Supporting Information

Unveiling the unique mechanism of the UV-sensitive phosphonate-based metal-organic frameworks

Wenzhuo Tan,ab Li Xu,ab Ziwei Liu,ab Jihu Su,c and Tao Zheng *ab

a School of Materials Science and Engineering, Northwestern Polytechnical University, Xi’an 710072, P. R. China. E-mail: zhengtao@nwpu.edu.cn
b Institute of Clean Energy, Yangtze River Delta Research Institute, Northwestern Polytechnical University, Suzhou 215400, P. R. China.
c Hefei National Laboratory for Physical Sciences at Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei 230026, P. R. China
# Contents

1. Results and Discussion.......................................................................................................................... 3

1.1 The Phosphonate Ligand and the Guest Molecules .............................................................................. 3

1.2 Crystal Data and Structures .................................................................................................................. 4

1.3 Analysis of Weak Interaction ............................................................................................................... 11

1.4 Powder X-ray Diffraction ..................................................................................................................... 15

1.5 IR and Raman Spectra ............................................................................................................................ 17

1.6 Thermal Gravimetric Analysis ............................................................................................................... 18

1.7 UV-vis Absorption Spectra .................................................................................................................... 19

1.8 Photoluminescence Spectra and Fluorescence Quenching Curves ....................................................... 20

1.9 Determination of detection limit ........................................................................................................... 30

1.10 EPR Spectra Before and After UV Irradiation ...................................................................................... 31

2. References .................................................................................................................................................. 32
1. Results and Discussion

1.1 The Phosphonate Ligand and the Guest Molecules

Figure S1. The TppmH₈ ligand and guest molecules.
## 1.2 Crystal Data and Structures

**Table S1.** Crystal data and refinement details for **UPF-112**, **UPF-113** and **UPF-114**.

<table>
<thead>
<tr>
<th></th>
<th><strong>UPF-112</strong></th>
<th><strong>UPF-113</strong></th>
<th><strong>UPF-114</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₄₀H₄₀O₁₇P₄N₃U</td>
<td>C₃₅H₃₂O₁₈P₄U₂N₂</td>
<td>C₇₄H₅₈O₃₀P₈U₃N₄</td>
</tr>
<tr>
<td>M</td>
<td>1196.68</td>
<td>1368.58</td>
<td>2445.14</td>
</tr>
<tr>
<td>CCDC No.</td>
<td>2295557</td>
<td>2295555</td>
<td>2295556</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P</td>
<td>C2/c</td>
</tr>
<tr>
<td>a / Å</td>
<td>13.0819(13)</td>
<td>10.7280(12)</td>
<td>21.053(6)</td>
</tr>
<tr>
<td>b / Å</td>
<td>24.404(2)</td>
<td>15.0760(16)</td>
<td>14.058(4)</td>
</tr>
<tr>
<td>c / Å</td>
<td>13.3433(12)</td>
<td>15.4046(18)</td>
<td>28.441(8)</td>
</tr>
<tr>
<td>α / deg</td>
<td>90</td>
<td>61.166(5)</td>
<td>90.000</td>
</tr>
<tr>
<td>β / deg</td>
<td>109.386(3)</td>
<td>71.045(5)</td>
<td>111.043(8)</td>
</tr>
<tr>
<td>γ / deg</td>
<td>90</td>
<td>80.722(5)</td>
<td>90.000</td>
</tr>
<tr>
<td>V /Å³</td>
<td>4018.3(6)</td>
<td>2064.2(4)</td>
<td>7856(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>ρcalcd / g cm⁻³</td>
<td>1.908</td>
<td>2.168</td>
<td>2.062</td>
</tr>
<tr>
<td>F (000)</td>
<td>2252</td>
<td>1258</td>
<td>4640</td>
</tr>
<tr>
<td>μ(Mo Kα) /mm⁻¹</td>
<td>4.277</td>
<td>8.068</td>
<td>6.421</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.030</td>
<td>1.092</td>
<td>1.021</td>
</tr>
<tr>
<td>R₁, wR₂, [I &gt; 2σ(I)]</td>
<td>0.0315, 0.0896</td>
<td>0.1013, 0.2887</td>
<td>0.0374, 0.0870</td>
</tr>
<tr>
<td>(Ap)max, (Ap)min / eÅ⁻³</td>
<td>2.33, -0.9</td>
<td>11.78, -5.58</td>
<td>2.22, -1.12</td>
</tr>
<tr>
<td>porosity</td>
<td>36%</td>
<td>30%</td>
<td>27%</td>
</tr>
</tbody>
</table>

*a* $R_1 = \Sigma ||F_o|| - |F_c|| / \Sigma |F_o||$, *b* $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$
Table S2. Bond lengths of UPF-112.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Lengths [Å]</th>
<th>Bond</th>
<th>Lengths [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1=O13</td>
<td>1.771(3)</td>
<td>P2-O4 HP</td>
<td>1.541(3)</td>
</tr>
<tr>
<td>U1=O14</td>
<td>1.773(3)</td>
<td>P2-O5 HP</td>
<td>1.546(4)</td>
</tr>
<tr>
<td>U1-O1</td>
<td>2.354(3)</td>
<td>P2=O6</td>
<td>1.484(3)</td>
</tr>
<tr>
<td>U1-O12A</td>
<td>2.354(3)</td>
<td>P3-O7 HP</td>
<td>1.556(3)</td>
</tr>
<tr>
<td>U1-O6B</td>
<td>2.361(3)</td>
<td>P3-O8 HP</td>
<td>1.516(3)</td>
</tr>
<tr>
<td>U1-O9C</td>
<td>2.371(3)</td>
<td>P3-O9</td>
<td>1.506(3)</td>
</tr>
<tr>
<td>U1-O1w</td>
<td>2.594(4)</td>
<td>P4-O10</td>
<td>1.549(4)</td>
</tr>
<tr>
<td>P1-O1</td>
<td>1.501(3)</td>
<td>P4-O11</td>
<td>1.519(4)</td>
</tr>
<tr>
<td>P1=O2</td>
<td>1.496(3)</td>
<td>P4-O12</td>
<td>1.515(3)</td>
</tr>
<tr>
<td>P1-O3p</td>
<td>1.582(4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Symmetric codes for UPF-112: A: 1/2+x, 3/2-y, 1/2+z; B: 3/2-x, 1/2+y, 3/2-z; C: x, y, 1+z. P: the oxygen atom is protonated. HP: the oxygen atom is half protonated.

Figure S2. Asymmetric building unit of UPF-112 with atomic labeling scheme at 50% probability. All hydrogen atoms and 4,4'-bpy molecules are omitted for clarity.
**Figure S3.** Crystal framework structures of UPF-112 (a, b, and c), viewed along $a$, $b$, and $c$ axis, respectively. UO$_2$ is represented by the yellow pentagonal bipyramid, while $\text{CPO}_3$ is represented as a purple tetrahedron, and the guest molecules are omitted for clarity.

UPF-112 crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one UO$_2^{2+}$ cation, one TppmH$_8$ ligand, one and a half 4,4'$'$-bpy, one coordinated water molecule, and two lattice water molecules (Fig. S2). UO$_2^{2+}$ cation adopts a pentagonal bipyramid coordination geometry, forming UO$_2$ units. O1, O1w, O12A, O6B, and O9C are in the equatorial plane (Figs. S3a-S3c).

The bond lengths of U=O and U-O are in the range of $1.771(3)$-$1.773(3)$ Å and $2.354(3)$-$2.371(3)$ Å, respectively. The bond length of U1-O1w is $2.594(4)$ Å, which is longer than other bonds between uranium atoms and coordinated water molecules. UO$_2$ units act as zero-dimensional secondary building units (0D-SBU) connecting four TppmH$_8$ ligands to give porous 3D frameworks with 4,4'$'$-bpy molecules filled inside (Figs. S3a and S3b). 4,4'$'$-bpy molecules are part or fully protonated to balance the charge, forming hydrogen bonds with the phosphonate groups in the framework structure. The P-O bond lengths in the range of $1.496(3)$-$1.516(3)$ Å ($1.496(3)$ Å of P1-O2, $1.484(3)$ Å of P2-O6, $1.506(3)$ Å of P3-O9, $1.515(3)$ Å of P4-O12) are assigned to P=O groups. The bond length of P1-O3, P2-O4, P2-O5, P3-O7, and P4-O10 is $1.582(4)$ Å, $1.541(3)$ Å, $1.546(4)$ Å, $1.556(3)$ Å, and $1.549(4)$ Å, respectively, showing that O3 is fully protonated and the other oxygen atoms are half protonated (Table S2).
Table S3. Bond lengths of UPF-113.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Lengths [Å]</th>
<th>Bond</th>
<th>Lengths [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1=O13</td>
<td>1.783(15)</td>
<td>U3-O7E</td>
<td>2.338(18)</td>
</tr>
<tr>
<td>U1=O13J</td>
<td>1.783(16)</td>
<td>U3-O10</td>
<td>2.40(2)</td>
</tr>
<tr>
<td>U1-O1</td>
<td>2.242(17)</td>
<td>U3-O1w</td>
<td>2.54(2)</td>
</tr>
<tr>
<td>U1-O1J</td>
<td>2.242(17)</td>
<td>P1-O1</td>
<td>1.502(18)</td>
</tr>
<tr>
<td>U1-O6A</td>
<td>2.308(17)</td>
<td>P1-O2</td>
<td>1.534(19)</td>
</tr>
<tr>
<td>U1-O6K</td>
<td>2.308(17)</td>
<td>P1-O3</td>
<td>1.527(17)</td>
</tr>
<tr>
<td>U2-O14</td>
<td>1.797(19)</td>
<td>P2-O4</td>
<td>1.50(2)</td>
</tr>
<tr>
<td>U2-O14I</td>
<td>1.797(19)</td>
<td>P2-O5P</td>
<td>1.56(2)</td>
</tr>
<tr>
<td>U2-O2B</td>
<td>2.180(18)</td>
<td>P2-O6</td>
<td>1.51(2)</td>
</tr>
<tr>
<td>U2-O2G</td>
<td>2.180(18)</td>
<td>P3-O7</td>
<td>1.485(18)</td>
</tr>
<tr>
<td>U2-O4</td>
<td>2.24(2)</td>
<td>P3-O9</td>
<td>1.517(16)</td>
</tr>
<tr>
<td>U2-O4I</td>
<td>2.24(2)</td>
<td>P3-O8P</td>
<td>1.590(18)</td>
</tr>
<tr>
<td>U3-O15</td>
<td>1.77(2)</td>
<td>P4-O10</td>
<td>1.508(17)</td>
</tr>
<tr>
<td>U3-O16</td>
<td>1.79(2)</td>
<td>P4-O11HP</td>
<td>1.541(18)</td>
</tr>
<tr>
<td>U3-O3C</td>
<td>2.312(16)</td>
<td>P4-O12HP</td>
<td>1.518(17)</td>
</tr>
<tr>
<td>U3-O9D</td>
<td>2.32(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Symmetric codes for UPF-113: A: 2-x, 1-y, 1-z; B: x, 1+y, z; C: x, y, 1+z; D: 1-x, 1-y, 2-z; E: 1+x, y, z; G: 1-x, 1-y, 1-z; I: 1-x, 2-y, 1-z; J: 2-x, -y, 1-z; K: x, -1+y, z. P: the oxygen atom is protonated. HP: the oxygen atom is half protonated.

Figure S4. Asymmetric building unit of UPF-113 with atomic labelling scheme at 50% probability. All hydrogen atoms and 2,2'-bpy molecules are omitted for clarity.
Figure S5. Crystal framework structures of UPF-113 (a, b, and c), viewed along α, β, and c axis, respectively. UO₆ and UO₇ are represented by the yellow tetragonal bipyramid and pentagonal bipyramid, while -CPO₃ is represented as a purple tetrahedron, and the guest molecules are omitted for clarity.

UPF-113 crystallizes in the triclinic space group P।. The asymmetric unit contains one and two half UO₂²⁺ cations, which are crystallography different, one TppmH₈ ligand, two half 2,2'-bpy molecules, one coordinated water molecule, and one lattice water molecule (Fig. S4†). As presented in Figure 1d-1f, UO₂²⁺ cations adopt tetragonal and pentagonal bipyramid coordination geometry, respectively. The bond lengths of U=O and U-O are in the range of 1.77(2)-1.797(2) Å and 2.18(2)-2.40(2) Å, respectively. And the bond length of U₃-O₁w is 2.54(2) Å. For U₁ and U₂ in UO₆ units, four oxygen atoms located at the equatorial plane are provided by four TppmH₈ ligands and 1D-SBUs are achieved along the a axis consisting of U₁ and U₂ in UO₆ units arranged alternatively. For U₃, O₉C, O₉D, O₇E, O₁₀, and O₁w are located in the equatorial plane, forming the UO₇ cluster. UO₇ units are connected by TppmH₈ ligands, giving porous layers, which are further linked by 1D-SBUs to construct the final 3D structure. The bond lengths of P₂-O₅, P₃-O₈, P₄-O₁₁, and P₄-O₁₂ are in the range of 1.52(2)-1.59(2) Å, showing that O₅ is protonated and the other oxygen atoms are half protonated (Table S3†).
Table S4. Bond lengths of UPF-114.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Lengths [Å]</th>
<th>Bond</th>
<th>Lengths [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1=O13</td>
<td>1.760(4)</td>
<td>P1-O2</td>
<td>1.497(4)</td>
</tr>
<tr>
<td>U1=O13E</td>
<td>1.761(4)</td>
<td>P1-O3</td>
<td>1.549(4)</td>
</tr>
<tr>
<td>U1-O2</td>
<td>2.278(4)</td>
<td>P2-O4</td>
<td>1.515(4)</td>
</tr>
<tr>
<td>U1-O2E</td>
<td>2.278(4)</td>
<td>P2-O5</td>
<td>1.567(4)</td>
</tr>
<tr>
<td>U1-O10A</td>
<td>2.294(4)</td>
<td>P2-O6</td>
<td>1.502(4)</td>
</tr>
<tr>
<td>U1-O10F</td>
<td>2.294(4)</td>
<td>P3-O7</td>
<td>1.494(4)</td>
</tr>
<tr>
<td>U2=O15</td>
<td>1.777(4)</td>
<td>P3-O8</td>
<td>1.511(4)</td>
</tr>
<tr>
<td>U2=O14</td>
<td>1.788(4)</td>
<td>P3-O9</td>
<td>1.551(4)</td>
</tr>
<tr>
<td>U2-O4B</td>
<td>2.243(4)</td>
<td>P4-O10</td>
<td>1.503(4)</td>
</tr>
<tr>
<td>U2-O7C</td>
<td>2.256(4)</td>
<td>P4-O11</td>
<td>1.496(4)</td>
</tr>
<tr>
<td>U2-O8D</td>
<td>2.295(4)</td>
<td>P4-O12</td>
<td>1.578(4)</td>
</tr>
<tr>
<td>P1-O1</td>
<td>1.498(4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Symmetric codes for UPF-114: A: x, -1+y, z; B: 1/2-x, -1/2+y, -z; C: 1/2-x, -1/2+y, -1/2-z; D: x, y, 1/2+z; E: x, y, -1/2-z; F: x, -1+y, -1/2-z. P: the oxygen atom is protonated. Hp: the oxygen atom is half protonated.

Figure S6. Asymmetric building unit of UPF-114 with atomic labeling scheme at 50% probability. All hydrogen atoms and phen molecules are omitted for clarity.
**Figure S7.** Crystal framework structures of UPF-114 (a, b, and c), viewed along a, b, and c axis, respectively. UO$_6$ is represented by the yellow tetragonal bipyramid, while -CPO$_3$ is represented as a purple tetrahedron, and the guest molecules are omitted for clarity.

UPF-114 crystallizes in the monoclinic space group C2/c. The asymmetric unit contains one and a half UO$_2^{2+}$ cations, one TppmH$_8$ ligand, and one phen molecule (Fig. S6). U1O$_6$ and U2O$_6$ units adopt tetragonal bipyramid coordination geometry, and four different TppmH$_8$ ligands provide four oxygen atoms in the equatorial plane. The bond lengths of U=O and U-O are in the range of 1.760(4)-1.788(4) Å and 2.243(4)-2.295(4) Å, respectively. One U1O$_6$ and two U2O$_6$ units are connected to give a trimer by corner-sharing of phosphonate groups, acting as 0D-node, further linked by TppmH$_8$, forming a porous 3D-MOF structure. To balance the charge, the protonated phen cations are filled in the space of the structure. UPF-114 has two kinds of channels that are not crosslinked (Figs. S7a-S7c). The bond lengths of P-O are in the range of 1.494(4)-1.578(4) Å. The bond lengths of P1-O3, P2-O5, P3-O9, and P4-O12 are 1.549(4), 1.567(4), 1.551(4), and 1.578(4) Å, respectively, which belong to P-O-H (Table S4).
1.3 Analysis of Weak Interaction

Figure S8. π-π interaction between guest molecules in the framework of UPF-114.
**Figure S9.** C-H···π interactions (blue dash line) between guest and framework. UO$_6$ and UO$_7$ are represented by the yellow tetragonal bipyramid and pentagonal bipyramid, and the hydrogen atoms are omitted for clarity.
**Figure S10.** Hydrogen bonding interactions (green dash line) between guest and framework. \( \text{UO}_6 \) and \( \text{UO}_7 \) are represented by the yellow tetragonal bipyramid and pentagonal bipyramid, and the hydrogen atoms are omitted for clarity.
Table S5. Bond lengths and bond angles for weak interaction forces between guest molecules and frameworks in **UPF-112**, **UPF-113**, and **UPF-114**.

<table>
<thead>
<tr>
<th>Species</th>
<th>π-π interaction</th>
<th>C-H···π interactions</th>
<th>hydrogen bonding interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bond length</td>
<td>bond length</td>
<td>bond length</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H14-π) = 3.1796 Å</td>
<td>d(P1-O2···H36) = 2.6170 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H18-π) = 3.1021 Å</td>
<td>d(P1-O3···H29) = 2.9000 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H24-π) = 2.8341 Å</td>
<td>d(P2-O4···H30) = 2.3305 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(P4-O11···H1-N1) = 1.9397 Å</td>
</tr>
<tr>
<td>UPF-112</td>
<td></td>
<td></td>
<td>d(U1-O1w···H26) = 2.7369 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U1-O13···H34) = 2.5025 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U1-O12···H3) = 2.8213 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U1-O14···H32) = 2.8293 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U1-O14···H35) = 3.0838 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O14···H33) = 2.7233 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H15-π) = 2.8274 Å</td>
<td>d(P4-O12···H27) = 3.7923 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H20-π) = 3.6250 Å</td>
<td>d(P1-O3···H33) = 3.4168 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O14···H28) = 2.4705 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U3-O10···H30) = 2.7621 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U3-O16···H32) = 1.9388 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U3-O14···H33) = 2.7233 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U3-O15···H35) = 3.0838 Å</td>
</tr>
<tr>
<td>UPF-113</td>
<td></td>
<td></td>
<td>d(U2-O14···H37) = 2.3336 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
<tr>
<td>UPF-114</td>
<td></td>
<td></td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H26-π) = 2.9604 Å</td>
<td>d(N2-H2···O8-P) = 3.3631 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H31-π) = 3.0568 Å</td>
<td>d(U2-O14···H37) = 2.3336 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d(H35-π) = 3.2510 Å</td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d(U2-O15···H28) = 3.6199 Å</td>
</tr>
</tbody>
</table>

|          |                 |                       | bond angle                 |
|          |                 |                       | 131°                       |
|          |                 |                       | 131°                       |
|          |                 |                       | 141°                       |
|          |                 |                       | 133°                       |
|          |                 |                       | 129°                       |
|          |                 |                       | 131°                       |
|          |                 |                       | 114°                       |
|          |                 |                       | 123°                       |
|          |                 |                       | 135°                       |
|          |                 |                       | 106°                       |
|          |                 |                       | 156°                       |
|          |                 |                       | 97°                        |
|          |                 |                       | 144°                       |
|          |                 |                       | 123°                       |
|          |                 |                       | 100°                       |
|          |                 |                       | 130°                       |
|          |                 |                       | 130°                       |
|          |                 |                       | 130°                       |
|          |                 |                       | 100°                       |
1.4 Powder X-ray Diffraction

Figure S11. Powder X-ray diffraction (PXRD) patterns of calculated (black), experimental (red) and UV irradiated (violet) for UPF-112, UPF-113 and UPF-114.
Figure S12. Ex-situ variable temperature powder X-ray diffraction (VT-PXRD) patterns of (a) UPF-112, (b) UPF-113, and (c) UPF-114 taken with a Cu Kα radiation source.
1.5 IR and Raman Spectra

**Figure S13.** IR and Raman spectra of (a) UPF-112, (b) UPF-113, (c) UPF-114.
1.6 Thermal Gravimetric Analysis

![TG patterns of UPF-112 (red), UPF-113 (yellow), and UPF-114 (violet).](image)

**Figure S14.** TG patterns of UPF-112 (red), UPF-113 (yellow), and UPF-114 (violet).

**UPF-112** started to lose two lattice water molecules and one coordinated water molecule above 120 °C, demonstrating a platform during 200-300 °C. The average weight loss is 4.44 %, similar to a calculated weight loss of 4.52 %. The lattice water molecules of **UPF-113** started to lose with the temperature increase and lost 1.35 % of total weight at 80 °C, similar to the 1.32% calculated by the formula. The aqua ligands of **UPF-113** are removed completely at 135 °C, and the weight loss is 2.72 %, similar to the calculated 2.63 %.
1.7 UV-vis Absorption Spectra

Figure S15. UV-vis absorption spectrum of UPF-112 (red line), UPF-113 (yellow line), and UPF-114 (violet line).
1.8 Photoluminescence Spectra and Fluorescence Quenching Curves

![Photoluminescence Spectra](image)

Figure S16. Photoluminescence spectra of UPF-112, UPF-113 and UPF-114 measured at room temperature.
Table S6. Quenching of UPF-112 at a peak of 497.65 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>(I₀-I)/I₀ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10⁻⁶</td>
<td>12.44</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10⁻⁶</td>
<td>24.51</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10⁻⁵</td>
<td>31.80</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10⁻⁵</td>
<td>42.01</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10⁻⁵</td>
<td>51.76</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10⁻⁵</td>
<td>57.82</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10⁻⁴</td>
<td>62.34</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10⁻⁴</td>
<td>65.67</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10⁻⁴</td>
<td>69.82</td>
</tr>
<tr>
<td>150</td>
<td>9000</td>
<td>3.39×10⁻⁴</td>
<td>73.93</td>
</tr>
<tr>
<td>180</td>
<td>10800</td>
<td>4.053×10⁻⁴</td>
<td>75.42</td>
</tr>
</tbody>
</table>
Table S7. Quenching of UPF-112 at a peak of 519.07 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>((I_o-I)/I_o) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10^{-6}</td>
<td>13.799</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10^{-6}</td>
<td>26.83</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10^{-5}</td>
<td>34.24</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10^{-5}</td>
<td>44.78</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10^{-5}</td>
<td>54.69</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10^{-5}</td>
<td>60.72</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10^{-4}</td>
<td>65.34</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10^{-4}</td>
<td>68.42</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10^{-4}</td>
<td>72.37</td>
</tr>
<tr>
<td>150</td>
<td>9000</td>
<td>3.39×10^{-4}</td>
<td>76.15</td>
</tr>
<tr>
<td>180</td>
<td>10800</td>
<td>4.053×10^{-4}</td>
<td>77.46</td>
</tr>
</tbody>
</table>

Figure S17. (a) Normalized intensity of UPF-112 at the peak of 519.07 nm measured at room temperature. (b) Relative fluorescence quenching of UPF-112 at a peak of 519.07 nm.
Table S8. Quenching of UPF-112 at a peak of 542.84 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>($I_0-I$)/$I_0$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10⁻⁶</td>
<td>14.80</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10⁻⁶</td>
<td>28.39</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10⁻⁵</td>
<td>35.87</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10⁻⁵</td>
<td>46.20</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10⁻⁵</td>
<td>55.96</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10⁻⁵</td>
<td>61.74</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10⁻⁴</td>
<td>66.48</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10⁻⁴</td>
<td>69.01</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10⁻⁴</td>
<td>72.71</td>
</tr>
<tr>
<td>150</td>
<td>9000</td>
<td>3.39×10⁻⁴</td>
<td>76.11</td>
</tr>
<tr>
<td>180</td>
<td>10800</td>
<td>4.053×10⁻⁴</td>
<td>77.58</td>
</tr>
</tbody>
</table>

Figure S18. (a) Normalized intensity of UPF-112 at the peak of 542.84 nm measured at room temperature. (b) Relative fluorescence quenching of UPF-112 at a peak of 542.84 nm.
Table S9. Quenching of UPF-113 at a peak of 499.96 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>(I₀-I)/I₀ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10⁻⁶</td>
<td>18.49</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10⁻⁶</td>
<td>30.93</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10⁻⁵</td>
<td>39.27</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10⁻⁵</td>
<td>50.93</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10⁻⁵</td>
<td>63.93</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10⁻⁵</td>
<td>70.80</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10⁻⁴</td>
<td>77.47</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10⁻⁴</td>
<td>80.93</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10⁻⁴</td>
<td>85.96</td>
</tr>
<tr>
<td>150</td>
<td>9000</td>
<td>3.39×10⁻⁴</td>
<td>88.09</td>
</tr>
<tr>
<td>180</td>
<td>10800</td>
<td>4.053×10⁻⁴</td>
<td>90.29</td>
</tr>
</tbody>
</table>
Table S10. Quenching of UPF-113 at a peak of 521.23 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>(I_0 - I)/I_0 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10^{-6}</td>
<td>16.65</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10^{-6}</td>
<td>29.01</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10^{-5}</td>
<td>39.57</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10^{-5}</td>
<td>49.05</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10^{-5}</td>
<td>61.69</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10^{-5}</td>
<td>67.76</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10^{-4}</td>
<td>73.92</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10^{-4}</td>
<td>77.96</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10^{-4}</td>
<td>82.23</td>
</tr>
<tr>
<td>150</td>
<td>9000</td>
<td>3.39×10^{-4}</td>
<td>86.05</td>
</tr>
<tr>
<td>180</td>
<td>10800</td>
<td>4.053×10^{-4}</td>
<td>87.34</td>
</tr>
</tbody>
</table>

Figure S19. (a) Normalized intensity of UPF-113 at the peak of 521.23 nm measured at room temperature. (b) Relative fluorescence quenching of UPF-113 at a peak of 544.72 nm.
Table S11. Quenching of UPF-113 at a peak of 544.72 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>(I₀-I)/I₀ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10⁻⁶</td>
<td>16.08</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10⁻⁶</td>
<td>29.05</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10⁻⁵</td>
<td>38.16</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10⁻⁵</td>
<td>47.65</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10⁻⁵</td>
<td>60.70</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10⁻⁵</td>
<td>66.25</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10⁻⁴</td>
<td>72.35</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10⁻⁴</td>
<td>76.07</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10⁻⁴</td>
<td>79.49</td>
</tr>
<tr>
<td>150</td>
<td>9000</td>
<td>3.39×10⁻⁴</td>
<td>82.80</td>
</tr>
<tr>
<td>180</td>
<td>10800</td>
<td>4.053×10⁻⁴</td>
<td>83.86</td>
</tr>
</tbody>
</table>

Figure S20. (a) Normalized intensity of UPF-113 at the peak of 544.72 nm measured at room temperature. (b) Relative fluorescence quenching of UPF-113 at a peak of 544.72 nm.
Table S12. Quenching of **UPF-114** at a peak of 505.37 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>((I_0 - I)/I_0) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10^{-6}</td>
<td>33.99</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10^{-6}</td>
<td>54.14</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10^{-5}</td>
<td>64.01</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10^{-5}</td>
<td>75.61</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10^{-5}</td>
<td>84.36</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10^{-5}</td>
<td>88.10</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10^{-4}</td>
<td>91.03</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10^{-4}</td>
<td>92.63</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10^{-4}</td>
<td>94.46</td>
</tr>
<tr>
<td>120</td>
<td>7200</td>
<td>2.701×10^{-4}</td>
<td>95.56</td>
</tr>
</tbody>
</table>
Table S13. Quenching of UPF-114 at a peak of 527.72 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>(I_0-I)/I_0 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10^{-6}</td>
<td>33.97</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10^{-6}</td>
<td>53.85</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10^{-5}</td>
<td>64.02</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10^{-5}</td>
<td>75.53</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10^{-5}</td>
<td>84.15</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10^{-5}</td>
<td>87.75</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10^{-4}</td>
<td>90.85</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10^{-4}</td>
<td>92.49</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10^{-4}</td>
<td>94.20</td>
</tr>
<tr>
<td>120</td>
<td>7200</td>
<td>2.701×10^{-4}</td>
<td>95.48</td>
</tr>
</tbody>
</table>

Figure S21. (a) Normalized intensity of UPF-114 at the peak of 527.72 nm measured at room temperature. (b) Relative fluorescence quenching of UPF-114 at a peak of 527.72 nm.
Table S14. Quenching of UPF-114 at a peak of 552.31 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Dosage (mJ)</th>
<th>(I₀-I)/I₀ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>2.252×10⁻⁶</td>
<td>33.66</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>6.755×10⁻⁶</td>
<td>53.65</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.126×10⁻⁵</td>
<td>63.67</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>2.252×10⁻⁵</td>
<td>75.35</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>4.503×10⁻⁵</td>
<td>83.97</td>
</tr>
<tr>
<td>30</td>
<td>1800</td>
<td>6.755×10⁻⁵</td>
<td>87.58</td>
</tr>
<tr>
<td>45</td>
<td>2700</td>
<td>1.013×10⁻⁴</td>
<td>90.33</td>
</tr>
<tr>
<td>60</td>
<td>3600</td>
<td>1.351×10⁻⁴</td>
<td>92.10</td>
</tr>
<tr>
<td>90</td>
<td>5400</td>
<td>2.026×10⁻⁴</td>
<td>93.87</td>
</tr>
<tr>
<td>120</td>
<td>7200</td>
<td>2.701×10⁻⁴</td>
<td>95.26</td>
</tr>
</tbody>
</table>

Figure S22. (a) Normalized intensity of UPF-114 at the peak of 552.31 nm measured at room temperature. (b) Relative fluorescence quenching of UPF-114 at a peak of 552.31 nm.
1.9 Determination of detection limit

Figure S23. Linear fitting from data points in the low dose range (0 - 1.2×10⁻⁵ mJ).

Based on the fluorescence measurement shown in Figure S23, the limit of detection can be determined by the following equations:

\[
DT = \frac{3\sigma}{k}
\]

\[
\sigma = 100 \times \frac{l_{S0}}{I_0}
\]

where the detection limit is noted as \( DT \); \( l_{S0} \) is the standard error of the luminescence intensity (as determined by the baseline measurement of blank samples); \( l_0 \) is the measured luminescence intensity; \( k \) is the slope obtained from the linear fit in the lower dosage range of the dosage-dependent luminescence intensity calibration curve.¹

On the basis of the acquired data, the detection limit of UPF-112 was determined to be 9.54×10⁻¹² J; the detection limit of UPF-113 was determined to be 5.98×10⁻¹² J; the detection limit of UPF-114 was determined to be 2.96×10⁻¹² J.

Table S15. Comparison of detection limits of ionizing radiation detectors.

<table>
<thead>
<tr>
<th>UV-detector</th>
<th>Ionizing radiation</th>
<th>Intensity decay to half (T½)</th>
<th>Limit of detection (LOD)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-di(1H-phenanthro[9,10-d]imidazol-2-yl)-biphenyl (DPI-BP)</td>
<td>γ-radiation</td>
<td>( \gamma )</td>
<td>7×10⁻³ Gy</td>
<td>¹</td>
</tr>
<tr>
<td>(TMA)₂[(UO₂)₃(ox)₃(L)]</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>1.64×10⁻⁴ Gy</td>
<td>²</td>
</tr>
<tr>
<td>[UO₂(L)(DMF)]</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>5.2×10⁻⁴ Gy</td>
<td></td>
</tr>
<tr>
<td>[Hphen]₂[(UO₂)₂(ox)₃]</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>2.4×10⁻⁷ J</td>
<td>³</td>
</tr>
<tr>
<td>UO₂(ox)(H₂O)·2H₂O</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>6.9×10⁻⁹ J</td>
<td>⁴</td>
</tr>
<tr>
<td>Ln-DBTPA</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>1.18×10⁻⁵ Gy</td>
<td>⁵</td>
</tr>
<tr>
<td>[4,4-bpyH]₅(UO₂)(TppmH₄)·(H₂O)·2H₂O (UPF-112)</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>1.42×10⁻³ Gy</td>
<td></td>
</tr>
<tr>
<td>[2,2-bpyH]₅(UO₂)(TppmH₄)(H₂O)·H₂O (UPF-113)</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>9.54×10⁻¹² J</td>
<td>This work</td>
</tr>
<tr>
<td>[phenH]₅(UO₂)₂(TppmH₄) (UPF-114)</td>
<td>UV radiation</td>
<td>( \gamma )</td>
<td>5.98×10⁻¹² J</td>
<td></td>
</tr>
</tbody>
</table>
1.10 EPR Spectra Before and After UV Irradiation

Figure S24. EPR spectra of **UPF-112** (a, b), **UPF-113** (c, d), and **UPF-114** (e, f) before and after UV irradiation for 3 hours and stored in the dark for 4 days.
2. References


