# Electronic Supplementary Information

## Layered Hybrid Zincophosphites for Room Temperature Phosphorescent Emission

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**Syntheses of QDU-7 and QDU-8**

All chemicals were reagent grade and used as purchased without further purification. To synthesize QDU-7, a mixture of ZnO (0.08 g), $H_3PO_3$ (0.20 g), tib (0.02 g), 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. Elemental analysis of QDU-7 (%): calcd for $C_{15}H_{19}N_6O_{11}P_3Zn_3$ (748.38): C, 24.07; H, 2.56; N, 11.23. Found: C, 24.25; H, 2.87; N, 10.96. For QDU-8, 0.04 g $Zn(NO_3)_2$ and 0.16 g $H_3PO_3$ were used and the reaction time shortened to 1 day. Others remained same as QDU-7. Elemental analysis of QDU-8 (%): calcd for $C_{30}H_{26}N_{14}O_{12}P_2Zn_3$ (1032.68): C, 34.89; H, 2.54; N, 18.99. Found: C, 35.21; H, 2.73; N, 19.26. Figure S1 and Figure S2 show the simulated and the experimental powder X-ray diffraction (PXRD) patterns of QDU-7 and QDU-8 are in well agreement, respectively, suggesting the pure phase of the as-synthesized products.

**Characterization**

Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert-MPD diffractometer by using Cu-Kα1 radiation (λ = 1.54076 Å). The photoluminescence spectra and time-resolved emission spectra were measured on a HORIBA Scientific Fluoromax-4P spectrophotometer. The phosphorescence spectra were taken by using a pulsed xenon lamp. The parameters were set as sample window of 100 ms, delay after flash of 1 ms, time per flash of 130 ms and flash count of 50. Excitation monochromator was set to 330 nm (QDU-7) and 310 nm (QDU-8), the emission wavelengths were set from 330 nm to 640 nm with an increment of 1 nm and a bandpass of 2 nm. A microsecond flash xenon arc lamp was used as excitation source for the phosphorescence decay spectra. The excitation wavelength was set to 310 nm and emission wavelength were set to 380&470 nm (QDU-7) and 370&510 nm (QDU-8), respectively, with the bandpass to 2.5 nm. The data obtained were analyzed using DAS6 software. The absolute luminescence quantum yields were measured on an Edinburgh FLSP 920 fluorescence spectrophotometer.

**Crystallography**

The crystallographic data of QDU-7 and QDU-8 were collected on a XtaLAB-mini diffractometer at 293(2) K with Mo-Kα radiation ($\lambda$ = 0.71073 Å) by ω scan mode. The structures were solved by the SHELX-2016 software.[1] The H-atoms for free water molecules (O10 and O11) in QDU-7 are not added. The B-alert (Low Bond Precision on C-C Bonds---) for QDU-7 are mainly attributable to the limited quality of the single crystal. We have recollected the SCXRD data of QDU-7, however, this B-alert still exists. The "SQUEEZE" command in PLATON software was used to deal with the highly disordered

$NO_3^-$ groups in QDU-8.[2] All the tib ligand, together with the oxygen-atoms of phosphite (P2) in QDU-8, are disordered, which leads to the B-alerts in the checkcif report. Detailed crystallographic data for QDU-7 and QDU-8 are summarized in Table S1 and the selected bond lengths and angles are given in Table S2 and Table S3. Full crystallographic data for QDU-7 and QDU-8 have been deposited with the CCDC (1864979 and 1864980), 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). Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. The point symbol for the net is calculated by the TOPOS program.[3]

**References**


1. Sheldrick, G. *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3-8.
2. Spek, A. L. *J. Appl. Crystallogr.*, **2003**, *36*, 7-13.
3. Blatov, V. A. *TOPOS, A multipurpose Crystallochemical Analysis with the Program Package*, Samara State University: Russia, 2004.

**Table S1**. Crystallographic data for QDU-7 and QDU-8.

| | QDU-7 | QDU-8 |
|---|---|---|
| Formula | $C_{15}H_{19}N_6O_{11}P_3Zn_3$ | $C_{30}H_{26}N_{14}O_{12}P_2Zn_3$ |
| $F_w$ | 748.38 | 1032.68 |
| $T$/K | 293(2) | 293(2) |
| $\lambda$/Å | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic |
| Space group | *P*-1 | *P*-1 |
| $a$/Å | 10.1977(13) | 12.3250(9) |
| $b$/Å | 10.736(2) | 12.3259(10) |
| $c$/Å | 13.092(3) | 15.1393(10) |
| $\alpha$/° | 112.83(2) | 104.315(6) |
| $\beta$/° | 106.471(15) | 112.272(6) |
| $\gamma$/° | 92.519(13) | 103.174(6) |
| $V$/Å$^3$ | 1247.4(4) | 1925.0(3) |
| $Z$ | 2 | 2 |
| $D_c$/g cm$^{-3}$ | 1.992 | 1.568 |
| $\mu$/mm$^{-1}$ | 3.122 | 1.994 |
| $F$ (000) | 748 | 916 |
| total reflns | 6440 | 10655 |
| unique reflns | 4394 | 6767 |
| $R_{int}$ | 0.0688 | 0.0347 |
| Final $R$ indices [$I>2\sigma(I)$] [a] | $R_1$ = 0.0711 | $R_1$ = 0.0845 |
| w$R_2$ (all data) [b] | w$R_2$ = 0.1696 | w$R_2$ = 0.2694 |
| | $R_1$ = 0.1204 | $R_1$ = 0.1084 |
| | w$R_2$ = 0.2136 | w$R_2$ = 0.2959 |
| GOF on $F^2$ | 1.001 | 1.114 |

Table S2. Selected bond lengths (Å) and angles (º) for QDU-7

| | | | |
|---|---|---|---|
| N(1)-Zn(1) | 2.011(9) | O(9)-Zn(3)#4 | 1.940(6) |
| O(2)-Zn(1) | 1.911(6) | O(1)-P(1) | 1.491(7) |
| O(3)-Zn(1)#3 | 1.898(6) | O(2)-P(1) | 1.521(7) |
| O(6)-Zn(1)#3 | 1.917(7) | O(3)-P(1) | 1.490(8) |
| N(3)-Zn(2)#1 | 1.983(8) | O(4)-P(2) | 1.518(8) |
| O(1)-Zn(2) | 1.930(8) | O(5)-P(2) | 1.511(7) |
| O(4)-Zn(2) | 1.884(7) | O(6)-P(2) | 1.488(7) |
| O(7)-Zn(2) | 1.930(7) | O(7)-P(3) | 1.488(7) |
| N(5)-Zn(3)#2 | 2.007(9) | O(8)-P(3) | 1.527(6) |
| O(5)-Zn(3) | 1.938(6) | O(9)-P(3) | 1.504(6) |
| O(8)-Zn(3) | 1.961(6) | | |
| | | | |
| O(3)#3-Zn(1)-O(2) | 116.8(3) | O(9)#4-Zn(3)-O(8) | 112.6(3) |
| O(3)#3-Zn(1)-O(6)#3 | 117.4(3) | O(5)-Zn(3)-N(5)#6 | 109.9(4) |
| O(2)-Zn(1)-O(6)#3 | 106.9(3) | O(9)#4-Zn(3)-N(5)#6 | 104.7(3) |
| O(3)#3-Zn(1)-N(1) | 104.9(4) | O(8)-Zn(3)-N(5)#6 | 102.6(3) |
| O(2)-Zn(1)-N(1) | 110.7(4) | O(3)-P(1)-O(1) | 113.8(5) |
| O(6)#3-Zn(1)-N(1) | 98.6(4) | O(3)-P(1)-O(2) | 113.7(5) |
| O(4)-Zn(2)-O(7) | 111.9(3) | O(1)-P(1)-O(2) | 112.4(5) |
| O(4)-Zn(2)-O(1) | 113.7(4) | O(6)-P(2)-O(5) | 111.6(6) |
| O(7)-Zn(2)-O(1) | 109.8(3) | O(6)-P(2)-O(4) | 112.5(5) |
| O(4)-Zn(2)-N(3)#5 | 110.5(3) | O(5)-P(2)-O(4) | 114.5(5) |
| O(7)-Zn(2)-N(3)#5 | 105.8(3) | O(7)-P(3)-O(9) | 112.0(4) |
| O(1)-Zn(2)-N(3)#5 | 104.6(4) | O(7)-P(3)-O(8) | 112.5(4) |
| O(5)-Zn(3)-O(9)#4 | 109.9(3) | O(9)-P(3)-O(8) | 112.5(4) |
| O(5)-Zn(3)-O(8) | 116.2(3) | | |

Symmetry codes: #1: x-1, y, z-1; #2: x, y+1, z-1; #3: -x, -y, -z+2; #4: -x+1, -y, -z+3; #5: x+1, y, z+1; #6: x, y-1, z+1.

Table S3. Selected bond lengths (Å) and angles (°) for QDU-8

| | | | |
|---|---|---|---|
| N(1)-Zn(1)#1 | 2.043(13) | N(9)-Zn(3)#3 | 1.966(14) |
| N(11)-Zn(1)#2 | 1.940(14) | O(2)-Zn(3) | 1.916(7) |
| N(1A)-Zn(1)#1 | 1.901(14) | O(5)-Zn(3) | 2.032(12) |
| N(11A)-Zn(1)#2 | 2.061(14) | O(5A)-Zn(3) | 1.874(13) |
| O(3)-Zn(1) | 1.893(9) | O(1)-P(1) | 1.483(6) |
| O(6)-Zn(1) | 1.958(11) | O(2)-P(1) | 1.464(7) |
| O(6A)-Zn(1) | 1.943(11) | O(3)-P(1) | 1.473(9) |
| N(3)-Zn(2) | 1.947(10) | O(4)-P(2) | 1.573(13) |
| N(7)-Zn(2) | 1.983(8) | O(5)-P(2) | 1.419(12) |
| O(1)-Zn(2) | 1.912(7) | O(6)-P(2) | 1.562(11) |
| O(4)-Zn(2) | 1.939(14) | O(4A)-P(2) | 1.407(13) |
| O(4A)-Zn(2) | 1.953(14) | O(5A)-P(2) | 1.581(13) |
| N(5)-Zn(3)#2 | 1.968(7) | O(6A)-P(2) | 1.492(11) |
| | | | |
| O(3)-Zn(1)-O(6A) | 107.2(5) | O(4A)-Zn(2)-N(7) | 97.8(5) |
| O(3)-Zn(1)-N(1A)#4 | 123.3(5) | O(5A)-Zn(3)-O(2) | 112.5(4) |
| O(6A)-Zn(1)-N(1A)#4 | 86.2(6) | O(5A)-Zn(3)-N(9)#6 | 99.3(6) |
| O(3)-Zn(1)-N(11)#5 | 119.1(6) | O(2)-Zn(3)-N(9)#6 | 106.9(5) |
| O(6A)-Zn(1)-N(11)#5 | 112.1(7) | O(5A)-Zn(3)-N(5)#5 | 120.2(6) |
| N(1A)#4-Zn(1)-N(11)#5 | 104.2(6) | O(2)-Zn(3)-N(5)#5 | 104.7(4) |
| O(3)-Zn(1)-O(6) | 106.9(5) | N(9)#6-Zn(3)-N(5)#5 | 112.6(5) |
| N(1A)#4-Zn(1)-O(6) | 111.8(7) | O(2)-Zn(3)-O(5) | 108.9(5) |
| N(11)#5-Zn(1)-O(6) | 85.3(6) | N(9)#6-Zn(3)-O(5) | 121.4(6) |
| O(3)-Zn(1)-N(11A)#5 | 98.2(5) | N(5)#5-Zn(3)-O(5) | 101.0(5) |
| O(6A)-Zn(1)-N(11A)#5 | 136.8(7) | O(3)-P(1)-O(2) | 112.7(5) |
| N(1A)#4-Zn(1)-N(11A)#5 | 108.3(6) | O(3)-P(1)-O(1) | 115.4(5) |
| O(6)-Zn(1)-N(11A)#5 | 106.5(6) | O(2)-P(1)-O(1) | 112.0(5) |
| O(3)-Zn(1)-N(1)#4 | 99.9(5) | O(4A)-P(2)-O(5) | 137.4(8) |
| O(6A)-Zn(1)-N(1)#4 | 107.7(6) | O(4A)-P(2)-O(6A) | 80.5(9) |
| N(11)#5-Zn(1)-N(1)#4 | 109.7(6) | O(5)-P(2)-O(6A) | 118.5(8) |
| O(6)-Zn(1)-N(1)#4 | 137.6(7) | O(4A)-P(2)-O(6) | 116.7(8) |
| N(11A)#5-Zn(1)-N(1)#4 | 101.3(6) | O(5)-P(2)-O(6) | 76.5(8) |
| O(1)-Zn(2)-O(4) | 112.1(5) | O(5)-P(2)-O(4) | 112.9(8) |
| O(1)-Zn(2)-N(3) | 110.1(5) | O(6A)-P(2)-O(4) | 110.5(8) |
| O(4)-Zn(2)-N(3) | 92.9(5) | O(6)-P(2)-O(4) | 139.3(7) |
| O(1)-Zn(2)-O(4A) | 108.3(5) | O(4A)-P(2)-O(5A) | 113.3(9) |
| N(3)-Zn(2)-O(4A) | 115.5(6) | O(6A)-P(2)-O(5A) | 144.8(7) |
| O(1)-Zn(2)-N(7) | 110.8(4) | O(6)-P(2)-O(5A) | 105.7(8) |
| O(4)-Zn(2)-N(7) | 116.0(6) | O(4)-P(2)-O(5A) | 84.4(8) |
| N(3)-Zn(2)-N(7) | 113.8(4) | | |

Symmetry codes: #1: x-1, y-1, z; #2: x-1, y-1, z-1; #3: x, y, z-1; #4: x+1, y+1, z; #5: x+1, y+1, z+1; #6: x, y, z+1.

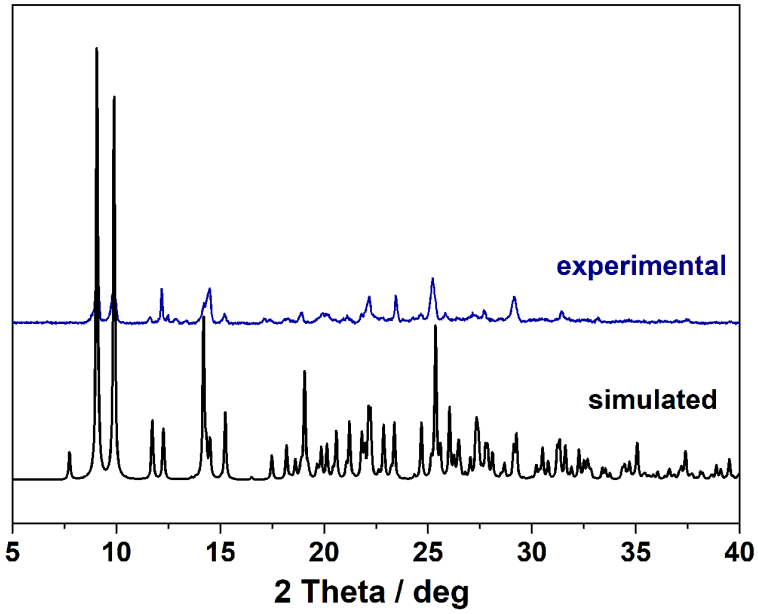


**Figure S1.** PXRD patterns of simulated and as-synthesized QDU-7.

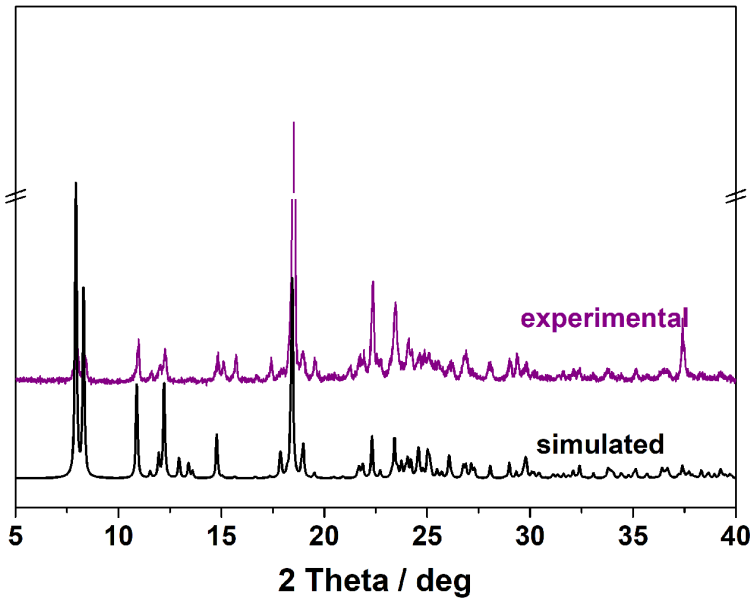


**Figure S2.** PXRD patterns of simulated and as-synthesized QDU-8.

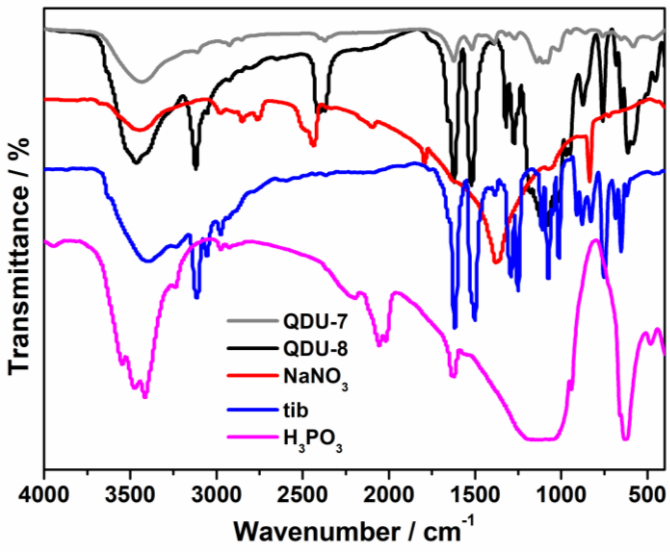


**Figure S3.** IR plots of QDU-7, QDU-8, $NaNO_3$, tib and $H_3PO_3$.

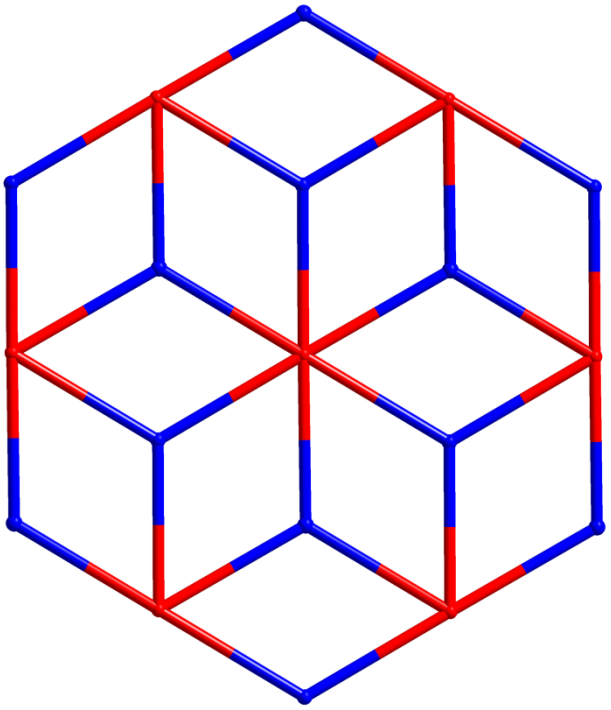

**Figure S4.** (3,6)-connected topological net of QDU-8.

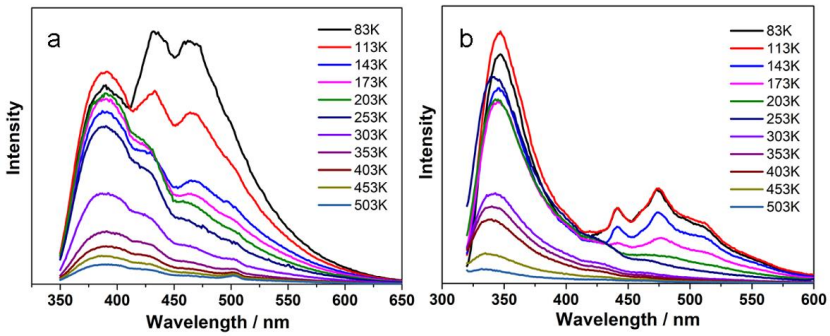


**Figure S5**. Temperature-dependent luminescent emission spectra of (a) QDU-7 and (b) QDU-8.