# Photoinduced Spin Centers in Photocatalytic Metal-Organic Framework UiO-66

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## Abstract

Metal-organic frameworks (MOFs) are promising candidates for the advanced photocatalytic active materials. These porous crystalline compounds have large active surface area and structural tunability, highly competitive with oxides, the well-established material class for the photocatalysis. However, due to their complex organic and coordination chemistry composition, photophysical mechanisms involved in the photocatalytic process in MOFs are still not well understood. Employing electron paramagnetic resonance (EPR) spectroscopy, we investigate the fundamental processes of electron and hole generation, as well as capture events that lead to the formation of various radical species in UiO-66, an archetypical MOF photocatalyst. As a result, we detected a manifold of photoinduced electron spin centers, which we subsequently analyzed and identified with the help of density-functional theory (DFT) calculations. Our findings provide new insights into the photo-induced charge transfer processes, which are the basis of photocatalytic activity in UiO-66. This sets the stage for further studies on photogenerated spin centers in this and similar MOF materials.

Keywords: metal-organic framework; MOF; EPR; DFT; photocatalysis

# 1. Introduction

A photocatalytic process is a photoreaction accelerated in the presence of a catalyst activated by light, with several reviews available in literature for each area of application [1-3]. At its core, it involves the absorption of light by a photocatalyst, which generates electron-hole pairs that initiate and accelerate chemical reactions without the catalyst itself being consumed or altered in the process. In other words, photocatalysis is the holy grail of clean technologies and sustainable energy, due to its application in pollutant degradation and water splitting for hydrogen generation [4].

The development of metal-organic frameworks (MOFs), one subfamily of coordination polymers, has significantly expanded the horizons of photocatalysis. MOFs are highly ordered, porous materials composed of metal ions or clusters coordinated to organic ligands. Their

chemical nature allows for the design of organometallic materials with synergic properties among coordination and organic chemistry [5].

The relevance of MOFs in photocatalysis lies in their unique set of properties [6-8]. First, the structural diversity and tunability of MOFs enable the precise control over the absorption of light across a broad range of wavelengths, including the visible spectrum, which is crucial for maximizing the use of solar light in photocatalytic processes [9-11]. Second, their high surface-to-volume ratio and porous nature facilitate the diffusion of reactant molecules to the active sites, thereby increasing the efficiency of the photocatalytic reaction. Furthermore, the ability to incorporate different metal ions or clusters within MOF structures allows for the generation of active sites tailored for specific reactions, enhancing both the activity and selectivity of the photocatalyst.

MOFs have shown exceptional performance in various photocatalytic applications, from the degradation of pollutants to CO<sub>2</sub> reduction and water splitting. Their modular nature allows for the integration of photocatalytic units that can absorb light and transfer electrons, thereby creating highly efficient photocatalytic systems. Moreover, the design flexibility of MOFs enables the construction of composite materials that combine the advantages of MOFs with other photocatalysts, such as semiconductors, to create hybrid systems that further boost photocatalytic performance [4, 12].

UiO-66 is an archetypical UV-responsive MOF photocatalyst (Fig. 1A) [13,14]. It exhibits exceptional thermal, chemical, and mechanical stability, and its photophysical properties can be enhanced by introducing structural defects and chemical modifications [15, 16]. This MOF is composed of organic terephthalate ligands connecting inorganic  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$  secondary building units (SBU) that consist of  $\mu_3$ -bridged  $Zr^{4+}$  ions. In the SBU, bridging hydroxyl groups and oxygen atoms are symmetrically distributed, capping the faces of the  $Zr_6$  octahedron. Like in the case of conventional solid-state photocatalysts, the catalytic activity of UiO-66 is associated with light-induced charge transfer and separation of electrons and holes (cf. Fig. 1B) between inorganic and organic moieties, followed by their trapping at defect or surface states and, finally, their transfer to adsorbed species [15].

At the same time, the fundamental mechanisms of charge transfer, separation and trapping in pristine UiO-66 are still not well understood. In previous studies of traditional solid-state photocatalysts such as TiO<sub>2</sub>, electron paramagnetic resonance (EPR) has established itself as the method of choice for elucidating the nature of charge traps and studying the dynamics of photogenerated radicals [17, 18]. While delocalized electrons in the conduction band are EPR silent, localized states such as holes trapped at oxygen anions and electrons trapped at coordinatively unsaturated metal cations are accessible to EPR spectroscopy. In the case of pristine UiO-66, however, no conclusive EPR observation of stable photoinduced electron and hole states has been reported so far [19]. This is an apparent contradiction with the known photo-responsiveness of this MOF and can be explained by assuming that the captured carriers are either short-lived at ambient temperatures or have too short electron spinrelaxation times to be detected and studied at these experimental conditions.

In this work, we used broadband UV irradiation and EPR spectroscopy to detect the elusive electron and hole states in the pristine UiO-66 MOF. We find that even at low temperature

(T = 6 K) and sufficiently long irradiation times it is possible to achieve an equilibrium concentration of spin centers detectable with EPR. Our experimental results indicate the presence of a manifold of photoinduced spin-carrying species, which we subsequently analyze and assign with the help of density functional theory (DFT) calculations. The results of this study not only provide fundamental insights into the photophysics of charge transfer, separation, and capture in UiO-66, but also pave the way to further experimental investigation of photogenerated spin centers in this and other MOF photocatalysts.

## 2. Results

As shown in Fig. 1C, broadband UV-irradiation of UiO-66 at low temperature (T = 6 K) results in the observation of a rich EPR spectrum that was previously unreported. The appearance of the spectrum suggests that it represents a superposition of various photogenerated paramagnetic centers. For the convenience of the following discussion, distinct groups of resonance signals constituting the spectrum are denoted as R0, R1, and R2.

The group R0 represents two or more partially overlapping lines situated around the freeelectron *g*-factor ( $g_e = 2.0023$ ). Additionally, the R0 region contains the contribution of the broad EPR line also observed without irradiation ("dark" spectrum in Fig. 1C). The group R1 appears upon illumination and contains two partially resolved EPR lines, at *g*-factors of 2.044 and 2.036. These lines can either belong to two different paramagnetic species, or one spin center with distinct magnetic anisotropy. As R2, we denote two narrow, symmetric resonance lines with equivalent intensities and equidistantly separated from  $g_e$ . In addition, we observe a weak photoinduced EPR signal in the region of 155 mT (g = 4.4), as shown in the inset to Fig. 1C, which can indicate the presence of a photoinduced triplet state (i.e., a center with the total spin S = 1) in the sample [10].



**Figure 1.** Detection of photoinduced spin centers in UiO-66. (A) Schematic atomic structure of UiO-66. (B) Scheme of UV-induced charge separation. Electrons are excited either from the valence band or from occupied mid-gap defect states near the valence band (VB) and can be subsequently trapped by defect or surface states near the conduction band (CB). The resulting localized electron and hole states can now be observed using EPR. (C) X-band CW EPR spectrum at T = 6 K upon broadband UV-irradiation (blue line) compared with the dark EPR spectrum measured at the same temperature (gray line). The inset shows the photoinduced EPR signal at about 155 mT (asterisk). (D) UV illuminated (blue trace) and

dark (gray trace) EPR spectra recorded at room temperature exhibit no presence of spin centers observed in (C). (E) TDDFT-calculated difference density (top) and excitation wavelength (bottom) of the lowest excited singlet state  $S_1$  in UiO-66. The yellow isosurface shows the increase of electron density, while the cyan isosurface indicates its depletion. This equals a charge transfer in between linker (e<sup>-</sup>) and metal cluster (h<sup>+</sup>).

After the light is switched off, the photoinduced EPR signals remain stable at T = 6 K for at least several hours. However, after heating the sample back to room temperature, they disappear, allowing us to exclude their connection to photoionization damage of the material. Additionally, the X-ray diffraction data (Fig. S1) demonstrates that UV irradiation and low experimental temperatures do not cause the loss of crystallinity. Therefore, it is reasonable to assign the observed EPR signals to metastable radical species formed by light-induced separation and subsequent trapping (localization) of charge carriers. We use UV light with a broad spectrum, covering the range between 280 nm and 390 nm. According to our time-dependent DFT (TDDFT) calculations, this range covers the energy required to excite UiO-66 to the lowest singlet excited state (S<sub>1</sub>; cf. Fig. 1E and Fig. S5 for UiO-66 absorption spectra).

The TDDFT-calculated transition density shown in Figure 1A, E indicates that photoexcitation to S<sub>1</sub> is accompanied by charge transfer from the oxygen atoms of the SBU to the linker. Therefore, it is a likely scenario that UV-irradiation leads to the formation of electron-deficient oxygen-related radical species, which give rise to some of the resonance signals in the measured EPR spectrum. Specifically, the *g*-factors of the R1 signals (~2.04) remarkably agree with those reported for oxygen anions (O<sup>-</sup>), commonly detected in metal oxide as a result of hole trapping by an oxygen atom at the surfaces. These species are characterized by axially symmetric *g*-tensors with the following relation between the axial ( $g_{||}$ ) and in-plane ( $g_{\perp}$ ) principal values:  $g_{\perp} > g_{||} \approx g_e$ . For instance, for MgO, a variety of O<sup>-</sup> centers with  $g_{\perp}$ values in the range of 2.045 – 2.021 was observed [18]. A comparable range of *g* values was predicted by our DFT calculation for the O<sup>-</sup> center (trapped hole) in the SBU of UiO-66 (cf. Supplementary Figure S4), supporting the tentative assignment of the R1 signals.

As for the R2 EPR lines, the splitting between them on the magnetic field axis of 50.6 mT (corresponding to 1.4 GHz) is too large to be attributed to *g*-factor anisotropy. It is also unlikely to be caused by electron-nuclear hyperfine splitting. While transition metal ions can exhibit large hyperfine splitting, the only magnetic isotope of Zr (<sup>91</sup>Zr; natural abundance 11.2 %) has a nuclear spin I = 5/2, which would result in six resonance transitions. A likely explanation of the splitting between R2 resonances is that it originates from the effect known as zero-field splitting (ZFS) typical for high-spin (S > 1/2) states, such as triplets (S = 1). ZFS can be as large as a few GHz even in organic systems. As we already mentioned, the EPR signal which is marked by an asterisk in Fig. 2C (see also the inset to Fig. 1C) can indicate a photoinduced triplet state, for which a half-field EPR signal corresponding to  $\Delta m_S = \pm 2$ , where  $m_S$  is a spin projection quantum number, the so-called spin-forbidden transition is also expected. Thus, it can originate from the same triplet spin center as the R2 lines.



**Figure 2. Identification of a triplet state in pristine UiO-66.** (A) TDDFT calculated energy level diagram and the corresponding SOC constants. Feasible excited states for singlet-to-triplet transformation are highlighted in blue. (B) The calculated spin-density distribution of the lowest excited triplet state, T<sub>1</sub>, along with the principal directions of the ZFS tensor,  $D_X$ ,  $D_Y$ , and  $D_Z$ . (C) Proposed simulation of the R2 EPR lines, and assuming the ZFS anisotropy of the T<sub>1</sub> triplet with  $D_Y$  = 465 MHz and distortion-induced strain applied in the  $D_X$  and  $D_Z$  directions. The asterisk marks the assumed half-field transition. Inset shows a typical powder-average EPR spectrum of a triplet with an anisotropic ZFS. The lines labeled X, Y, and Z correspond to the single-crystal contributions with the external magnetic field aligned with  $D_X$ ,  $D_Y$ , and  $D_Z$ , respectively. (D) Comparison of the EPR spectra of UiO-66 irradiated with broadband UV and with 280 nm.

To theoretically investigate possible mechanisms of a triplet center formation in pristine UiO-66, we analyzed the results of our TDDFT. Fig. 2A shows the energy level diagram of the lowest singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>-T<sub>4</sub>) excited states, as well as the spin orbit coupling (SOC) values between S<sub>1</sub> and the triplet states. Typically, an excited triplet can be accessed via an intersystem crossing (ISC) from the low-lying excited singlet followed by the internal conversion (IC) within the triplet manifold. The ISC process involves a spin-forbidden (singlettriplet) horizontal transition driven by efficient SOC between the singlet and triplet wavefunctions. As a rule of thumb, facile ISC channels require small singlet-triplet gap ( $\Delta E_{S-T}$ < ±0.37 eV) and high SOC values (>0.04 meV or 0.3 cm<sup>-1</sup>) [23, 24]. As shown in Fig. 2A, there are excited states in the triplet manifold (such as T<sub>3</sub>) close to S<sub>1</sub> in energy and exhibiting strong SOC to facilitate efficient ISC. The spin density distribution of the resulting relaxed triplet state T<sub>1</sub> is illustrated in Fig. 2B and is almost entirely localized on the organic linker of UiO-66. The principal values and principal directions of its ZFS tensor are determined predominantly by spin-spin interaction between unpaired electrons and, therefore, reflect the spatial distribution of the spin density [25]. Expectedly, the calculated ZFS tensor is highly anisotropic with the principal values  $D_X$  = 1282 MHz,  $D_Y$  = 785 MHz, and  $D_Z$  = -2068 MHz (and the respective principal directions shown in Fig. 2B). The calculated *g*-tensor of the triplet is almost isotropic and close to free electron g-factor  $g_e$ .

As schematically illustrated in the inset of Fig. 2C, the ZFS anisotropy of the T<sub>1</sub> triplet state should manifest in six EPR lines. They originate from ensemble-averaging of the different molecular orientations with respect to an external magnetic field, denoted as X, Y, and Z, each of them exhibiting two  $\Delta m_s = 1$  resonance transitions. We do not observe the X and Z components – at least, at the field positions expected from the DFT calculated ZFS tensor. However, we can explore a scenario, in which the X and Z components are suppressed by orientation-dependent line broadening. Such broadening, often observed in CW EPR spectra of various organic and inorganic compounds, is conventionally described by the statistical distribution of the principal values of the *g*-tensor around their mean values and is referred to as "*g*-strain" [26]. For example, in organic nitroxide radicals, the *g*-strain is most pronounced for the  $g_x$  values and is explained by site-to-site local structural variations [27, 28].

The atomic structure of UiO-66 can exhibit a certain degree of variability (due to intrinsic dynamic flexibility causing local structural deformations [29]) and, therefore, can favor the observation of the *g*-strain. To illustrate this idea, Fig. 2C shows the simulated EPR spectrum of a triplet state with the  $D_Y$  value fitted to the resonance transition fields of the R2 lines ( $D_Y$  = 465 MHz), the  $D_Z$  value kept as in the DFT results, and 4% statistical variation (strain) applied to the  $g_X$  and  $g_Z$  parameters. This relatively small *g*-strain can lead to the disappearance of the X and Z components from the ensemble-averaged (powder) EPR spectrum. It is important to note that we cannot exclude the possibility that the R2 signals are related to other paramagnetic species such as impurities in the pores of the MOF samples. However, our analysis strongly supports their assignment to the excited triplet state inherent to the structure of UiO-66, providing compelling evidence for this interpretation.

Finally, Fig. 2D compares the EPR spectra obtained by excitation with a broadband UV source and a target wavelength of 280 nm from the LED. While broadband excitation is expected to address a vast ensemble of mid-gap defect states and higher excited states, the 280 nm wavelength should more specifically excite the lowest singlet state (S<sub>1</sub> in Fig. 2A), facilitating the pathway of the triplet formation predicted by TDDFT. Thereby, selective photoexcitation allows the separation of the described triplet state from the other photoexcitable centers in the structure of UiO-66.

The EPR spectrum taken at 280 nm excitation exhibits substantial differences in its central region. In contrast, the R2 signal retains, although with reduced intensity, supporting its association with the triplet state. It is important to note that the power of the light sources is comparable and is therefore not responsible for the lower signal intensity of R2.

Consequently, these findings strongly imply a significant role of mid-gap defect states in the photoexcitation process and the dynamics of photoexcited carriers within UiO-66.

Following the tentative assignment of the observed photogenerated spin centers, we aimed to explore their thermal stability. For this purpose, we measured the temperature dependence of the EPR spectrum after the UV source was turned off (Fig. 3A). As mentioned above, the observed centers are stable at 6 K after irradiation. But due to their distinct chemical reactivity and electron spin relaxation characteristics, the R0, R1 and R2 centers are expected to exhibit varied behaviors upon heating. At first, the R2 resonance signal disappears between 15 and 25 K. The R1 EPR signals region become undetectable at around 50 K. If we assume that R1 is associated with electron-deficient oxygen species (such as O<sup>-</sup> radicals, as discussed previously), this behavior seems expected. In many metal oxides, the surface-bound O<sup>-</sup> radical is only observed at low temperatures due to fast spin-lattice relaxation [21].

The temperature dependence of R1 and R2 explains why these EPR signals were never previously observed. Our results show that sufficiently low temperatures (T< 15 K) are required to reach a detectable signal of the photoinduced radical species in pristine UiO-66. However, most of the earlier studies were performed at room temperature, with a few going down to liquid nitrogen temperatures (T> 77 K). This approach is understandable since some chemical modifications of UiO-66 exhibit photoinduced EPR spectra already at room temperature. The activation energy or rather trapping energy of the spin center R1 and R2 can be very roughly estimated from the temperature behavior of their disappearance and should be on the order of magnitude of thermal energy  $k_BT \sim 3$ meV.



**Figure 3. Thermal stability of photoinduced radical species.** (A) Evolution of the EPR spectrum upon heating after UV switched off. (B) The EPR spectrum observed at 180 K in (A), which is attributed to the superoxide radical adsorbed at the unsaturated metal site (see the structural model shown below) and simulated using the corresponding spin Hamiltonian parameters discussed in the main text.

For example, NH<sub>2</sub>-UiO-66, a modification of UiO-66 that contains 2-aminoterephthalic acid as a linker, exhibits a photoinduced EPR signal at room temperature that is interpreted as a superoxide radical,  $O_2^{\bullet-}$  [30]. This radical is believed to be formed upon the reduction of  $O_2$ adsorbed at the unsaturated Zr<sup>4+</sup> site of a defective SBU by a photogenerated electron. Notably, an EPR signal with similar principal values of the *g*-tensor is observed in Figure 3A upon the thermal reduction of other species (at T  $\ge$  45 K). As shown in Figure 3B, this signal can be simulated using an anisotropic *g*-factor with the principal values  $g_X = 2.002$ ,  $g_Y = 2.009$ ,  $g_Z = 2.033$ . These values agree with the DFT calculations the  $O_2^{\bullet-}$  radical adsorbed at the missing-linker site of SBU:  $g_X = 2.0037$ ,  $g_Y = 2.0109$ ,  $g_Z = 2.0264$ . Our results suggest that, while never detected before, Zr-bound superoxide radicals are formed in the pristine UiO-66, just like in NH<sub>2</sub>-UiO-66. But either due to lower thermal stability or because of lower equilibrium concentration, it can only be detected with conventional EPR at cryogenic temperatures.

# Conclusions

Our work advances the understanding of the photophysics of MOF materials by revealing previously undiscovered details on photoinduced charge transfer, separation, and capture within pristine UiO-66, an archetypical MOF photocatalyst. We demonstrate for the first time that photo-induced charge carriers can be detected in this MOF under specific conditions, namely cryogenic temperatures (T < 20 K) and sufficiently long UV-irradiation time. These conditions compensate for the thermal instability of the photogenerated spin species associated with their rapid recombination and/or fast electron spin relaxation. The detectability of trapped photoinduced charge carriers by means of EPR spectroscopy offers a promising tool for understanding and tuning the photocatalytic properties of this and other types of MOF materials. Therefore, by establishing the experimental conditions that favor the observation of these photogenerated spin centers, we provide the guidelines for subsequent investigations of MOF photocatalysts.

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# Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

# **Conflicts of interest**

There are no conflicts to declare.

## **Supplementary Materials**

Supporting Information contains supplementary explanation and data, including XRD and UV-VIS analysis, additional EPR spectra and DFT simulations. SI includes Figures S1 – S5.

### **Authors contributions**

A.K. performed the magnetic resonance measurements and evaluated the data with help of A.S. and V. D., T. B. performed the DFT calculations. E.O. and M.C. performed the chemical synthesis and UV-VIS characterization. P.D. did XRD characterization and characterization of light sources. All the authors contributed to analysis of the data, discussions and to the writing of the paper.

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# Supporting Information for

# Photoinduced Spin Centers in Photocatalytic Metal-Organic Framework UiO-66

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### METHODS

## Sample preparation

UiO-66 was synthesized using a modified procedure previously reported by Katz et al. [1S]. In a 500 ml Schott Duran flask, 300 ml of DMF and 20 ml of concentrated HCl were mixed under a fume hood. To this solution, 2.51 g of ZrCl<sub>4</sub> was added in small portions, also under the fume hood. The solid dissolved quickly, and then 2.49 g of terephthalic acid was added to the resultant solution. To facilitate the dissolution of terephthalic acid, the mixture was subjected to an ultrasonic bath for 30 minutes. After complete dissolution, the screw-cap bottles were sealed and maintained at 120°C for 12 hours. The solids were isolated by centrifugation and washed twice with DMF and  $CH_2Cl_2$ .

## Continuous wave electron paramagnetic resonance experiment

CW EPR was done on a commercial Magnettech CW spectrometer MS5000 outfitted with an Oxford ESR 900 He flow cryostat. The deviation of the temperature was less than 0.2 K. Two types of light sources were used, a broadband Dymax BlueWave 50 UV lamp (280 nm to 450 nm, see Fig. S6) and a LED source with a wavelength of 280 nm from Thorlabs. The characteristic wavelengths of high intensity of the broadband lamp are 310 nm, 370 nm, 400 nm and 440 nm. The power of the LED and UV lamp were measured considering the distance between the sources and the irradiated sample. Thus, the LED with a wavelength of 280 nm has a power of 6.5 mW at a distance of 11 cm at the sample, and the broadband UV lamp 5.1 mW respectively. A microwave power of 1 mW was chosen for optimal signal-to-noise ratio of the main EPR spectra without saturation effects. However, experiments on saturation behavior have also been conducted.

### **EPR spectra simulations**

For the simulations of EPR spectra, we used EasySpin software based on MatLab [2S]. For the centers with the total spin S = 1/2, the spin Hamiltonian included only the Zeeman interaction term expressed as:

$$H_Z = \beta_e SgB = \beta_e [g_x S_x B_x + g_y S_y B_y + g_z S_z B_z]$$
(1)

where  $\beta_e$  is the Bohr magneton; **B** is the external magnetic field vector, **S** is the electron spin operator, and **g** is the is the electron *g*-tensor with the principal values  $g_x$ ,  $g_y$ , and  $g_z$ . In case of an *g*-tensor,  $g_x = g_y = g_{\perp}$  and  $g_y = g_{\parallel}$ .

In case of triplet (S = 1) states, anisotropic magnetic dipole-dipole interaction between two unpaired electrons results in lifting of degeneracy among the three spin sublevels, even without an external magnetic field. This phenomenon is known as the zero-field splitting (ZFS) interaction and can be described by the spin Hamiltonian equation:

$$H_{zfs} = SDS = D_x S_x^2 + D_y S_y^2 + D_z S_z^2 = D\left(S_z^2 - \frac{1}{3}S^2\right) + E\left(S_x^2 - S_y^2\right)$$
(2)

where  $D_x$ ,  $D_y$ ,  $D_z$  are the principal values of the ZFS tensor **D**. The ZFS interaction is typically specified by the two parameters  $D = \frac{3}{2}D_z$  and  $E = \frac{1}{2}(D_x - D_y)$  by the reason of traceless nature of it [3S, 4S].

#### **DFT** calculations

The DFT calculations were performed with the ORCA program package [5S] using the TPSSh exchange-correlation functional [6S] and the def2-TZVP basis set [7S] combined with the RIJCOSX approximation and the corresponding auxiliary basis set [8S]. Both ground-state and excited state calculations were performed using a cluster model cut from the crystal structure of UiO-66. The cluster model consisted of one linker and two SBUs with the remaining (unsaturated) coordination sites of the SBUs terminated by HCOO<sup>-</sup> anions. During geometry optimization, the coordinates of the carbon atoms of each HCOO<sup>-</sup> were fixed. For the excited states, TDDFT calculations [9S] were used with the optimized ground-state atomic structures. For the calculation of the ZFS tensor, the lowest excited triplet state was modeled by constraining the spin multiplicity. The calculated ZFS included both the spin-spin and spin-orbit contributions. To diminish the spin contamination error in the spin-spin ZFS [10S], it was calculated using the unrestricted natural orbital (UNO) approach [11S] and the generalized gradient (GGA) based PBE functional [12S].

## X-ray diffraction

X-Ray diffraction (XRD) measurements were performed using a General Electric XRD 3003 TT with a monochromatic Cu-K $\alpha$  radiation source (U = 40 kV, I = 40 mA) with a wavelength  $\lambda$  of 1.5406 Å. The measurements were performed at room temperature. Simulations were performed with Diamond software. The structure has a cubic space group Fm-3m (225).

### **ADDITIONAL RESULTS**



**Figure S1.** X-Ray diffraction pattern for UiO-66 powder sample after UV irradiation at T = 6 K and heating back to the room temperature. No significant broadening of the peaks was found, indicating that the crystallinity of the structure was not lost after UV irradiation and low experimental temperatures.



**Figure S2**. Time dependence of R2 signal intensity growth. One of the signal peaks corresponding to one of the  $\Delta m_s = \pm 1$  transitions was chosen to measure the time dependence. The measurements were performed at T = 6 K and fixed modulation amplitude and microwave power for each scan. Also, the receiver gain remained the same throughout the experiment.



**Figure S3**. The microwave dependence of R0, R1 and R2. The different behavior under microwave power saturation displays differences in spin-spin and spin-lattice relaxation times due to the different nature and coordination environment of the R0, R1, and R2 centers.



**Figure S4**. Two representative DFT models of a hole trapped at a  $\mu_3$ -O atom of the UiO-66 SBU (i.e., the O<sup>-</sup> radical anion) with different arrangements of the surrounding  $\mu_3$ -O and  $\mu_3$ -OH groups. The electron spin densities are shown as yellow isosurfaces and the calculated principal values of the g-tensors are shown below each structure, illustrating the range of the principal *g*-values expected for this center.



Figure S5. UV-visible DRS absorption spectra of UiO-66 samples.



Figure S6. Spectrum of the used broadband Dymax BlueWave 50 UV lamp.

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