Supporting Information

Upcycling of nonporous coordination polymers: controllable-conversion toward porosity-tuned N-doped carbons and their electrocatalytic activity in seawater battery

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Table S1. X-ray crystallographic data of $ZnCP_{azo}$-1.

Compound	$ZnCP_{azo}$-1
formula	$Zn_4C_{104}N_{24}O_{20}H_{88}$
crystal system	*Triclinic*
space group	*P-1*
fw	2255.46
a, Å	15.014(3)
b, Å	18.539(4)
c, Å	19.763(4)
α, deg	89.57(3)
β, deg	78.43(3)
γ, deg	70.48(3)
V, Å^3	5068(2)
Z	2
ρ_{calcd}, g cm^{-3}	1.478
temp , K	173(2)
λ, Å	0.69999
μ, mm^{-1}	1.019
goodness-of-fit (F^2)	1.084
F(000)	2320
reflections collected	49468
independent reflections	22567 [*R*(int) = 0.0488]
completeness to θ_{max}, %	98.8
data/parameters/restraints	22567/1369/0
θ range for data collection, deg	3.01-27.48
diffraction limits (*h*, *k*, *l*)	$-19 \le h \le 19$, $-23 \le k \le 24$, $-25 \le l \le 25$
refinement method	Full-matrix least-squares on F^2
R_1, wR_2 [$I>2\sigma(I)$]	0.0499[a], 0.1367[b]
R_1, wR_2 (all data)	0.0906[a], 0.1693[b]
largest peak, hole, eÅ^{-3}	0.755, -0.693

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR(F^2) = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ where $w = 1/[\sigma^2(Fo^2) + (0.0573P)^2 + (0.0000)P]$, $P = (Fo^2 + 2Fc^2)/3$.

Table S2. Selected bond distances (Å) and angles (deg) of $ZnCP_{azo}$-1.

Zn(1)-O(1)	2.077(3)	Zn(1)-O(2)	2.087(3)
Zn(1)-O(3)	2.046(3)	Zn(1)-O(11)$^{\#1}$	2.173(2)
Zn(1)$^{\#4}$-O(11)	2.173(2)	Zn(1)-N(1)	2.198(4)
Zn(1)-N(4)	2.209(3)	Zn(2)-O(7)	2.023(3)
Zn(2)-O(9)$^{\#2}$	2.081(3)	Zn(2)-O(5)	2.120(3)
Zn(2)-N(7)	2.188(4)	Zn(2)-N(10)	2.193(4)
Zn(2)-O(6)	2.287(3)	Zn(2)-C(4)	2.551(4)
Zn(2)$^{\#2}$-O(9)	2.081(3)	Zn(3)-O(12)	2.014(3)
Zn(3)-O(14)$^{\#3}$	2.036(3)	Zn(3)-O(16)	2.045(3)
Zn(3)-N(13)	2.217(4)	Zn(3)-N(16)	2.264(4)
Zn(3)$^{\#3}$-O(14)	2.173(2)	Zn(4)-O(18)	2.047(3)
Zn(4)-O(19)	2.087(3)	Zn(4)-O(8)	2.100(3)
Zn(4)-O(20)	2.100(3)	Zn(4)-N(19)	2.188(4)
Zn(4)-N(22)	2.200(4)		
O(3)-Zn(1)-O(1)	175.28(12)	O(3)-Zn(1)-O(2)	94.55(10)
O(1)-Zn(1)-O(2)	87.20(10)	O(3)-Zn(1)-O(11)$^{\#1}$	99.40(10)
O(1)-Zn(1)-O(11)$^{\#1}$	79.20(10)	O(2)-Zn(1)-O(11)$^{\#1}$	165.52(10)
O(3)-Zn(1)-N(1)	87.78(12)	O(1)-Zn(1)-N(1)	87.78(13)
O(2)-Zn(1)-N(1)	91.70(13)	O(11)#1-Zn(1)-N(1)	92.70(12)
O(3)-Zn(1)-N(4)	88.91(12)	O(1)-Zn(1)-N(4)	95.52(12)
O(2)-Zn(1)-N(4)	88.81(12)	O(11)$^{\#1}$-Zn(1)-N(4)	87.60(11)
N(1)-Zn(1)-N(4)	176.69(13)	O(7)-Zn(2)-O(9)$^{\#2}$	103.27(10)
O(7)-Zn(2)-O(5)	172.45(10)	O(9)$^{\#2}$-Zn(2)-O(5)	84.10(10)
O(7)-Zn(2)-N(7)	92.67(12)	O(9)$^{\#2}$-Zn(2)-N(7)	91.68(13)
O(5)-Zn(2)-N(7)	88.70(12)	O(7)-Zn(2)-N(10)	92.00(12)
O(9)$^{\#2}$-Zn(2)-N(10)	90.87(13)	O(5)-Zn(2)-N(10)	86.18(12)
N(7)-Zn(2)-N(10)	174.02(13)	O(7)-Zn(2)-O(6)	113.51(10)
O(9)$^{\#2}$-Zn(2)-O(6)	143.20(10)	O(5)-Zn(2)-O(6)	59.10(9)

N(7)-Zn(2)-O(6)	87.91(13)	N(10)-Zn(2)-O(6)	86.81(13)
O(7)-Zn(2)-C(4)	143.30(11)	O(9)$^{\#2}$-Zn(2)-C(4)	113.39(11)
O(5)-Zn(2)-C(4)	29.28(11)	N(7)-Zn(2)-C(4)	88.11(13)
N(10)-Zn(2)-C(4)	85.91(13)	O(6)-Zn(2)-C(4)	29.81(10)
O(12)-Zn(3)-O(14)$^{\#3}$	106.94(10)	O(12)-Zn(3)-O(16)	159.54(10)
O(14)$^{\#3}$-Zn(3)-O(16)	93.52(11)	O(12)-Zn(3)-N(13)	95.98(12)
O(14)$^{\#3}$-Zn(3)-N(13)	89.23(12)	O(16)-Zn(3)-N(13)	84.01(13)
O(12)-Zn(3)-N(16)	93.33(12)	O(14)$^{\#3}$-Zn(3)-N(16)	87.08(13)
O(16)-Zn(3)-N(16)	87.61(13)	N(13)-Zn(3)-N(16)	170.63(12)
O(18)-Zn(4)-O(19)	96.88(11)	O(18)-Zn(4)-O(8)	98.10(10)
O(19)-Zn(4)-O(8)	164.84(10)	O(18)-Zn(4)-O(20)	176.40(13)
O(19)-Zn(4)-O(20)	84.34(11)	O(8)-Zn(4)-O(20)	80.56(11)
O(18)-Zn(4)-N(19)	87.33(13)	O(19)-Zn(4)-N(19)	88.59(13)
O(8)-Zn(4)-N(19)	89.86(12)	O(20)-Zn(4)-N(19)	89.32(13)
O(18)-Zn(4)-N(22)	89.10(13)	O(19)-Zn(4)-N(22)	91.96(13)
O(8)-Zn(4)-N(22)	90.52(13)	O(20)-Zn(4)-N(22)	94.25(13)
N(19)-Zn(4)-N(22)	176.43(13)		

Symmetry transformation used to generate equivalent atoms:
$^{\#1}$, x, y+1, z; $^{\#2}$, -x+1, -y+1, -z+2; $^{\#3}$, -x+1, -y, -z+1; $^{\#4}$, x, y-1, z.

Table S3. X-ray crystallographic data of $ZnCP_{azo}$-2.

Compound	$ZnCP_{azo}$-2
formula	$Zn_1C_{19}N_3O_4H_{13}$
crystal system	*Monoclinic*
space group	$P2_1/c$
fw	412.69
a, Å	12.076(2)
b, Å	10.117(2)
c, Å	15.042(3)
α, deg	90
β, deg	111.41(3)
γ, deg	90
V, Å^3	1710.9(7)
Z	4
ρ_{calcd}, g cm^{-3}	1.602
temp , K	100(2)
λ, Å	0.700
μ, mm^{-1}	1.407
goodness-of-fit (F^2)	1.144
F(000)	840
reflections collected	13700
independent reflections	5565 [R(int) = 0.0744]
completeness to θ_{max}, %	94.9
data/parameters/restraints	5565/245/0
θ range for data collection, deg	1.78-33.33
diffraction limits (h, k, l)	$-17 \leq h \leq 14$, $-12 \leq k \leq 13$, $-21 \leq l \leq 21$
refinement method	Full-matrix least-squares on F^2
R_1, wR_2 [$I>2\sigma(I)$]	0.0429[a], 0.1160[b]
R_1, wR_2 (all data)	0.0525[a], 0.1293[b]
largest peak, hole, eÅ^{-3}	1.249, -1.597

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR(F^2) = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ where $w = 1/[\sigma^2(Fo^2) + (0.0573P)^2 + (0.0000)P]$, $P = (Fo^2 + 2Fc^2)/3$.

Table S4. Selected bond distances (Å) and angles (deg) of $ZnCP_{azo}$-2.

Zn(1)$^{\#3}$-O(2)	1.9911(11)	Zn(1)-O(3)	1.9448(11)
Zn(1)-O(1)	1.9586(11)	Zn(1)-O(2)$^{\#3}$	1.9911(11)
Zn(1)-N(1)	2.0078(14)	O(1)-C(1)	1.2641(15)
O(3)-C(5)	1.2922(19)	O(4)-C(5)	1.2384(19)
O(3)-Zn(1)-O(1)	114.30(5)	O(3)-Zn(1)-O(2)$^{\#3}$	100.75(5)
O(1)-Zn(1)-O(2)$^{\#3}$	114.32(5)	C(1)-O(2)-Zn(1)$^{\#3}$	128.08(9)
O(1)-Zn(1)-N(1)	99.12(4)	O(2)$^{\#3}$-Zn(1)-N(1)	97.43(5)
C(1)-O(1)-Zn(1)	128.44(9)	C(5)-O(3)-Zn(1)	105.01(9)
C(13)-N(1)-Zn(1)	120.42(9)	C(9)-N(1)-Zn(1)	121.19(9)
O(3)-Zn(1)-N(1)	130.18(5)		

Symmetry transformation used to generate equivalent atoms:
$^{\#1}$, -x+2, -y, -z+1; $^{\#2}$, -x+1, -y+1, -z+1; $^{\#3}$, -x+1, -y, -z+1.

Table S5. Summary of nitrogen adsorption of $ZnCP_{azo}$-2 and thermally converted materials of $ZnCP_{azo}$-2.

Sample Name	S_{BET}[a] ($m^2\ g^{-1}$)	V_{tot}[b] ($cc\ g^{-1}$)	V_{meso}[c] ($cc\ g^{-1}$)	V_{micro}[d] ($cc\ g^{-1}$)
Converted material at 750 °C	1195	0.68	0.28	0.40
Converted material at 1000 °C	1334	0.70	0.24	0.46
$ZnCP_{azo}$-2	1.720	0.003	0.002	0.001

[a] The specific surface area (S_{BET}) was calculated by Brunauer-Emmet-Teller (BET) method.

[b] V_{tot} represented the total pore volume at $P/P_0 = 0.99$.

[c] The mesopore volume (V_{meso}) was determined by applying Barrett-Joyner-Halenda (BJH) analysis.

[d] The micropore volume (V_{micro}) was obtained by substracting the mesopore volume from total pore volume.

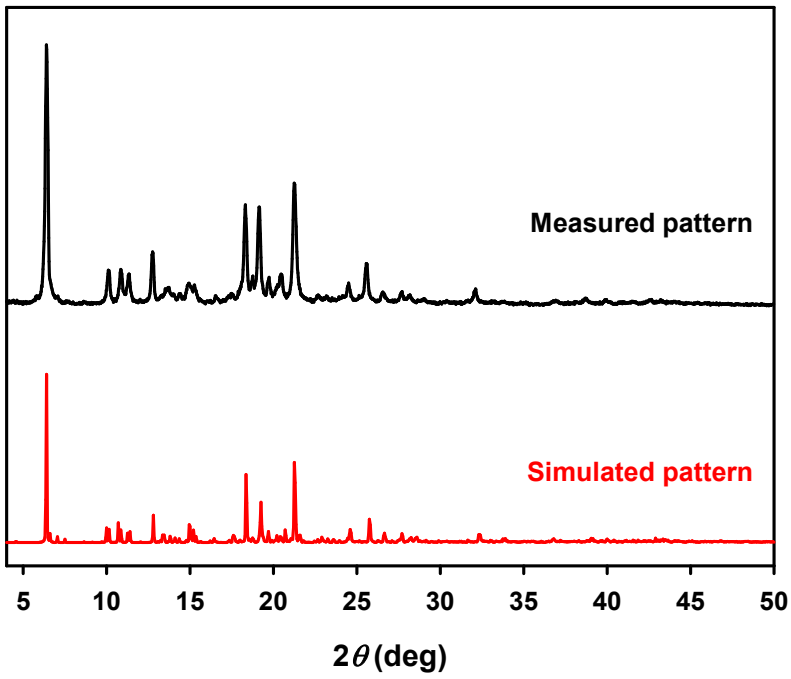

Figure S1. XRPD patterns of $ZnCP_{azo}$-1: measured pattern of as-synthesized $ZnCP_{azo}$-1 and simulated pattern from the single-crystal X-ray diffraction data.

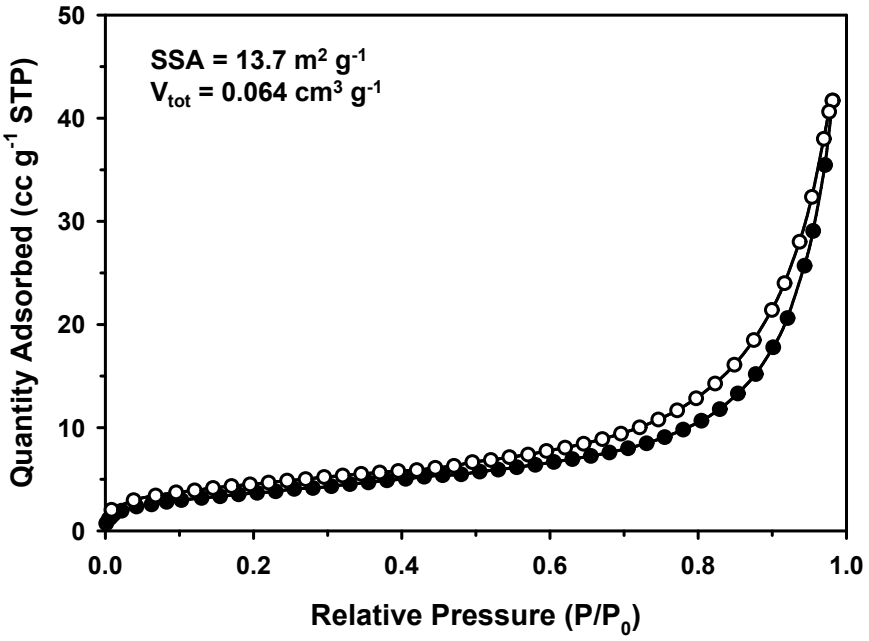

Figure S2. Nitrogen adsorption-desorption isotherm of $ZnCP_{azo}$-1.

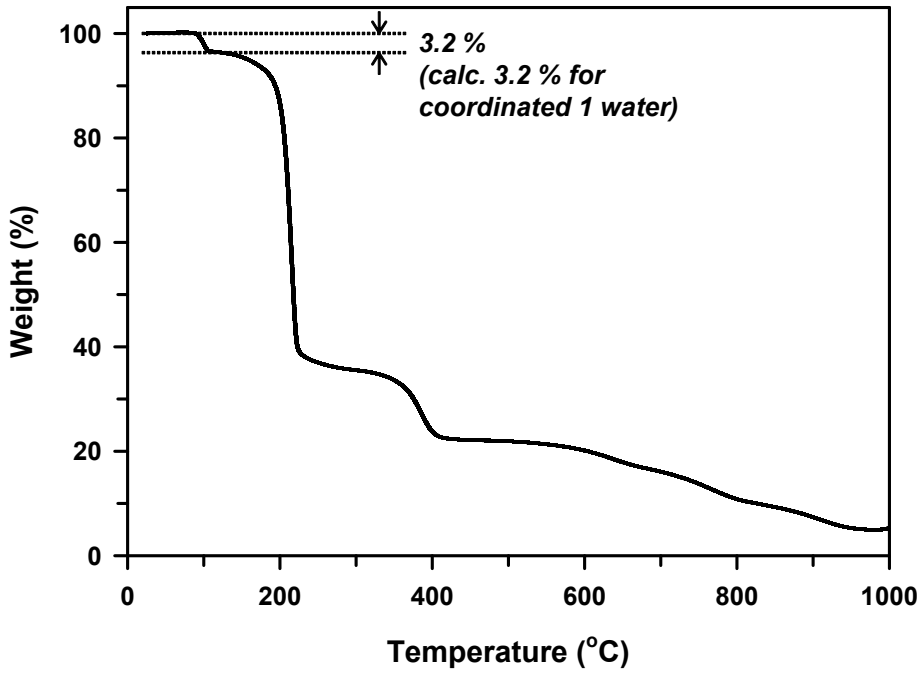

Figure S3. TGA trace of $ZnCP_{azo}$-1 obtained under a nitrogen atmosphere with 5 °C/min ramping rate. The result indicated 3.2% weight loss at 100 °C for one coordinating water (clac. 3.2%).

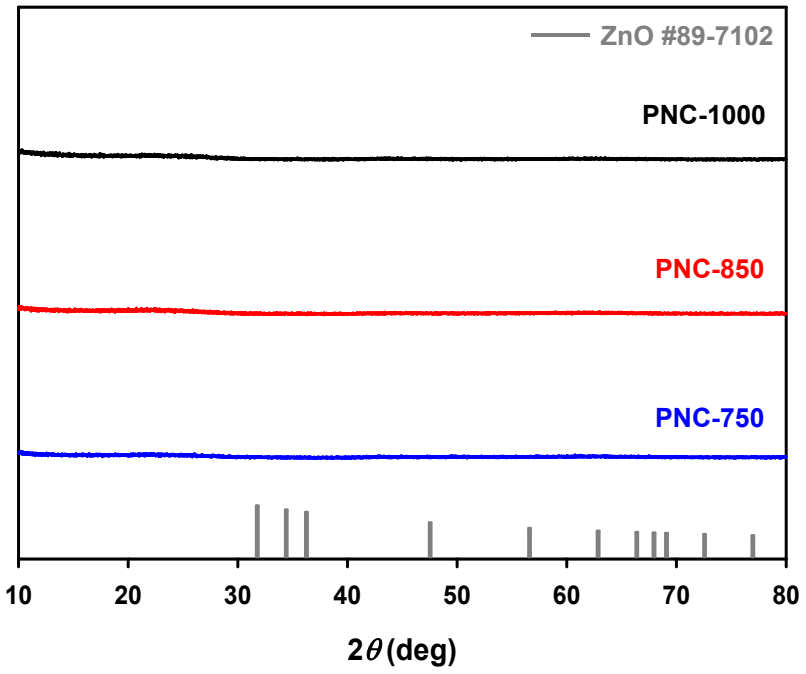

Figure S4. XRPD patterns of PNC-750, -850, and -1000.

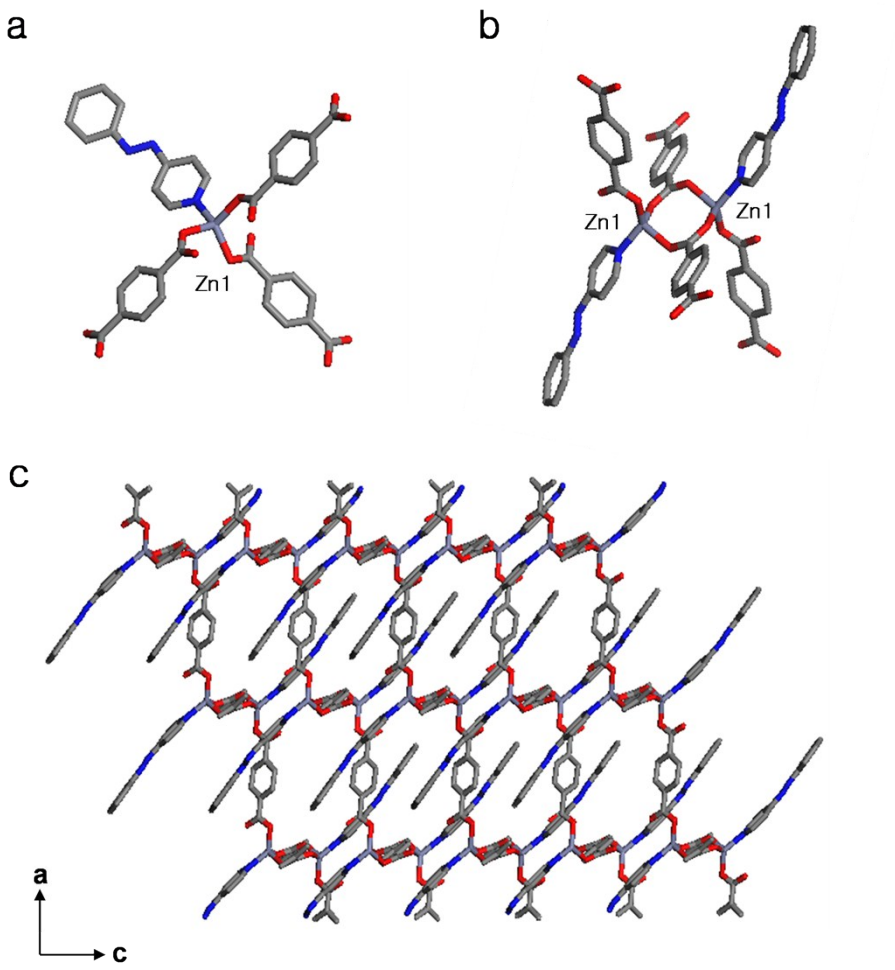

Figure S5. Single-crystal X-ray structure of $ZnCP_{azo}$-2 (a), (b) The coordination modes of the BDC^{2-} and pyridines. (c) Structure projected along the b-axis, showing nonporous framework. Hydrogen atoms are omitted for clarity. Color scheme: C, gray; O, red; N, blue; and Zn, purple.

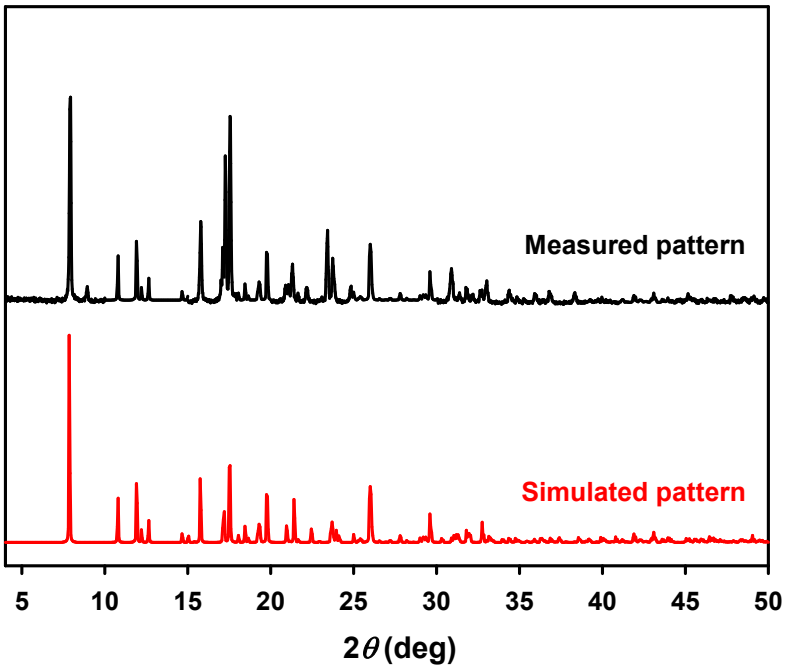

Figure S6. XRPD patterns of $ZnCP_{azo}$-2: measured pattern of as-synthesized $ZnCP_{azo}$-2 and simulated pattern from the single-crystal X-ray diffraction data.

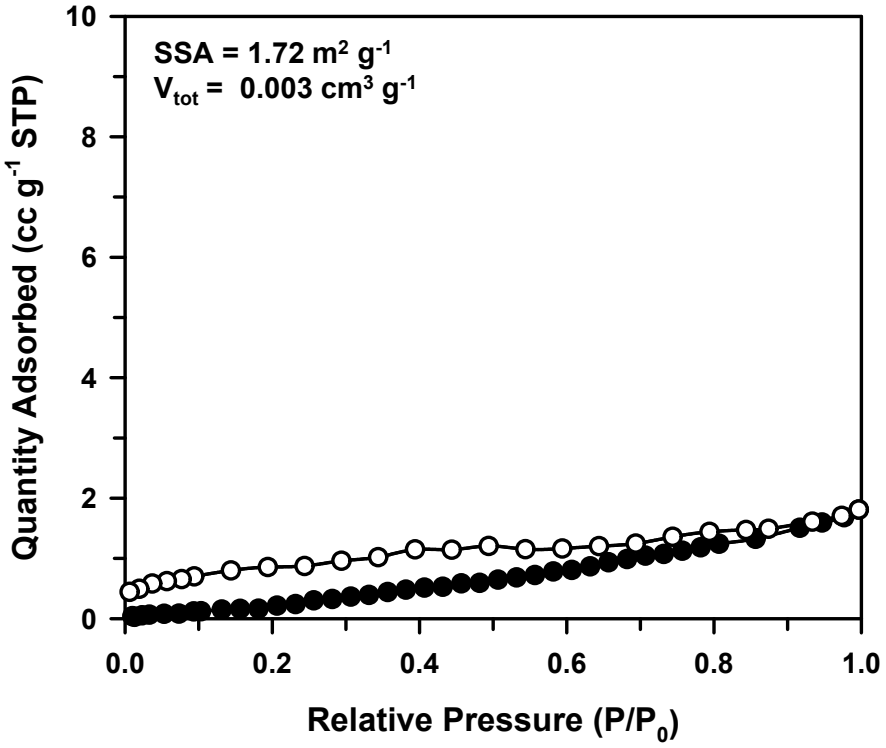

Figure S7. Nitrogen adsorption-desorption isotherm of $ZnCP_{azo}$-2.

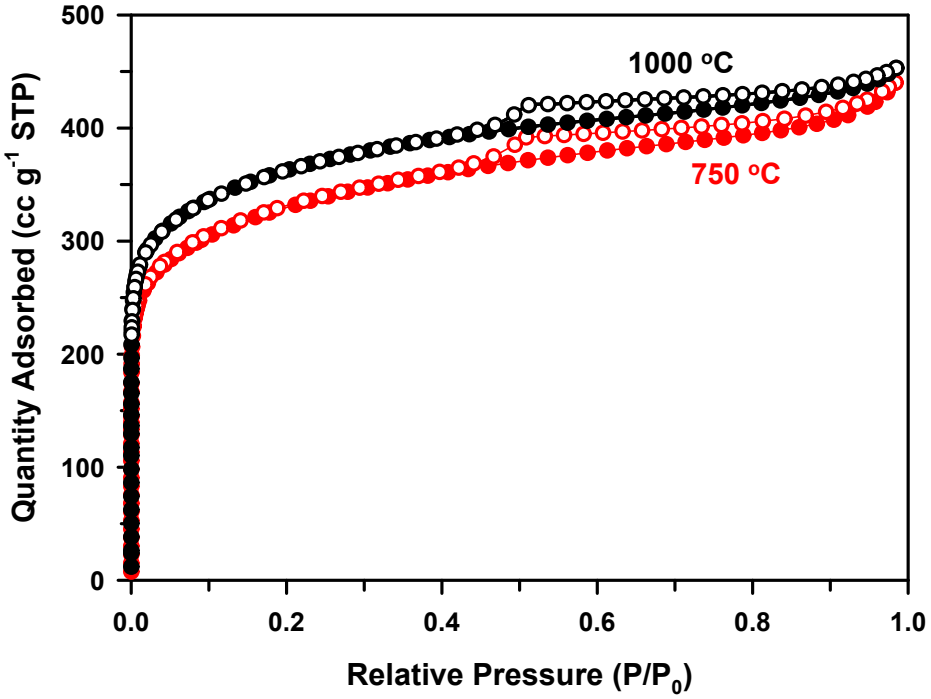

Figure S8. Nitrogen adsorption-desorption isotherm of thermally converted materials of $ZnCP_{azo}$-2.

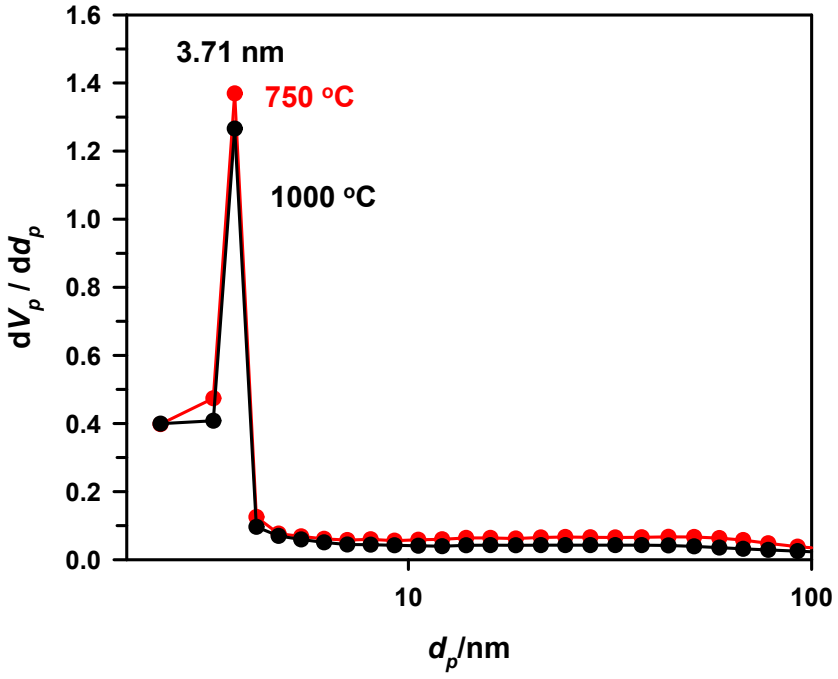

Figure S9. BJH pore size distribution curves of thermally converted materials of $ZnCP_{azo}$-2.