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Electronic Supplementary Information

An Organic-Inorganic Hybrid Zincophosphite Framework with Room Temperature Phosphorescence

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Synthesis of QDU-5

All chemicals were reagent grade and used as purchased without further purification. A mixture of ZnO (0.04 g, 0.49 mmol), H_3PO_3 (0.20-0.24 g, 2.44-2.93 mmol), tib (0.02 g, 0.07 mmol), DMF (N,N-dimethylformamide) (0.5 ml) and H_2O (1.5 ml) was sealed in a Teflon-lined autoclave (20 mL) and heated to 145 °C for 7 days then slowly cooled to 30 °C in 12 h. Yield: ca. 25% based on tib. It is notable that the crystallization time appears to be crucial to the yield and crystallinity of the product (**Table S1**).

Table S1. The relationship between the reaction time (r.t.) and yield

ZnO/g	H_3PO_3/g	tib/g	r.t./day	Yield based on tib	crystal quality
0.04	0.20-0.24	0.02	1	≤5%	poor
0.04	0.20-0.24	0.02	3	ca. 10%	poor
0.04	0.20-0.24	0.02	5	ca. 17%	ordinary
0.04	0.20-0.24	0.02	7	ca. 25%	good
0.04	0.20-0.24	0.02	9	almost powder	no crystalline product

Characterization

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). Elemental analysis (%): calcd for $C_{30}H_{44}N_{12}O_{30}P_8Zn_8$ (1823.80): C, 19.76; H, 2.43; N, 9.22. Found: C, 19.95; H, 2.82; N, 8.96. The photoluminescence spectra were measured on a HORIBA Scientific Fluoromax-4P spectrophotometer. The lifetime, steady state and time-resolved emission spectra, temperature dependent photoluminescence spectra and absolute luminescence quantum yield were measured on an Edinburgh FLSP 920 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900), a microsecond flash-lamp (uF2), a picosecond pulsed diode laser (EPL-280), a closed cycle cryostate (CS202*I-DMX-1SS, Advanced Research Systems) and an integrating sphere, respectively. The photos were recorded by iPhone7 plus. The variable-temperature powder XRD (VT-PXRD) was carried out on a modified Bruker D8 Advance diffractometer equipped with MRI high temperature attachment.

X-ray Crystallography.

The crystallographic data of **QDU-5** was collected on a XtaLAB-mini

diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The structure was solved by the SHELX-2016 software.[1] Detailed crystallographic data is summarized in Table S2 and the selected bond lengths and angles are given in Table S3. Full crystallographic data has been deposited with the CCDC (1819521), which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

Table S2. Crystal data and structure refinement parameters for **QDU-5**

	QDU-5	
Formula	$C_{30}H_{44}N_{12}O_{30}P_8Zn_8$	
*M*r (g mol^{-1})	1823.80	
Space group	$P3_2$	
Crystal system	Trigonal	
a (Å)	15.2377(9)	
b (Å)	15.2377(9)	
c (Å)	21.055(2)	
α (°)	90	
β (°)	90	
γ (°)	120	
V (Å^3)	4233.8(6)	
Z	3	
F(000)	2724	
Dc (gcm^{-3})	2.146	
μ (mm^{-1})	3.666	
R_{int}	0.0447	
limiting indices	-22≤ h ≤22 -6≤ k ≤6 -23≤ l ≤23	
Collected reflections	15862	
Unique reflections	13492	
GOF on F^2	1.074	
R_1, wR_2 [I>2σ(I)]	0.1015	0.2526
R_1, wR_2 [all data]	0.1302	0.2683

Table S3. Selected bond lengths (Å) and angles (°) for **QDU-5**

O(1)-P(1)	1.509(17)	N(7)-Zn(2)	1.922(10)
O(2)-P(1)	1.533(16)	O(5)-Zn(2)	1.885(19)
O(3)-P(1)	1.397(16)	O(7)-Zn(2)	1.880(19)
O(4)-P(2)	1.558(15)	O(23)-Zn(2)#7	1.937(14)
O(5)-P(2)	1.568(15)	O(2)-Zn(3)	1.910(18)
O(6)-P(2)	1.498(16)	O(10)-Zn(3)	2.028(14)
O(7)-P(3)	1.498(18)	O(21)-Zn(3)#6	2.017(15)
O(8)-P(3)	1.518(15)	O(24)-Zn(3)#7	1.92(2)
O(9)-P(3)	1.57(2)	O(8)-Zn(4)#5	1.896(15)
O(10)-P(4)	1.515(14)	O(10)-Zn(4)	2.044(16)
O(11)-P(4)	1.491(16)	O(15)-Zn(4)#6	1.888(15)
O(12)-P(4)	1.530(16)	O(21)-Zn(4)#6	1.996(17)
O(13)-P(5)	1.465(19)	N(11)-Zn(5)#1	1.918(11)
O(14)-P(5)	1.548(17)	O(6)-Zn(5)	1.894(19)
O(15)-P(5)	1.536(15)	O(11)-Zn(5)	1.95(2)
O(16)-P(6)	1.438(16)	O(13)-Zn(5)	1.884(19)
O(17)-P(6)	1.487(17)	N(1)-Zn(6)	1.962(11)
O(18)-P(6)	1.476(17)	O(12)-Zn(6)	1.923(18)
O(19)-P(7)	1.512(15)	O(14)-Zn(6)	1.908(14)
O(20)-P(7)	1.513(14)	O(16)-Zn(6)	1.940(17)
O(21)-P(7)	1.560(16)	N(6)-Zn(7)#2	1.974(11)
O(22)-P(8)	1.595(19)	O(3)-Zn(7)#4	1.981(15)
O(23)-P(8)	1.457(17)	O(17)-Zn(7)	1.956(18)
O(24)-P(8)	1.467(18)	O(19)-Zn(7)	1.947(17)
N(9)-Zn(1)#3	2.00(2)	N(4)-Zn(8)#1	2.053(17)
O(1)-Zn(1)	1.881(14)	O(9)-Zn(8)#2	1.838(17)
O(4)-Zn(1)	1.915(17)	O(18)-Zn(8)	1.967(18)
O(20)-Zn(1)#3	1.941(16)	O(22)-Zn(8)	1.882(17)
O(3)-P(1)-O(1)	117.6(12)	O(2)-Zn(3)-O(24)#2	120.2(7)
O(3)-P(1)-O(2)	110.2(12)	O(2)-Zn(3)-O(21)#8	107.1(8)
O(1)-P(1)-O(2)	117.0(12)	O(24)#2-Zn(3)-O(21)#8	116.3(8)
O(6)-P(2)-O(4)	112.9(9)	O(2)-Zn(3)-O(10)	108.0(6)
O(6)-P(2)-O(5)	111.7(10)	O(24)#2-Zn(3)-O(10)	117.0(7)
O(4)-P(2)-O(5)	112.5(9)	O(21)#8-Zn(3)-O(10)	81.3(7)
O(7)-P(3)-O(8)	109.1(11)	O(15)#8-Zn(4)-O(8)#9	117.1(6)
O(7)-P(3)-O(9)	114.7(13)	O(15)#8-Zn(4)-O(21)#8	118.7(7)
O(8)-P(3)-O(9)	111.2(11)	O(8)#9-Zn(4)-O(21)#8	112.6(7)
O(11)-P(4)-O(10)	111.8(11)	O(15)#8-Zn(4)-O(10)	113.9(7)
O(11)-P(4)-O(12)	115.3(12)	O(8)#9-Zn(4)-O(10)	107.1(7)
O(10)-P(4)-O(12)	107.9(10)	O(21)#8-Zn(4)-O(10)	81.4(6)

O(13)-P(5)-O(15)	110.5(13)	O(13)-Zn(5)-O(6)	122.5(8)
O(13)-P(5)-O(14)	114.3(14)	O(13)-Zn(5)-N(11)#10	108(4)
O(15)-P(5)-O(14)	110.5(12)	O(6)-Zn(5)-N(11)#10	110(3)
O(16)-P(6)-O(18)	113.0(12)	O(13)-Zn(5)-O(11)	102.2(10)
O(16)-P(6)-O(17)	111.4(11)	O(6)-Zn(5)-O(11)	105.8(7)
O(18)-P(6)-O(17)	112.6(11)	N(11)#10-Zn(5)-O(11)	107(5)
O(19)-P(7)-O(20)	114.8(10)	O(14)-Zn(6)-O(12)	111.1(8)
O(19)-P(7)-O(21)	112.9(10)	O(14)-Zn(6)-O(16)	113.7(8)
O(20)-P(7)-O(21)	107.4(9)	O(12)-Zn(6)-O(16)	110.9(7)
O(23)-P(8)-O(24)	110.4(14)	O(14)-Zn(6)-N(1)	101.8(8)
O(23)-P(8)-O(22)	115.8(14)	O(12)-Zn(6)-N(1)	107.6(9)
O(24)-P(8)-O(22)	106.6(11)	O(16)-Zn(6)-N(1)	111.2(8)
O(1)-Zn(1)-O(4)	116.4(8)	O(19)-Zn(7)-O(17)	105.8(7)
O(1)-Zn(1)-O(20)#4	108.4(8)	O(19)-Zn(7)-N(6)#7	101(5)
O(4)-Zn(1)-O(20)#4	106.8(6)	O(17)-Zn(7)-N(6)#7	114(4)
O(1)-Zn(1)-N(9)#4	106.4(10)	O(19)-Zn(7)-O(3)#3	115.8(8)
O(4)-Zn(1)-N(9)#4	109.1(8)	O(17)-Zn(7)-O(3)#3	109.6(8)
O(20)#4-Zn(1)-N(9)#4	109.6(8)	N(6)#7-Zn(7)-O(3)#3	110(4)
O(7)-Zn(2)-O(5)	114.7(7)	O(9)#7-Zn(8)-O(22)	112.0(11)
O(7)-Zn(2)-N(7)	103.2(8)	O(9)#7-Zn(8)-O(18)	107.7(9)
O(5)-Zn(2)-N(7)	109.3(7)	O(22)-Zn(8)-O(18)	122.4(8)
O(7)-Zn(2)-O(23)#2	112.0(11)	O(9)#7-Zn(8)-N(4)#10	105.9(11)
O(5)-Zn(2)-O(23)#2	112.1(8)	O(22)-Zn(8)-N(4)#10	99.4(8)
N(7)-Zn(2)-O(23)#2	104.6(8)	O(18)-Zn(8)-N(4)#10	107.9(8)

Symmetry codes: #1: x-1, y-1, z; #2: x, y-1, z; #3: x-1, y, z; #4: x+1, y, z; #5: -x+y+2, -x+1, z+1/3; #6: -x+y+2, -x+2, z+1/3; #7: x, y+1, z; #8: -y+2, x-y, z-1/3; #9: -y+1, x-y-1, z-1/3; #10: x+1, y+1, z.

References

1. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

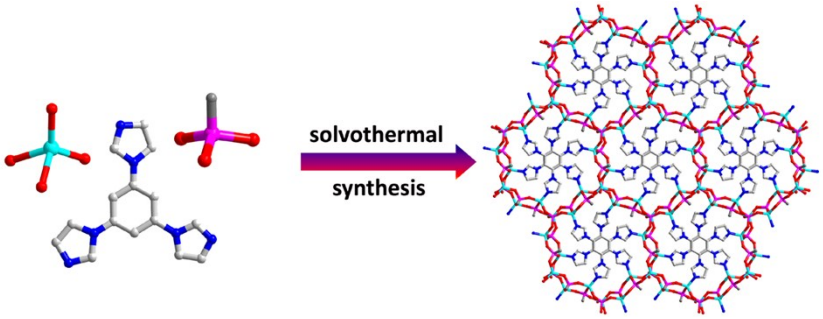

Fig. S1. The reaction scheme of the solvothermal synthesis.

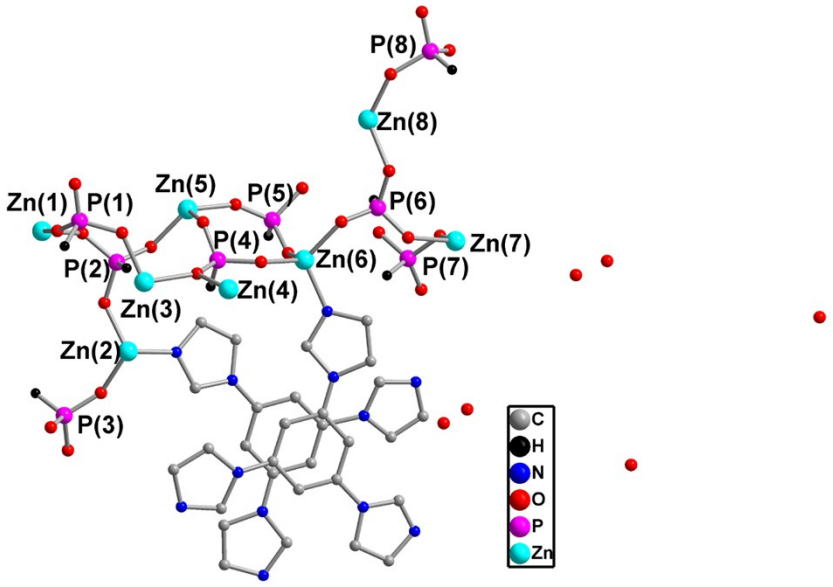

Fig. S2. The asymmetric unit of QDU-5.

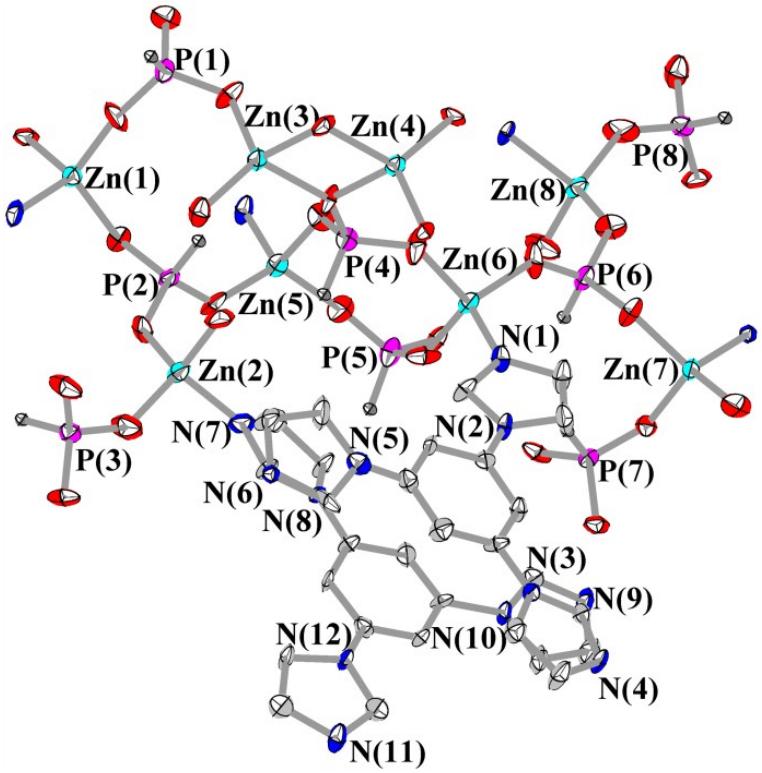

Fig. S3. The coordination environment of the Zn atoms in QDU-5.

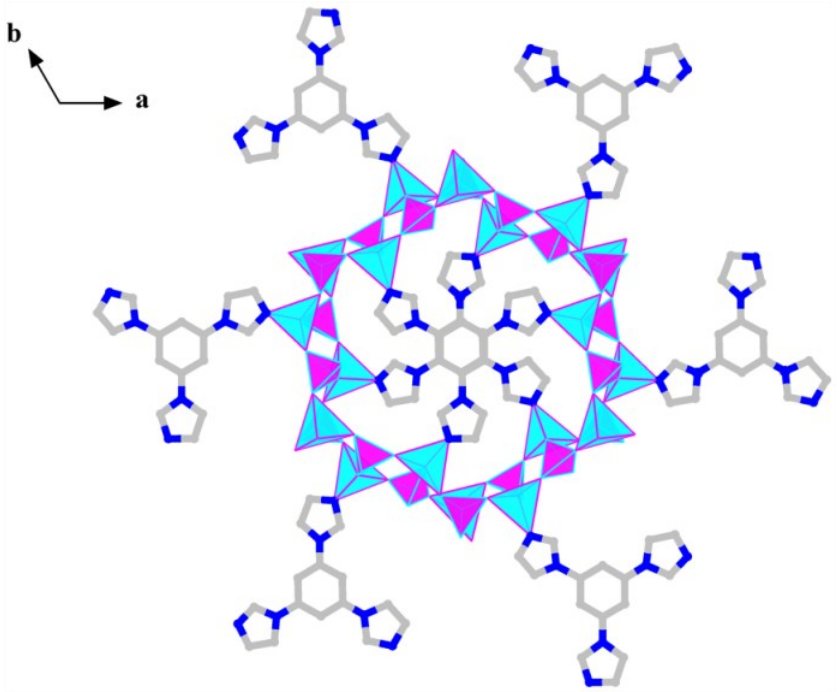

Fig. S4. View of the $[Zn_{18}(HPO_3)_{18}(tib)_8]$ secondary building unit of QDU-5.

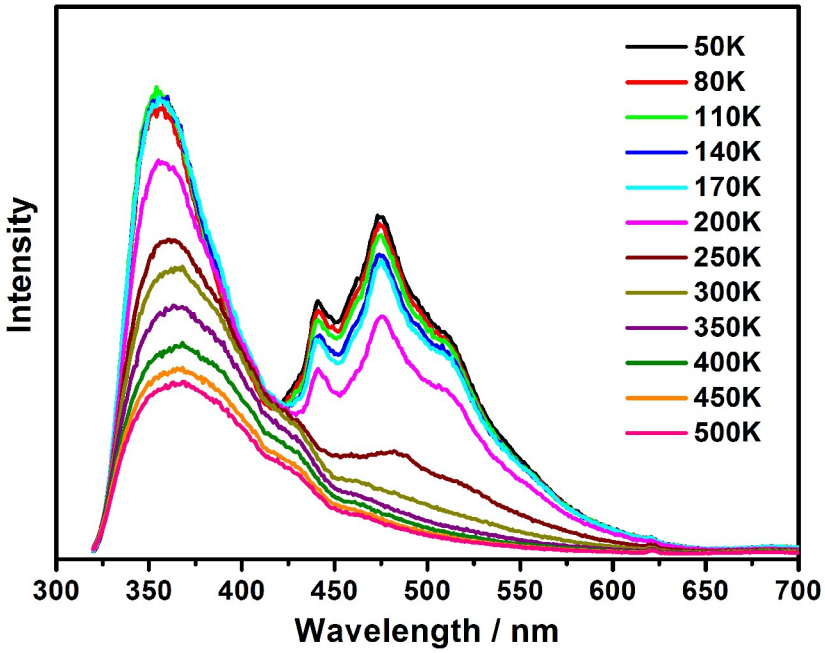

Fig. S5. Temperature-dependent luminescent emission spectra of QDU-5.

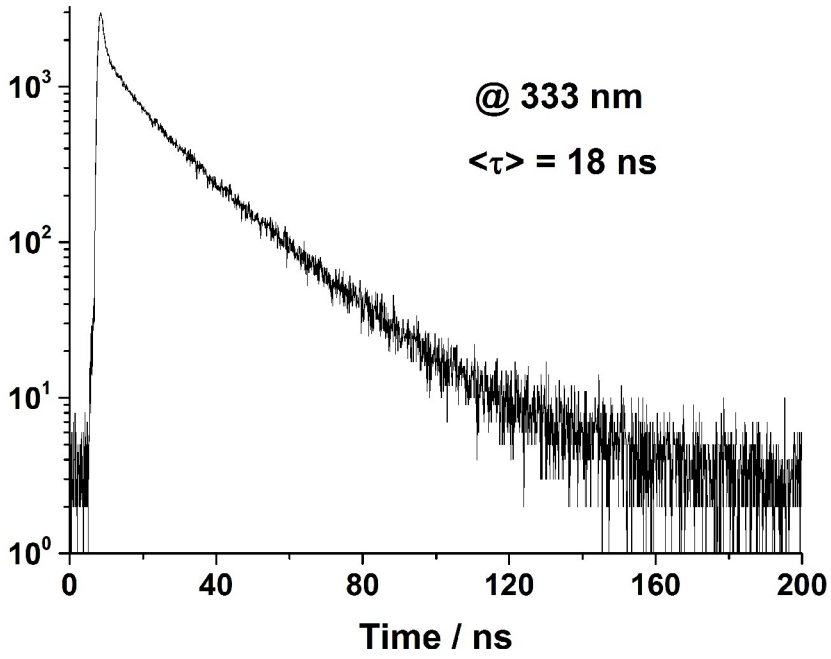

Fig. S6. PL decay spectra of compound QDU-5 excited by a picosecond pulsed diode laser.

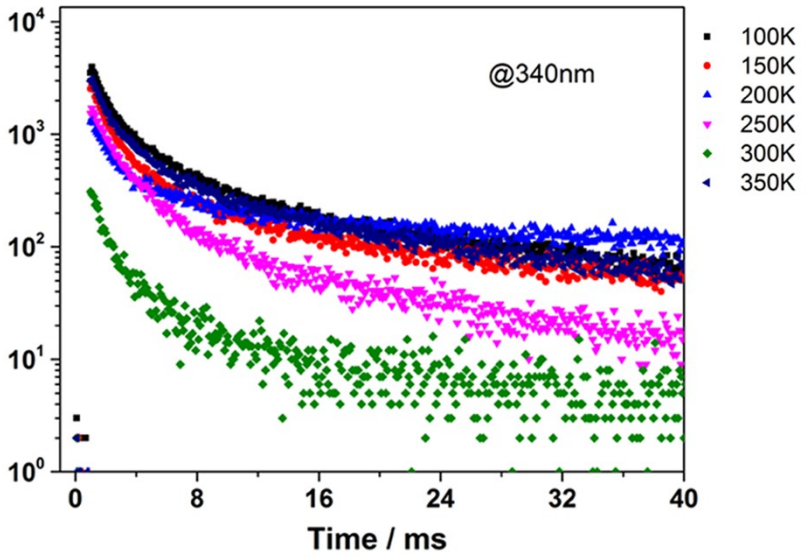

Fig. S7. Time-resolved PL decay curves of QDU-5 detected at 340 nm from 100 to 350 K.

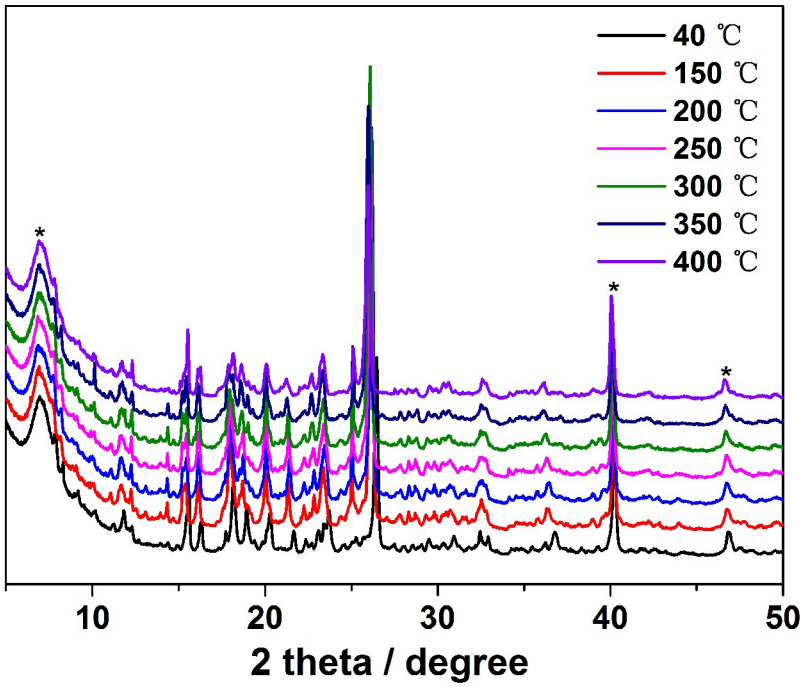

Fig. S8. The variable-temperature powder XRD plots of QDU-5 (the marked peaks are from the background).