

A Layered Uranyl Coordination Polymer with UV Detection Sensitivity, Stability, and Reusability

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Abstract: The sensitive detection of UV light is critical in industrial production and for personal protection, and the aim of this research is to develop novel UV detection materials. The uranyl unit generally exhibits relatively high UV absorption efficiency and strong fluorescence intensity. Hence in this work, a uranyl coordination polymer compound $[(\text{TEA})_2(\text{UO}_2)_5(\text{PhPC})_6]$ (TEA = tetraethylammonium ion, PhPC = (2-carboxyethyl)phenylphosphinic acid, denoted as UPhPC-1) was successfully synthesized *via* the hydrothermal method. The structural analysis of UPhPC-1 based on the single crystal XRD data elucidates that there are three crystallographically unique uranyl centers. Two uranyl units are in the pentagonal bipyramidal geometry, while the third one is in the tetragonal bipyramidal geometry. All three uranyl units are connected by the ligands to form infinite uranyl layers in the $[bc]$ plane, which are packed *via* hydrogen bonding networks and π - π interactions to yield the overall layered structure. The stability test results of UPhPC-1 demonstrate that the compound exhibits good thermal and hydrolytic stability with high radiation resistance. Moreover, results of the UV irradiation experiments show that the intrinsic luminescence of UPhPC-1 is highly sensitive to 365 nm UV irradiation with a low detection limit and a fast response rate. A negative correlation between the emission intensity and the UV irradiation dosage was then established. The electron paramagnetic resonance data analysis strongly supports the production of radicals in UPhPC-1 under UV radiation, which leads to the partial quenching of the uranyl fluorescence. Furthermore, the radicals in the quenched sample can be readily eliminated by heating, resulting in the recovery of the photoluminescence intensity of UPhPC-1. The current results suggest suitable application potential of UPhPC-1 in the field of quantitative UV detection.

Key words: uranyl coordination polymer; luminescence spectroscopy; UV detection; structural chemistry

For decades, ultraviolet radiation receives rapidly growing attention due to its indispensable role in industrial production, security and anti-counterfeiting, health care, and other related fields^[1-4]. However, excessive ultraviolet radiation would cause irreversible damage to human, such as epidermal hyperplasia, DNA damage, and melanoma skin cancers^[5-6]. Since UV light is invisible to the naked eyes, the development of UV light detection materials is essential for the purpose of protection and radiation control. Various types of semiconductor photodetectors have been fabricated and commercialized,

including photodiodes detectors^[7], thermoelectric sensors^[8], metal-semiconductor-metal detectors^[9], and Schottky barrier detectors^[10]. However, those materials still face several disadvantages. For example, the defects of semiconductor materials could significantly affect their sensitivity and efficiency, therefore high production standards are required.

Compared with traditional semiconductors, luminescent methods show clear advantages in high sensitivity, fast response rate, and low cost^[11]. Over the years, many luminescent materials have been developed for this pur-

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pose, among which luminescent Coordination Polymers (CPs) or Metal Organic Frameworks (MOFs) have been widely investigated primarily due to their advantages of structure diversity and adjustable functionality that can be readily realized by various selections of organic linkers and metal nodes^[12-19]. Lanthanide and transition metals are two major groups of elements utilized to build luminescent CPs or MOFs.

The 5f element uranium is an emerging element used as photosensitive and luminescent materials. The hexavalent uranium generally exists as the divalent linear dioxo unit of UO_2^{2+} . The photoluminescence property of the uranyl unit originates from the HOMO-LUMO transition of hybridized molecular orbitals, which is not Laporte-forbidden, and hence the UV absorption efficiency and emission intensity of the uranyl often exceeds those of lanthanides^[20-24]. Furthermore, owing to the participation of the uranyl 5f/6d orbitals in bonding, the uranyl luminescence intensity is extremely sensitive to the variation of its coordination environment, endowing uranium bearing materials with high detection sensitivity^[25-31]. The ongoing research regarding uranyl-based UV detection systems, though limited, has demonstrated their great application potential. For example, a uranyl carboxylate coordination polymer has been reported for the first time to have excellent detection capability of X- or γ -ray and sensitive response to the UV light^[32]. In this work, the luminescence of the uranyl unit is proposed to be quenched by the free radicals generated by the bond breaking of the carboxylate group under UV radiation. Then, Liu, *et al.*^[33] reported that the presence of coordinated DMF units of uranyl phthalate layers would significantly lower down the UV detection limit, due to the interaction between the uranyl unit and the radicals generated on the DMF units by the UV light. The authors have prepared convenient UV-test strips using this material. Moreover, the insertion of highly photosensitive molecules such as phenanthroline between uranyl oxalate layers would further extend the detection limit to the 10^{-9} J level. The irradiation of this compound would result in the photo-exfoliation of the layered compound to monolayer nanosheet, which is an irreversible process^[34]. Besides actinide carboxylate compounds, a number of actinide phosphonate compounds with high structural diversity have also been reported, by virtue of the strong metal binding affinities of the phosphonate ligands^[35-39]. However, their UV detection properties have rarely been reported.

Here, a bifunctional ligand containing both phosphinate and carboxylate moieties was utilized and a luminescent uranyl layered compound $[(\text{TEA})_2(\text{UO}_2)_5(\text{PhPC})_6]$ (TEA = tetraethylammonium ion, PhPC = (2-carboxyethyl)

phenylphosphinic acid, denoted as UPhPC-1) was synthesized *via* the hydrothermal method. The structure of UPhPC-1 was revealed by single crystal XRD technique, showing that both phosphinate and carboxylate groups are coordinated to the uranyl ions. The experimental results demonstrate that UPhPC-1 not only shows good thermal stability, hydrolytic stability, and radiation resistance, but also exhibits a fast response rate of 365 nm UV radiation with a low detection limit of 3.9 μJ . The relationship between the UV radiation dosage and the uranyl emission intensity was established and the fluorescence quenching mechanism is proposed to be a radical-induced quenching process. Further studies suggest that the radicals can be readily eliminated by heating, leading to the recovery of the photoluminescence intensity of UPhPC-1.

1 Experimental

1.1 Materials and synthesis

Materials (2-carboxyethyl)phenylphosphinic acid (98%, Energy Chemical) and tetraethylammonium hydroxide (25wt% solution in H_2O , J&K Scientific) were used directly without further purification. While uranium compounds used in laboratories contain depleted uranium, standard procedures for handling radioactive materials should be followed.

Synthesis A mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.05 g, 0.1 mmol), (2-carboxyethyl)phenylphosphinic acid (0.04 g, 0.2 mmol), tetraethylammonium hydroxide (0.2 mL), and H_2O (2 mL) was added into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated to 220 $^\circ\text{C}$ for 3 d, and then cooled to room temperature in 24 h. Brown yellow crystals were isolated as UPhPC-1.

1.2 Characterization

X-ray crystallography Single crystal X-ray diffraction data acquisition was carried out on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo- $\text{K}\alpha$ radiation, $\lambda=0.071073$ nm) adopting the direct-drive rotating anode technique and a CMOS detector at 298 K. The data frames were collected using the program APEX3 and processed using SAINT routine in APEX3. The structure of UPhPC-1 was solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL program.

Powder X-ray diffraction (PXRD) PXRD patterns were collected on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu $\text{K}\alpha$ radiation ($\lambda=0.154056$ nm) and a Lynxeye one-dimensional detector from 5° to 50° with a step of 0.02° in 2θ .

Photoluminescence and UV-Vis absorption spectroscopy The crystals were placed on quartz slides and

photoluminescence and UV-Vis absorption spectra were acquired after auto-set optimization by Craic Technologies microspectrophotometer. The photoluminescence spectra of the solid samples before and after X-ray irradiation were collected by Steady State & Transient State Fluorescence Spectrofluorometer.

Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of the solid samples before and after irradiation were recorded in the range of 4000–400 cm^{-1} with the Thermo Nicolet iS 50 spectrometer.

Thermogravimetric analysis (TG)

TG analysis was carried out using a NETZSCH STA449F3 instrument in the temperature range from 30–900 $^{\circ}\text{C}$ under a nitrogen flow at a heating rate of 10 K/min for the dried sample.

Elemental analysis

Elemental analysis (C, H, and N) was performed with a Vario EL CHNOS elemental analyzer.

Electron paramagnetic resonance (EPR) spectroscopy

The EPR data of the pristine sample and samples irradiated for 90 min by UV light and 226 s by X-ray were recorded on a Bruker EMXplus 10/12 EPR spectrometer equipped with an Oxford Instruments EPR901 liquid helium continuous-flow cryostat fitted with a super-high-Q cavity, respectively.

UV detection experiments

UV detection studies were carried out and luminescence spectra were recorded at various exposure time under 365 nm light.

X-ray irradiation experiments

The experiments were carried out using a RS-2000 Pro Biological Irradiator equipped with Cu $K\alpha$ radiation at a dose rate of 26.5 Gy/min and the samples were irradiated for 226 s.

Hydrolytic stability measurements

The hydrolytic stability evaluation of UPhPC-1 was performed by soaking the samples in HNO_3/NaOH aqueous solutions in the pH range from 5 to 12 and shaking for 24 h. The soaked samples were isolated and dried for PXRD pattern analysis.

2 Results and discussion

2.1 Structural elucidation

Single crystal X-ray diffraction analysis reveals that UPhPC-1 crystallizes in the centrosymmetric space group, $P\bar{1}$. As shown in Fig. 1 and Table S1, the asymmetric unit consists of two and a half unique uranyl ions, three PhPC ligands, and one distinctive tetraethylammonium ion.

The U1 and U3 units are in the pentagonal bipyramidal geometry with axial $\text{U}=\text{O}$ bond distances ranging from 0.1781(5) to 0.1789(4) nm. The U2 unit sits at the inversion center and is in tetragonal bipyramidal geometry with the typical uranyl bond distance of 0.1777(4) nm. All equatorial-bonding oxygen atoms of three uranyl units are provided from the PhPC ligand with bond distances

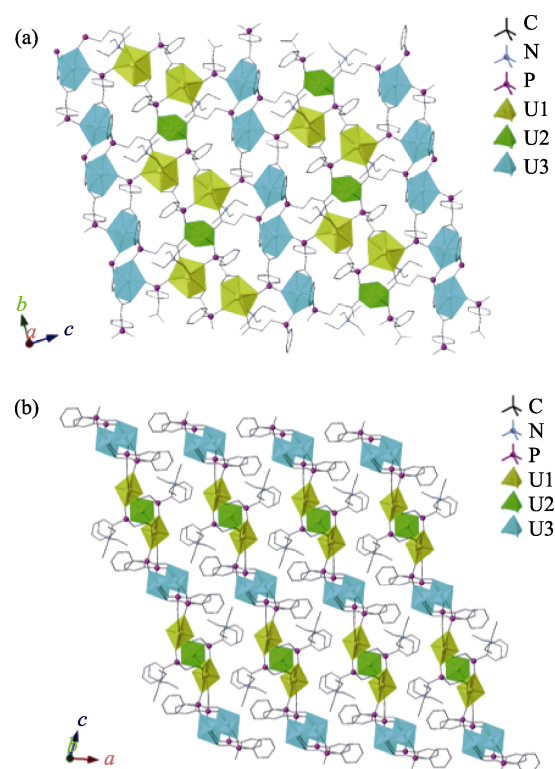


Fig. 1 Structural depiction of UPhPC-1

(a) View of the layer topology in the $[bc]$ plane; (b) View of the stacking mode of the uranyl layers

ranging from 0.2309(5) to 0.2491(4) nm. The bond valence sum values of the U1, U2, and U3 are calculated to be 6.019, 5.739, and 6.094, respectively. As shown in Fig. 1, all uranyl units are connected by the PhPC ligands to form the uranyl layers, which are packed *via* hydrogen bonding networks and π - π interactions to yield the overall layered structure. In the free space, there are tetraethylammonium cations to compensate the negative charge of the uranyl layers. The formula of UPhPC-1 is determined to be $(\text{TEA})_2(\text{UO}_2)_5(\text{PhPC})_6$ taken the results of single crystal structural analysis and elemental analysis (Table S2) into consideration. The FT-IR spectrum of UPhPC-1 was collected without KBr at room temperature. As shown in Fig. S1, the characteristic vibration peaks of the phenyl rings and the carboxylate units are identified between 1720 and 1250 cm^{-1} [40-42]. The vibration peaks of the phosphinate groups are located in the range from 1200 and 950 cm^{-1} . The peak at ~ 920 cm^{-1} is assigned to the stretching vibration of the $\text{O}=\text{U}=\text{O}$ unit[43-44].

2.2 Irradiation dosage dependent luminescence spectra

The photoluminescence spectrum of UPhPC-1 was collected under 365 nm excitation light at room temperature. As shown in Fig. S2, the spectrum of UPhPC-1 exhibits the characteristic emission peaks at 495, 516, 539, 565, and 592 nm, corresponding to the $S_{10}-S_{0\nu}$ ($\nu =$

0-4) transitions of the uranyl unit. Compared with the emissive spectrum of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the peak position of UPhPC-1 was red-shifted by *ca.* 7 nm, probably caused by the coordination of the uranyl unit and the PhPC ligand, which is generally observed in uranyl coordination polymers^[45-48]. The maximum UV-Vis absorption peak position of UPhPC-1 was also slightly shifted comparing to the reported data of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, as shown in Fig. S3.

To our surprise, the luminescent emission of UPhPC-1 was quenched rapidly after UV light irradiation, which could be observed by naked eyes. This phenomenon strongly suggests the potential of this material being used as a dosimeter for ultraviolet radiation. As shown in Fig. 2, the emission intensity of UPhPC-1 decreased significantly with the accumulative increase of the UV radiation dosage, indicating that the luminescence intensity of UPhPC-1 is responsive to the dosage of UV light not only instantly but also accumulatively. The emission peak intensity of UPhPC-1 was decreased by 79% after being exposed to 0.84 mJ 365 nm radiation and was almost completely quenched after 1.5 h exposure (Fig. 2(a)). To quantitatively describe the negative correlation between luminescence intensity and UV radiation dosage, the quenching ratio of UPhPC-1 was calculated and expressed as $(I_0 - I)/I_0$, where I_0 is the initial luminescence intensity and I is the luminescence intensity after irradiation by ultraviolet light. The detection limit of UPhPC-1 can be determined by the following equations:

$$DT = 3\sigma / k \quad (1)$$

$$\sigma = 100 \times (I_{SE} / I_0) \quad (2)$$

Here DT is the detection limit; I_{SE} is the standard error of the luminescence intensity; I_0 is the measured initial luminescence intensity of UPhPC-1; k is the slope obtained from the linear fit in the low dosage range of the dosage-dependent luminescence intensity calibration curve.

The linear fitting can be achieved for the curve of the quenching ratio *versus* the dosage of UV irradiation in the low dose range (Fig. 2(b)). The detection limit of UPhPC-1 was determined to be 3.9 μJ . Besides, the response rate of UPhPC-1 is faster than the uranyl-oxalate based UV detection material, demonstrating the high sensitivity of UPhPC-1 for the low dosage ultraviolet radiation. When exposed with 100 Gy X-ray, the luminescence intensity of UPhPC-1 was quenched by 66% (Fig. 3(a)).

2.3 Stability evaluation

The stability of UPhPC-1 was investigated in this work. The PXRD and FT-IR data show that the structural integrity of UPhPC-1 was maintained after UV light and X-ray irradiation without any light-induced crystal degradation (Fig. S1 and Fig. S4). Those results demonstrate the high radiation resistance of UPhPC-1, which is comparable to other uranyl-based detection materials. The hydrolytic stability of UPhPC-1 was evaluated by soaking the crystalline samples in HNO_3/NaOH aqueous solutions in the pH range from 5 to 12 and shaking for 24 h. The experimental PXRD patterns of the soaked samples match well with the pattern of the pristine UPhPC-1 sample, indicating the excellent hydrolytic stability of UPhPC-1 (Fig. S4). Thermogravimetric analysis reveals that UPhPC-1 experienced several stages of weight loss in the temperature range from 30 to 900 °C. As shown in Fig. S5, the first weight-loss of 1.72% before 380 °C is assigned to the loss of surface water molecules during the heating process. The loss of tetraethylammonium ion occurred at temperature above 400 °C, resulting in the 10.7% loss in weight and the disruption of the overall structure. This decomposition temperature is higher than that of a previous reported two-dimensional uranyl-oxalate compound of 306 °C^[32].

2.4 Quenching mechanism and reusability investigation

The EPR analyses were performed on the irradiated and pristine crystalline samples to further investigate the fluorescence quenching mechanism (Fig. 3(b)). It was observed that the peak intensity of the irradiated samples increased significantly compared to the original sample, implying the generation of radicals, yet further theoretical

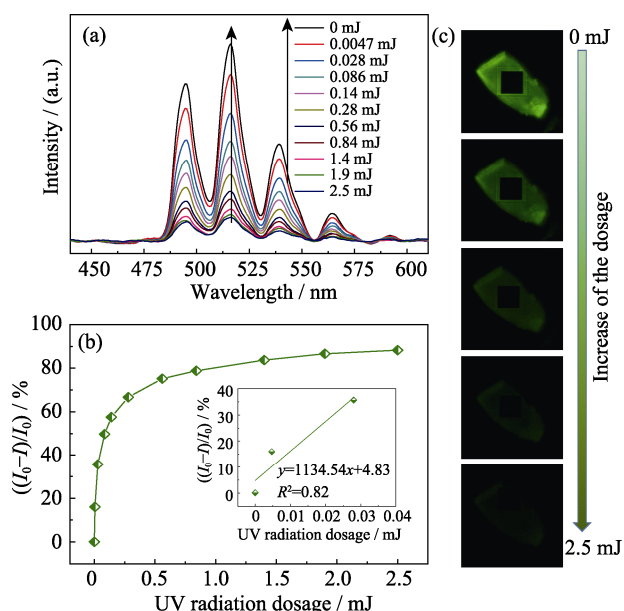


Fig. 2 Luminescence spectra (a) of UPhPC-1 with increasing doses of UV radiation, correlation between the quenching ratio and the UV radiation dose (b) (measured at 516 nm), and corresponding photographs (c) of the single crystal under continuous UV irradiation

The inset is the linear fitting of the point data in the low dose range (0–0.028 mJ)

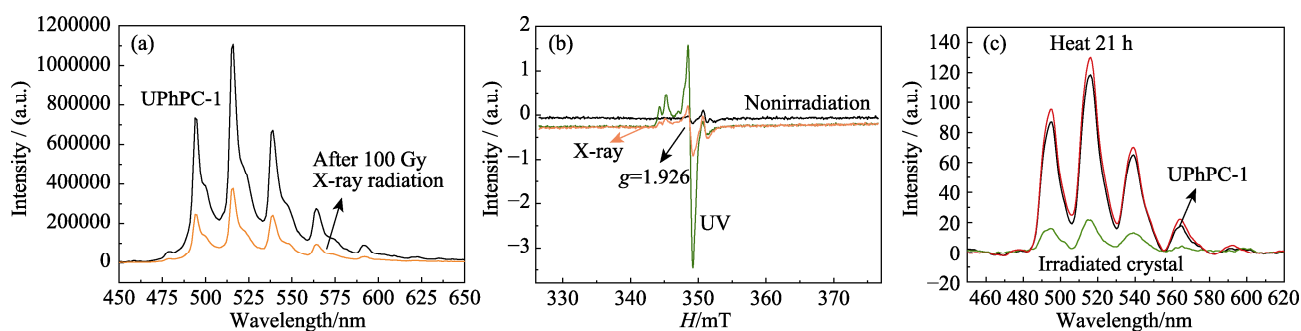


Fig. 3 Photoluminescence spectra (a) of UPhPC-1 before and after X-ray irradiation, EPR spectra (b) of UPhPC-1 before and after UV and X-ray irradiation, luminescence intensities (c) of UPhPC-1 before and after UV irradiation, and after the heating recovery process

calculation is necessary to identify those radicals. On the basis of the obtained data, we speculate that the most plausible quenching mechanism is the production of radicals possibly from the partial bond break of the ligand in the irradiated crystal, resulting in the energy transfer from the uranyl center to the nearby generated radicals, which leads to the quenching of the luminescence of UPhPC-1^[33-34].

The reusability of UV detection materials is also critical for their industrial development. Generally, it is not easy to obtain a reusable uranyl-based UV detection material since the recovery of the material requires not only the easy elimination of irradiation induced radicals, but also the ability to maintain the structural integrity during the irradiation and the recovery processes to restore its original photophysical properties. Generally, free radicals will not be able to stable for a long time, and heating accelerates the quenching process. The thermal elimination of radicals has been widely studied ever since 1970's and has already been applied in the industrial production^[49-51]. Here in this work, we have demonstrated that the radicals in the quenched UPhPC-1 samples could be eliminated after heating at 150 °C for 21 h. During the irradiation and heating process, the overall structure of UPhPC-1 is retained, and the uranyl fluorescence intensity could be fully restored (Fig. 3(c)). Therefore, the UPhPC-1 could be reused in a recovery way that is executable and cost-effective. A similar heating induced recovery was reported by Xie, *et al.*^[33].

3 Conclusion

In conclusion, we herein report a novel uranyl layered compound UPhPC-1 with high thermal and hydrolytic stability and radiation resistance. The intrinsic luminescence of UPhPC-1 was found to be highly sensitive to UV and 100 Gy X-ray irradiation, and a negative correlation between the emission intensity and the irradiation dosage was established with a low detection limit. The EPR data indicate that the production of free radicals

after irradiation is responsible for the quenching of the uranyl emission. Therefore, we can reasonably conclude that UPhPC-1 exhibits suitable application potential in the field of quantitative UV radiation detection and provides a new application platform for a large inventory of depleted uranium.

Supporting Materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20200139>.

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具有 UV 探测灵敏性、稳定性和重复利用性的层状铀酰配位聚合物研究

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摘要: 灵敏的 UV 探测对于工业生产和个人防护非常重要, 本研究旨在开发新型 UV 探测材料。一般而言, 铀酰单元具有相对高的 UV 吸收效率和荧光强度。本课题组成功地在水热条件下制备了一例铀酰配位聚合物 $[(\text{TEA})_2(\text{UO}_2)_5(\text{PhPC})_6]$ (TEA = 四乙基胺离子, PhPC = (2-羧基乙基)苯膦酸, 标记为 UPhPC-1)。基于单晶 XRD 数据的结构分析表明 UPhPC-1 中有三个不同的铀酰中心, 其中两个铀酰单元为五角双锥构型, 而第三个铀酰单元为四角双锥构型。全部三个铀酰中心与配体在 $[bc]$ 平面配位形成无限的铀酰层。通过氢键网络和 π - π 相互作用, 这些铀酰层堆积成整体的层状结构。此化合物具有很好的热稳定性、水稳定性和高抗辐照能力。UV 辐照实验结果表明 UPhPC-1 的本征荧光强度对 365 nm 的 UV 辐射高度敏感, 检测下限低且响应速率快, 而发光强度与 UV 辐照剂量呈负相关。电子顺磁共振谱分析证实了在 UV 光照射下, UPhPC-1 中极有可能产生自由基, 造成铀酰荧光部分淬灭。进一步, 被淬灭样品中的自由基能够在加热后被去除, 从而实现 UPhPC-1 发光强度的快捷恢复。目前的结果表明 UPhPC-1 在 UV 辐照的定量探测领域具有一定的发展潜力。

关键词: 铀酰配位化合物; 荧光光谱; UV 探测; 结构化学

中图分类号: TQ174 文献标识码: A

Supporting information:

A Layered Uranyl Coordination Polymer with UV Detection Sensitivity, Stability, and Reusability

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Table S1 Crystallographic data of UPhPC-1 (CCDC No. 1978001)

Formula	[N(C ₂ H ₅) ₄] ₂ (UO ₂) ₅ [C ₆ H ₅ PO ₂ C ₂ COO] ₆
Mr/(g·mol ⁻¹)	2883.45
Color and habit	Yellow, block
Crystal system	Triclinic
Space group	P $\bar{1}$
<i>a</i> /nm	1.0802(4)
<i>b</i> /nm	1.2288(5)
<i>c</i> /nm	1.7544(5)
α /(°)	86.856(13)
β /(°)	78.009(10)
γ /(°)	86.530(18)
<i>V</i> /nm ³	2.2714(15)
<i>Z</i>	1
ρ calcd/(g·cm ⁻³)	2.108
<i>T</i> /K	298
<i>R</i> (F) for F _o ² > 2 σ (F _o ²) ^a	0.0322
<i>R</i> _w (F _o ²) ^b	0.0816
^a $R(F) = \frac{\sum F_o - F_c }{\sum F_o }$	
^b $R_w(F_o^2) = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}}{\sum wF_o^2}$	

Table S2 The elemental analyses of UPhPC-1

	Content/%	Peak area	Daily factor
N	0.0832	929	0.9751
C	28.68	20169	0.9846
H	3.409	6670	0.9800

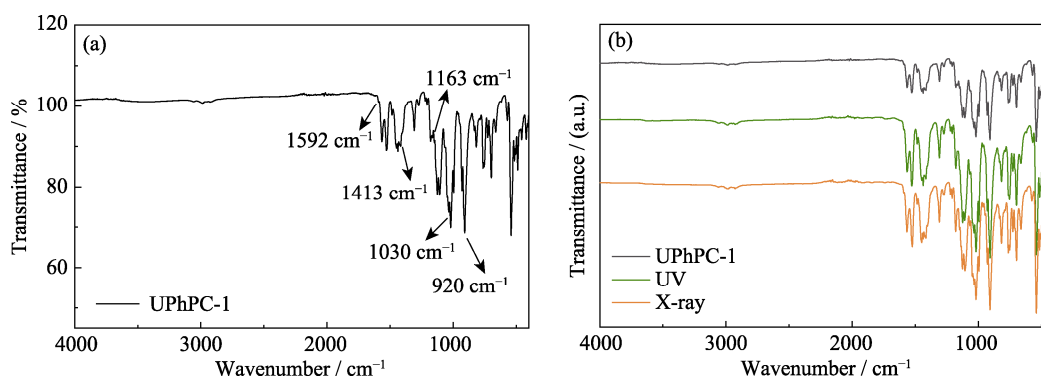


Fig. S1 FT-IR spectra of the pristine UPhPC-1 (a), and UPhPC-1 after UV irradiation and 100 Gy X-ray irradiation (b)

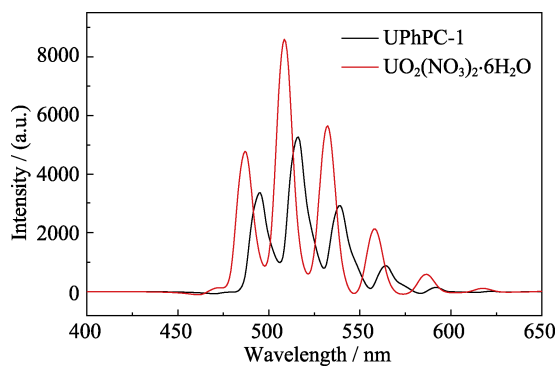


Fig. S2 Photoluminescent spectra of UPhPC-1 ($\lambda_{\text{ex}} = 365 \text{ nm}$) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

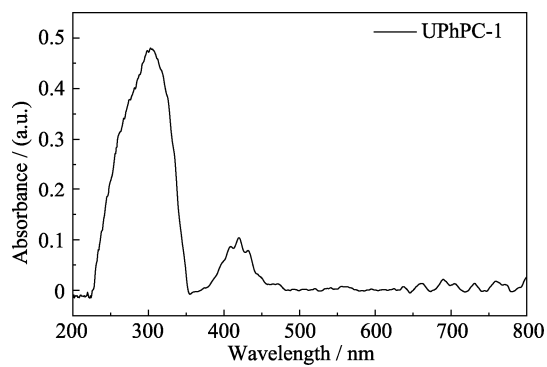


Fig. S3 UV-Vis absorption spectrum of UPhPC-1 at 298 K

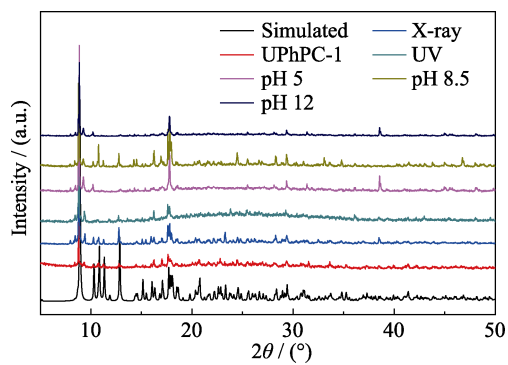


Fig. S4 PXRD patterns of samples irradiated by UV and X-ray radiation and soaking in HNO_3/NaOH aqueous solutions at pH range from 5 to 12 for 24 h

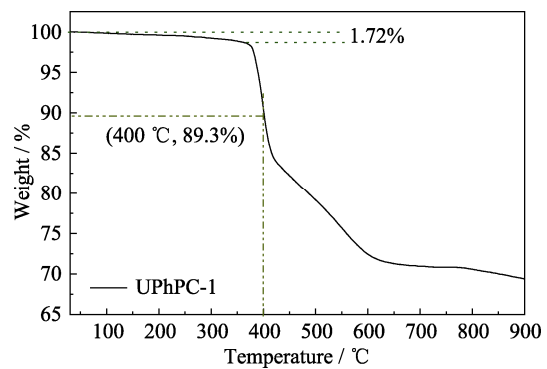


Fig. S5 Thermogravimetric analysis curve of UPhPC-1