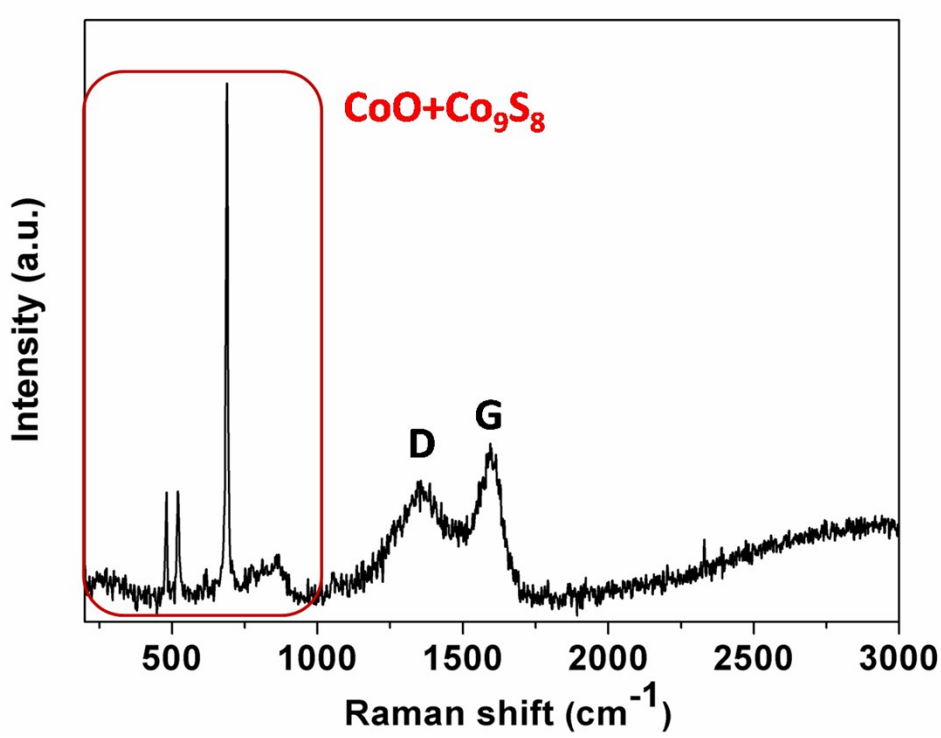

Fig. S6 The Raman spectra of CoO/Co_9S_8@CN

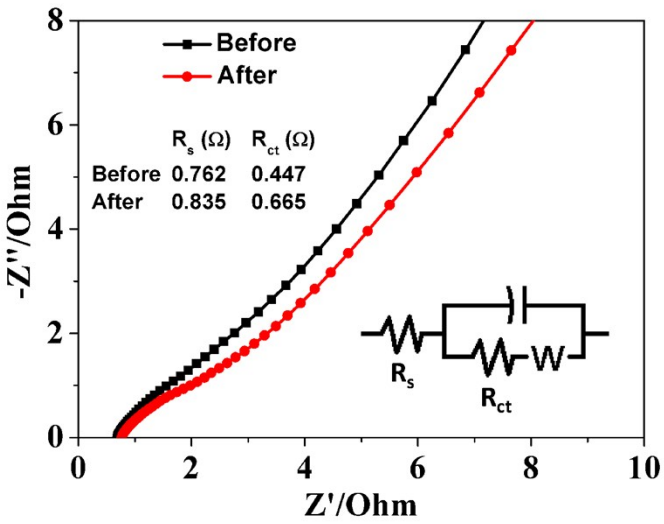

Fig. S7 Nyquist plots before and after 1000 cycles of CoO/Co_9S_8@CN/NF

The impedance measurements were applied for the NF-supported CoO/Co_9S_8@CN in range of 100 kHz -0.01 Hz. The Nyquist plots before and after 1000 cycles are composed of a depressed semicircle in the high frequency region and a almost straight line in the low frequency, which is characteristic of capacitive behavior and representative of ion diffusion in the electrode. The fitted charge transfer impedance (Rct) and the total resistance of solution resistance between the working electrode and the reference electrode (Rs) did not show any essential difference indicating the good stabilities of the fabricated CoO/Co_9S_8@CN/NF for supercapacitors.

Table S1 Crystal Data and Structural Refinement Parameters for **1**

Formula	$C_{180}H_{287}Cl_3Co_{14}N_{62}O_{43}S_{12}$
Mr	5323.79
Crystal system	Hexagonal
space group	$P6_3/m$ (No.176)
Temperature (K)	150
a(Å)	26.6695 (5)
b(Å)	26.6695 (5)
c(Å)	21.9235 (5)
α(º)	90
β(º)	90
γ(º)	120
Volume(Å^3)	13504.2 (6)
Z	2
D_c(g/cm^3)	1.196
μ(mm^{-1})	1.020
Reflections collected	95276
Unique data(R_{int})	8190
GOF on F^2	1.07
R_1 [I>2sigma(I)]	0.0745
wR_2	0.2467

$^aR_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $^bwR_2 = \{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

Table S1 Selected bond lengths (Å) of **1**

Co(1)-O(1)	1.994(3)	Co(3)-O(4)	2.092(6)
Co(1)-O(2)#1	2.028(4)	Co(3)-O(4)#3	2.092(6)
Co(1)-N(1)	2.049(5)	Co(3)-O(4)#4	2.092(5)
Co(1)-N(5)	2.142(5)	Co(3)-N(8)	2.135(6)
Co(1)-S(1))#1	2.4707(17)	Co(3)-N(8)#3	2.135(6)
Co(1)-Cl(1)	2.702(1)	Co(3)-N(8)#4	2.135(6)
Co(2)-O(3)	1.994(3)		
Co(2)-O(2)	2.032(4)		
Co(2)-N(3)#2	2.039(7)		
Co(2)-N(6)#1	2.150(5)		
Co(2)-S(2)	2.4786(16)		
Co(2)-Cl(1)	2.682(1)		

#1: x,y,-z+3/2 , #2:1-y,x-y,3/2-z, #3: 1-y,x-y,z, #4:1-x+y,1-x,z