Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Stabilization of Radical Active Species in a MOF Nanospace to Exploit Unique Reaction Pathways

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<Chemicals>

Dimethyl 5-hydroxyisophthalate, 1-bromo-2-chloroethane, sodium iodine (NaI), ~~,~~ lithium hydroxide (LiOH), 1,2-dibromoethane, ammonium chloride (NH_4Cl), sodium chloride (NaCl) and potassium *tert*-butoxide (^{t}BuOK) were purchased from Tokyo Chemical Industry, 5-hydroxyisophthalic acid, potassium carbonate (K_2CO_3), potassium iodine (KI), dimethyl sulfoxide (DMSO), zinc actetate dihydrorate ($Zn(OAc)_2 \cdot 2H_2O$), tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) were from Wako Pure Chemical Industries Ltd, sodium hydroxide (NaOH), , hydrochloric acid (HCl), were from Kanto Chemical Co., Inc., acetone, methanol (MeOH), dimethyl sulfoxide-d_6 (DMSO-d_6), chloroform-d ($CDCl_3$) were from Nacalai Tesque. All chemicals were used without further purification.

<Organic Synthesis>

・Synthesis of 5-(2-iodoethoxy)isophthalic acid (H_2lip)

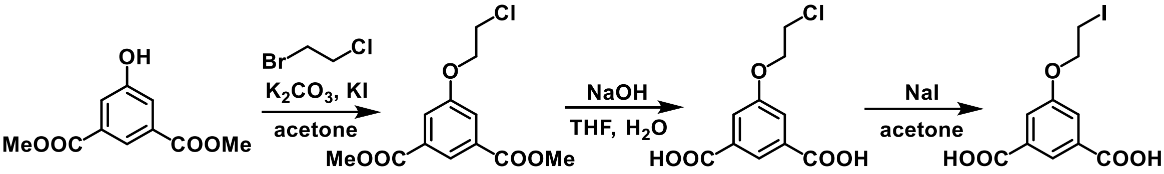

Fig. S1 Synthetic scheme of H_2lip.

Step1: Synthesis of dimethyl 5-(2-chloroethoxy)isophthalate

Dimethyl 5-hydroxyisophthalate (10.5 g, 50.0 mmol) was dissolved in acetone (500 mL) into 1 L recovery flask. K_2CO_3 (10.0 g, 72.4 mmol) and KI (90.0 mg, 0.54 mmol) were slowly added into the solution and stirred at room temperature for 30 min. Then, 1-Bromo-2-chloroethane (5.2 mL, 62.5 mmol) were added slowly at room temperature and heated at 65 ^{o}C for one week. After cooling to room temperature, the reaction mixture was filter off and evaporated to get the solid crude compound. The crude compound was purified by column chromatography (CH_2Cl_2) to get white solid (3.3 g, 12.1 mmol, yield: 31 %).^{1}H NMR (DMSO-d_6, 300 MHz) δ8.10 (t, 1H, J=1.4 Hz), 7.71 (d, 2H, J=1.5 Hz), 4.40 (t, 2H, J=4.9 Hz); 3.98 (t, 2H, J=5.1 Hz), 3.89 (s, 6H).

Step2: Synthesis of 5-(2-chloroethoxy)isophthalic acid (H_2Clip)

Dimethyl 5-(2-chloroethoxy)isophthalate (3.3 g, 12.1 mmol) was dissolved in THF (100 mL) into 200 mL recovery flask. Then NaOH saturated aqueous solution (10 mL, NaOH:1.5 g, 37.5 mmol) were slowly added into the solution and heated at 40 ^{o}C for a day. After cooling to room temperature, the reaction mixture was evapolated to remove THF, and 6 M HCl aqueous solution was added to the solution by pH = 1.

Finally, the white solid was filtered off and dried *in vacuo* at room temperature for 24 h to get the product (2.6 g, 10.6 mmol, yield: 88%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 13.3 (s, 2H), 8.10 (t, 1H, *J* = 1.4 Hz), 7.67 (d, 2H, *J* = 1.4 Hz), 4.39 (t, 2H, *J* = 4.9 Hz); 3.98 (t, 2H, *J* = 5.1 Hz).

Step3: Synthesis of 5-(2-iodoethoxy)isophthalic acid

5-(2-chloroethoxy)isophthalic acid (2.6 g, 10.6 mmol) was dissolved in acetone (100 mL) into 200 mL recovery flask. Then sodium iodine (5.0 g, 33.4 mmol) were added to the solution and heated at 65 °C for 3 days. After cooling to room temperature, the reaction mixture was filtered to remove sodium chloride and evaporated. Finally, the white solid was washed with water (300 mL) and dried *in vacuo* at room temperature for 24 h to get the product (2.38 g, 7.1 mmol, yield: 91.7%).^{1}H NMR (DMSO-d_6, 300 MHz) δ 13.3 (s, 2H), 8.09 (t, 1H, *J* = 1.4 Hz), 7.65 (d, 2H, *J* = 1.4 Hz), 4.38 (t, 2H, *J* = 6.0 Hz); 3.54 (t, 2H, *J* = 6.0 Hz).

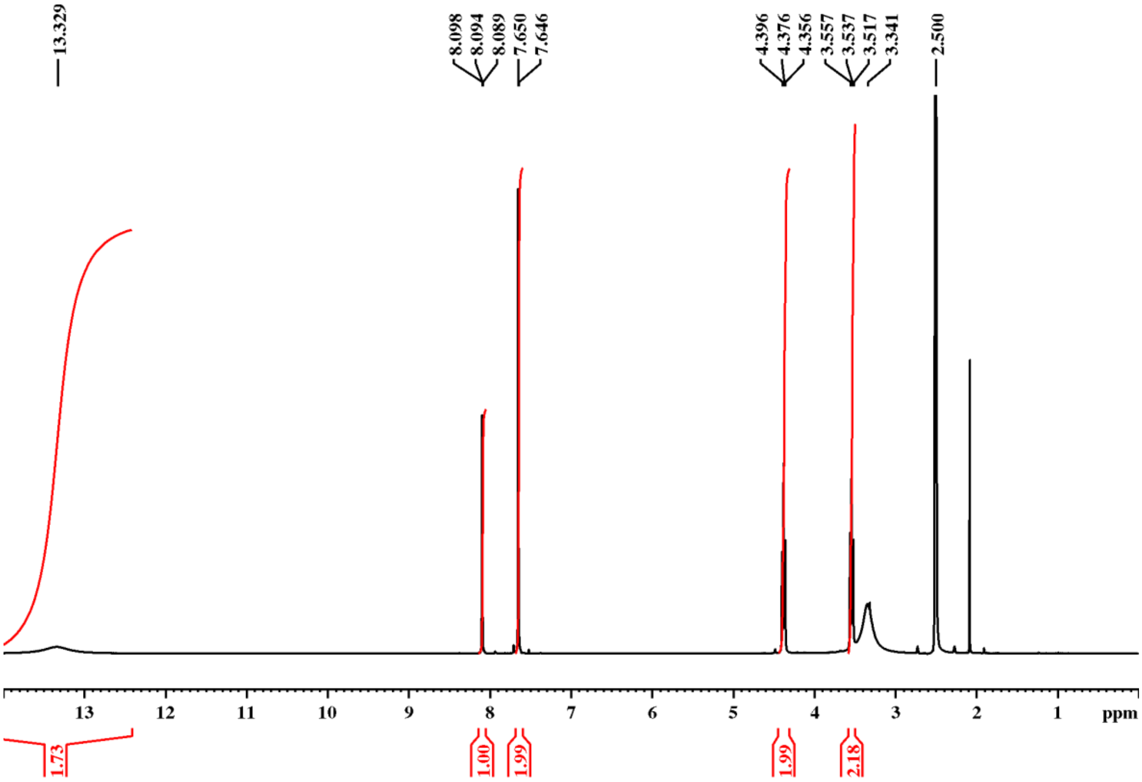

Fig. S2 ^{1}H NMR spectrum of H_2lip.

<Photoirradiation experiment>

First, the organic ligand (H_2lip) and MOF (**Znlip**) were ground for 20 min to align the particle size. Then, we conducted SEM measurements to confirm the particle sizes of the samples. The SEM images showed that the particle size of H_2lip and **Znlip** range between *ca.* 200~500 nm (Fig. S3 (a), (b)). Next, 5 mg of H_2lip or **Znlip** were put into a quartz tube, and the samples were heated at 120 ^{o}C *in vacuo* for 6 hours to activate. After cooling to room temperature, the samples were filled with helium (He) and cooled to 80 K with liquid nitrogen (N_2). Then, the light was irradiated using an USHIO OpticalModulex high-pressure Hg lamp (12 A) for 1 h with stirring the sample.

The yield of photoproduct of H_2lip was 19% for 5-hydroxyisophthalic acid, whereas that of **Znlip** was 33%, including 22% for 5-hydroxyisophthalic acid and 11% for 5-(ethenyloxy)isophthalic acid, respectively.

We also performed the same photoirradiation experiment using a **Znlip** sample with larger particle sizes (*ca.* 50 μm, Fig. S3 (c)). The total product yield for the larger particle size was 20%, which was lower than that of smaller particle sizes (33%) because of the smaller light penetration for larger crystals. However, the value is much higher than the surface ratio (0.029%), further supporting that the reaction occurred inside the crystals.

Furthermore, the yields of 5-hydroxyisophthalic acid and 5-(ethenyloxy)isophthalic acid were 22% and 11% from the smaller **Znlip** particle (Fig. S3(b)), and 13% and 7% from the larger **Znlip** particle(Fig. S3(c)), respectively. The product ratios are both *ca.* 2 : 1, indicating that the product distribution of the photoreaction does not tend to be affected by the particle size.

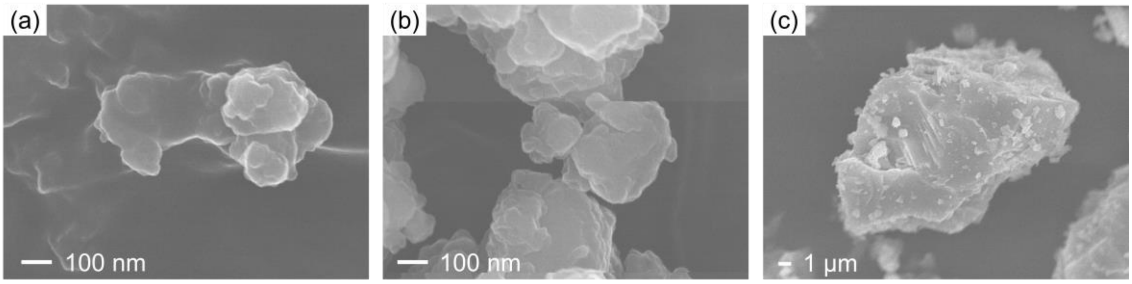

Fig. S3 SEM image of (a) H_2lip. (b), (c) **Znlip** with (b) smaller particle size, (c) larger particle size.

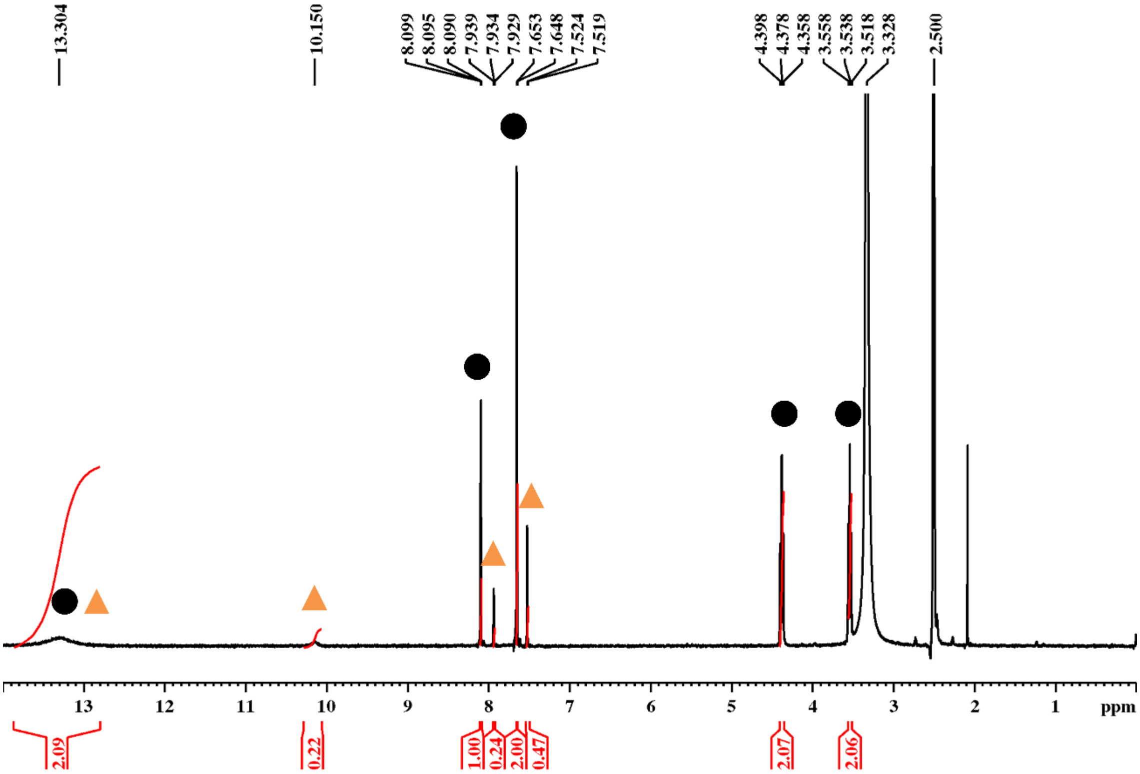

Fig. S4 ^{1}H NMR spectrum of H_2lip after photoirradiation. (black circle) the peaks of H_2lip, (orange triangle) the peaks of 5-hydroxyisophthalic acid.

<Organic Synthesis (for photoproduct identification)>

・Synthesis of 5-(ethenyloxy)isophthalic acid

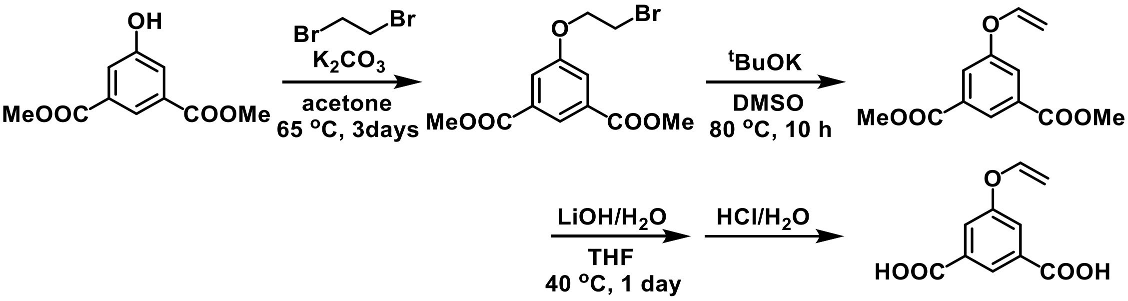

Fig. S5 Synthetic scheme of 5-ethenyloxy isophthalic acid.

Step1: Synthesis of Dimethyl 5-(2-bromoethoxy)isophthalate

Dimethyl 5-(2-bromoethoxy)isophthalate was synthesized according to the literature with minor modification.[1] Dimethyl 5-hydroxyisophthalate (2.1 g, 10.0 mmol) was dissolved in acetone (500 mL) into 1 L recovery flask. K_2CO_3 (4.0 g, 72.4 mmol) and 1,2-dibromoethane (4.3 mL, 51.5 mmol) were slowly added into the solution heated at 60 °C for 3 days. After cooling to room temperature, ammonium chloride saturated aqueous solution was added into the solution and stirred for 30 min. The solution was evaporated to get the solid compound. The crude compound was dissolved in CH_2Cl_2 (50 mL) and washed with H_2O (50 mL×2) and NaCl saturated aqueous solution (50 mL). The crude compound was dehydrated by magnesium sulfate ($MgSO_4$), filtered off to remove $MgSO_4$ and evaporated. Then the solid was dissolved in cyclohexane (50 mL) and stirred for 10 min at room temperature. Finally, the solution was evaporated and dried *in vacuo* at room temperature for 24 h to get white solid (1.83 g, 5.8 mmol, yield: 63 %). ^1H NMR ($CDCl_3$, 300 MHz) δ 8.26 (t, 1H, J = 1.4 Hz), 7.70 (d, 1H, J = 1.4 Hz), 3.94 (s, 6H).

Step2: Synthesis of Dimethyl 5-(ethenyloxy)isophthalate

Dimethyl 5-(ethenyloxy)isophthalate was synthesized refer to the literature.[2] Dimethyl 5-(2-bromoethoxy)isophthalate (1.83 g, 5.8 mmol) was dissolved in DMSO (10 mL) into 30 mL recovery flask. Potassium *tert*-butoxide (1.0 g, 8.9 mmol) were added to the solution and stirred at 80 °C for 10 h. After cooling to room temperature, the solution was cooled down to 0 °C by ice, and 6 M HCl was added dropwise to pH = 1. Then, the mixture was extracted with diethyl ether (10 mL×3) and washed with $NaHCO_3$ saturated aqueous solution (30 mL). The organic solution was dried by magnesium sulfate. Finally, the solution was evaporated and dried *in vacuo* at room temperature for 24 h to get the product (0.48 g, 2.0 mmol, yield: 34%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.14 (t, 1H, *J* = 1.5 Hz), 7.73 (d, 1H, *J* = 1.5 Hz), 6.96 (dd, 1H, *J* = 6.0 and 13.5 Hz), 4.87 (dd, 1H, *J* = 1.8 and 13.5 Hz), 4.65 (dd, 1H, *J* = 1.8 and 6.0 Hz) 3.90 (s, 6H).

Step3: Synthesis of 5-(ethenyloxy)isophthalic acid

Dimethyl 5-(ethenyloxy)isophthalate (0.48 g, 2.0 mmol) was added into 100 mL recovery flask and was dissolved in THF (20 mL). Then LiOH (0.2 g, 4.8 mmol) dissolved in H_2O (30 mL) were slowly added in the solution and heated at 60 ^{o}C for a day. After cooling to room temperature, the solution was evapolated to remove THF. Then, 6 M HCl aqueous solution was added to the solution by pH=1. Finally, the white solid was washed with water (30 mL) and dried *in vacuo* at room temperature for 24 h to get the product (0.23 g, 1.1 mmol, yield: 54%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 13.4 (s, 2H), 8.19 (t, 1H, *J* = 1.5 Hz), 7.74 (d, 2H, *J* = 1.4 Hz), 6.97 (dd, 1H, *J* = 6.0 and 13.5 Hz), 4.86 (dd, 1H, *J* = 1.7 and 13.5 Hz), 4.63 (dd, 1H, *J* = 1.7 and 6.0 Hz).

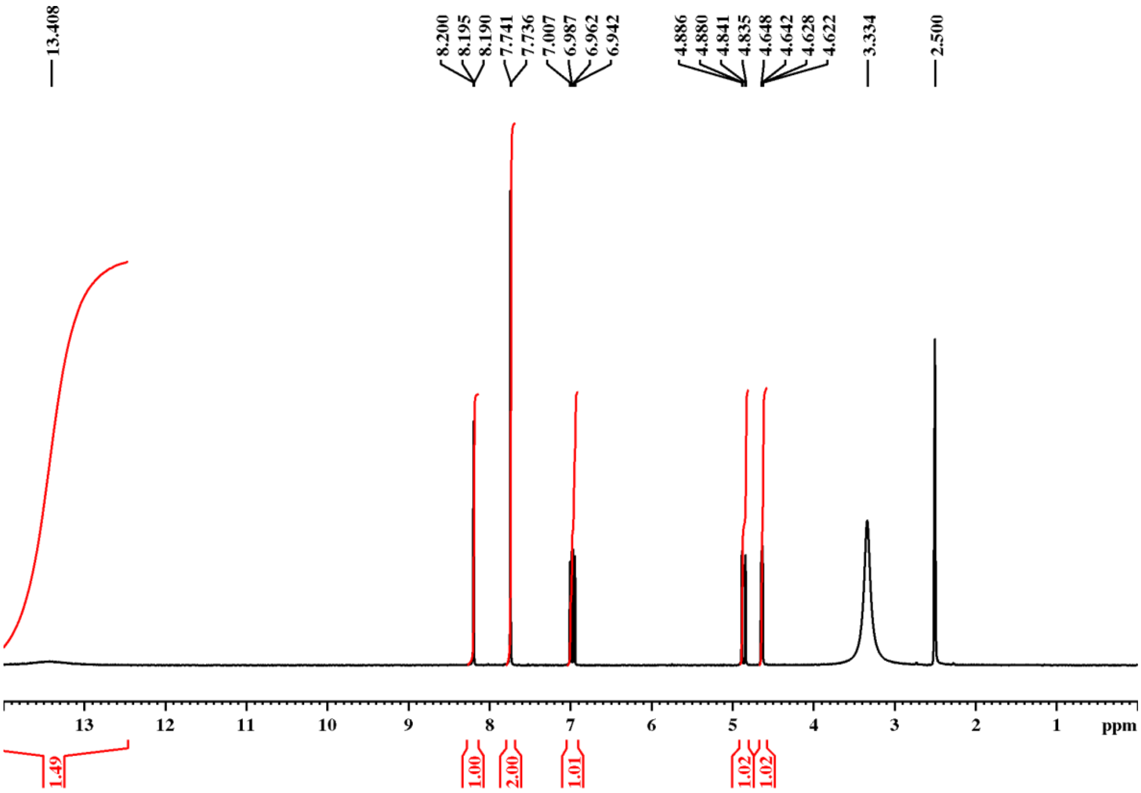

Fig. S6 ^{1}H NMR spectrum of 5-(ethenyloxy)isophthalic acid.

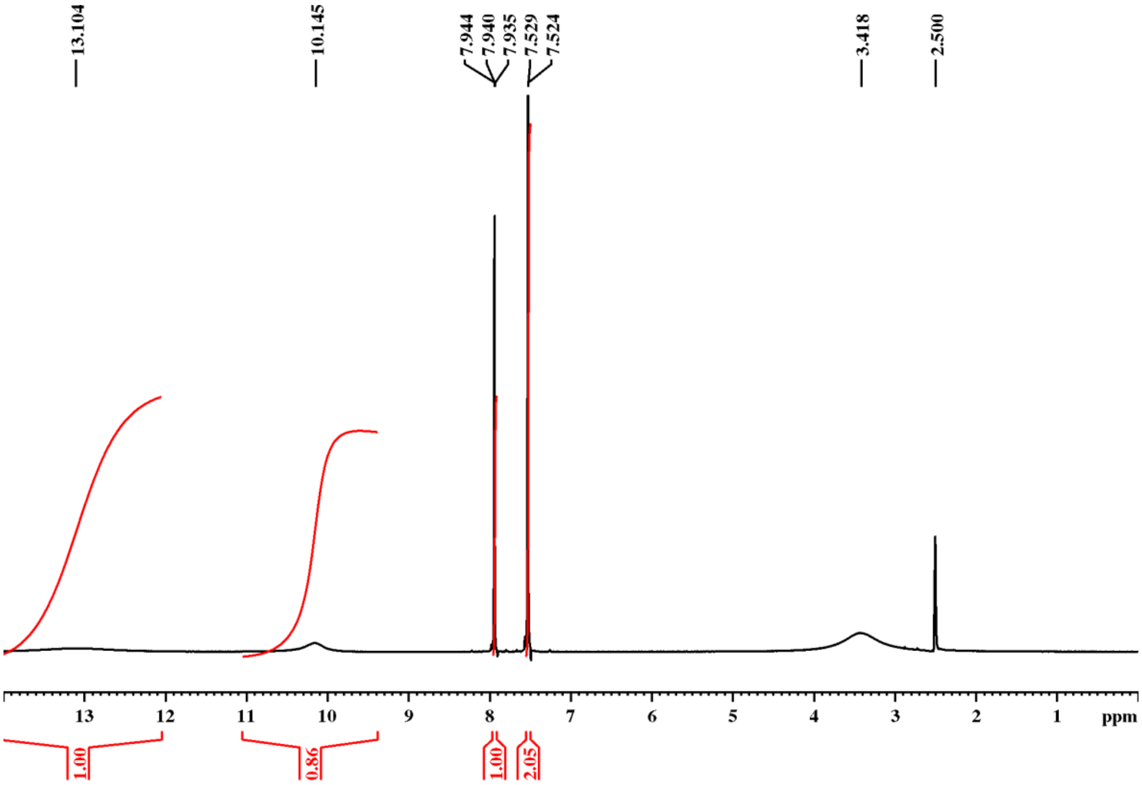

Fig. S7 ^{1}H NMR spectrum of 5-hydroxyisophthalic acid. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 13.1 (s, 1H), 10.1 (s, 1H), 7.94 (t, 1H, *J* = 1.5 Hz), 7.53 (d, 2H, *J* = 1.5 Hz).

<MOF Synthesis>

Synthesis of $[Zn_2(Iip)_2(H_2O)]$ **(ZnIip)**

$Zn(OAc)_2 \cdot 2H_2O$ (43.9 mg, 0.20 mmol) were dissolved in H_2O (5 mL). Also, H_2Iip (67.2 mg, 0.20 mmol) were dissolved in MeOH (5 mL). Next, in the glass tube (8 mm diameter and 200 mm length), the metal solution was slowly poured to the bottom layer and the organic ligand solution to the top layer. After that, the glass tube was put into the oven and heated at 323 K for 3 days. After cooling to the mixture, transparent colorless crystal was formed in the middle of glass tube. Then the crystals were collected by filtration and washed with H_2O (10 mL×2) and MeOH (10 mL×2) (64.3 mg, 0.079 mmol, yield: 39%).

Table S1. Crystallographic parameters for **ZnIip**

	ZnIip
Formula	$C_{20}H_{16}I_2O_{11}Zn_2$
Crystal system	Trigonal
Space group	R -3
a [Å]	27.5610 (10)
b [Å]	27.5610 (10)
c [Å]	17.9581 (6)
α [°]	90
β [°]	90
γ [°]	120
V [Å^3]	11813.6 (9)
Z	18
Diffractometer	CCD
μ [cm^{-1}]	42.32
Radiation type	Mo $K\alpha$
Radiation wavelength	0.71073
F [000]	7020
Goodness of fit	1.823
Temperature [K]	233
Reflections collected	17180
Independent reflections	6025
R_1 [$I > 2\sigma[I]$]^{*a}	0.1068
wR_2 [all data]^{*b}	0.3887

$^{*a}R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $^{*b}wR_2 = [\sum w|F_o^2 - F_c^2|^2 / \sum w(F_o^2)^2]^{1/2}$

<Instruments and measurement details>

Single-crystal X-ray diffraction data were collected on a RIGAKU XtaLab P200 CCD system with VariMax Mo Optic with Mo Kα radiation (λ = 0.71073 Å) and a confocal monochromator, with a constant temperature of 233 K by flowing nitrogen gas. The structure was solved by direct methods and refined by full-matrix least-squares cycles using SHELX.[3] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. All powder x-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex600 operating at 40 kV/15 mA producing Cu Kα radiation (λ = 1.5406 Å) at room temperature ranging from 3˚ to 55˚ with the scan rate of 5˚/min. Thermal gravimetric analysis (TGA) was performed using a Rigaku TP-EVO2 SL DyTG/DTA TypeJ under nitrogen stream scanning from 40 ^{o}C to 500 ^{o}C with the temperature ramp of 5 ^{o}C/min. Scanning electron microscope (SEM) measurements were performed with a JEOL Model JSM-7500F operating at 10 kV. The samples were put on the carbon tape and coated with osmium prior to the measurements. Energy dispersive X-ray spectroscopy (EDX) analyses attributed of SEM were carried out with a JEOL Model JED-2300F operating at 15 kV. The adsorption isotherms of N_2 at 77 K were obtained on a BELSORP-Max volumetric-adsorption instrument from microtrac-BEL, Inc. The measurement temperature was controlled by cryostat. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Bruker model Av 300 using tetramethylsilane as an internal reference. All ESR measurements were performed with a JEOL JES-X320 ESR system, and the temperature was controlled by JEOL ES-CT470 with flowing nitrogen gas.

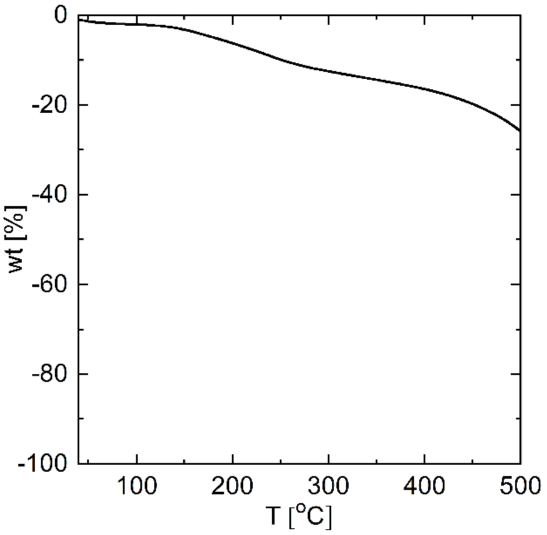

Fig. S8 TG data of **Znlip**.

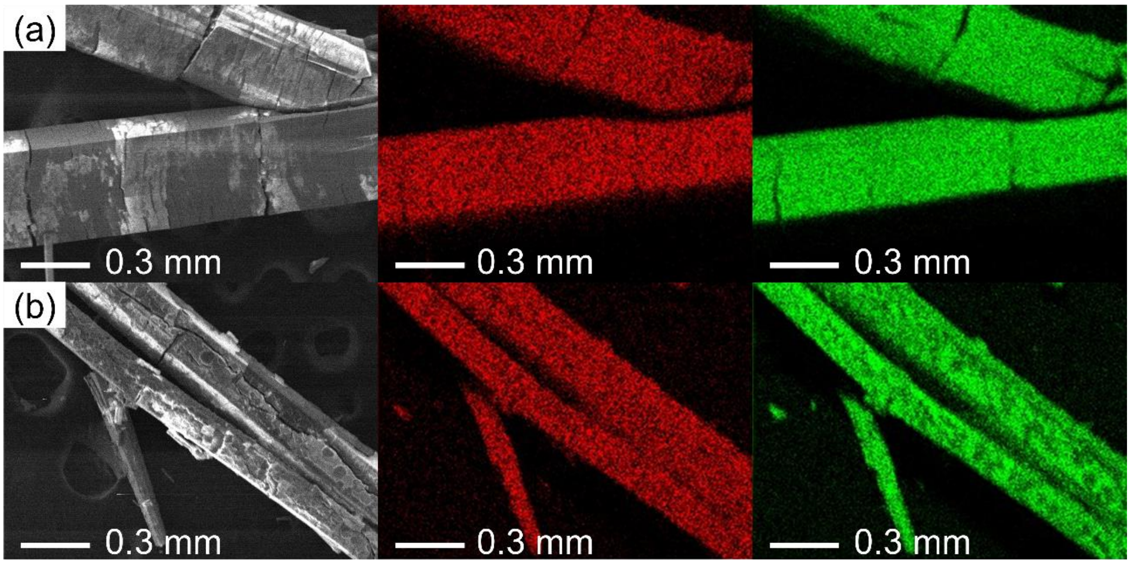

Fig. S9 SEM images and EDX mapping of **Znlip**. (red) zinc or (green) iodine. (a) before photoirradiation, (b) after photoirradiation.

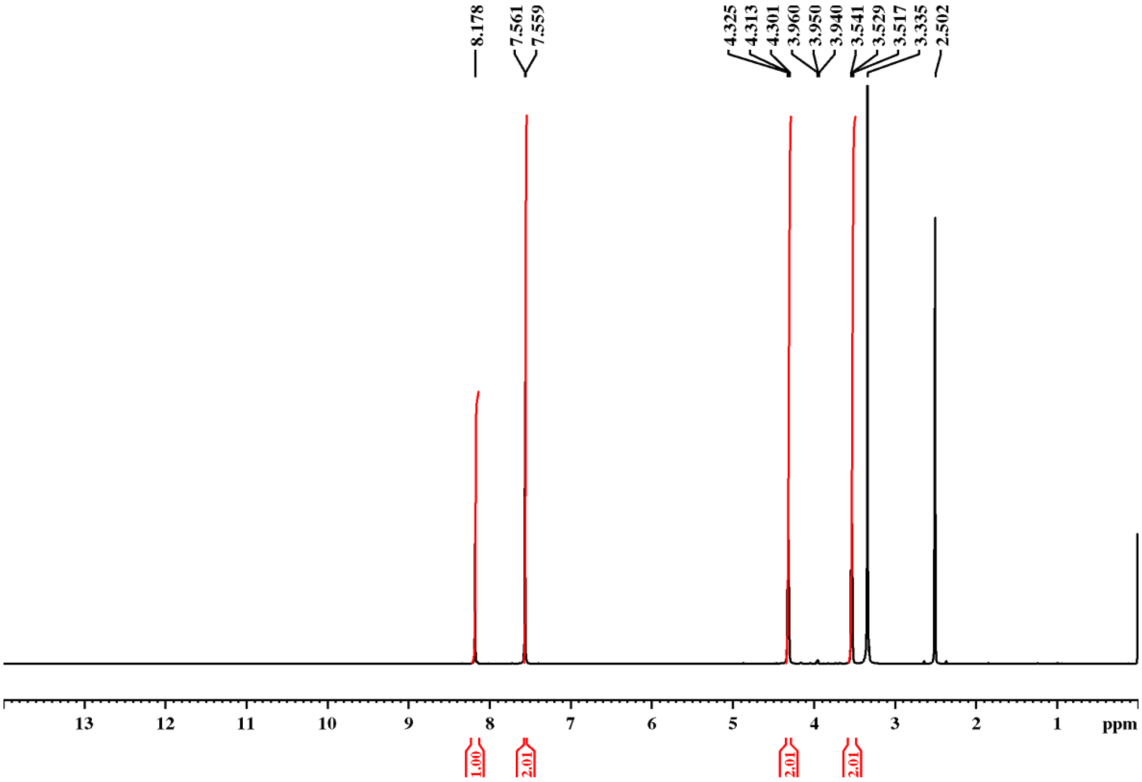

Fig. S10 ^{1}H NMR spectrum of **Znlip**.

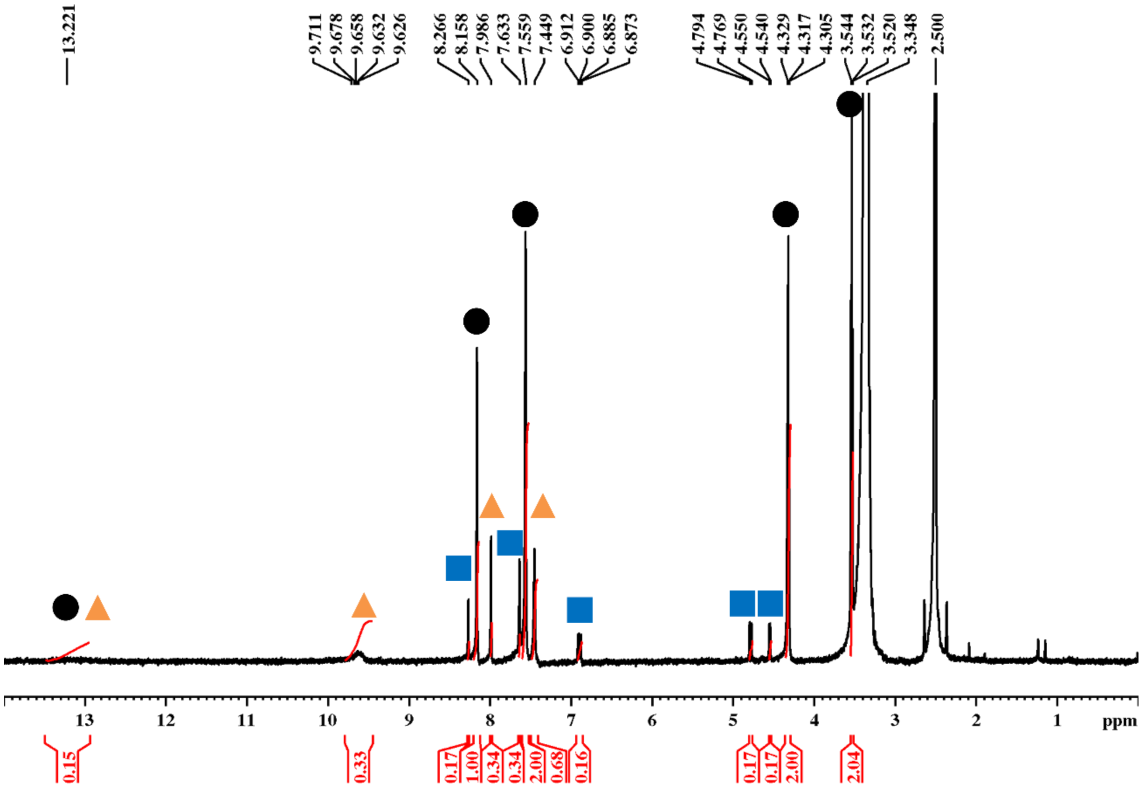

Fig. S11 ^{1}H NMR spectrum of **ZnIip** after photoirradiation. (black circle) the peaks of H_2Iip, (orange triangle) the peaks of 5-hydroxyisophthalic acid, (blue square) the peaks of 5-ethenyloxy isophthalic acid.

<ESR Measurement>

5 mg of H_2lip or **Znlip** were put into a Φ5 quartz tube, and the samples were evacuated by a pump. Then the samples were heated at 120 ^{o}C *in vacuo* for 6 hours to activate. After cooling to room temperature, the samples were cooled to 80 K with liquid nitrogen (N_2) and filled with Helium (He). After that, ESR measurement was carried out under photoirradiation by using an USHIO OpticalModulex high-pressure Hg lamp (12 A) at regular time intervals up to 24 h. Finally, the samples were dissolved in DMSO-d_6 and measured NMR spectrum to check the product by photoirradiation.

<Thermal Stability of Radicals>

The samples were pretreated and photoirradiated under the same condition as described above. After the photoirradiation, the temperature was raised from 80 K to 300 K by 10 K/min and was maintained the set temperature (100 K, 150 K, 200 K, 250 K, 300 K) for 10 min. Then, the samples were recooled at 80 K and measure ESR spectrum.

<Chemical Stability of Radicals>

The samples were degassed and photoirradiated under the same condition as described above. After the photoirradiation, the samples were vacuumed less than 10^{-3} bar. Then, the temperature was increased at 90 K, oxygen (O_2) was introduced into the sample at 100 kPa and ESR measurement was carried out at regular time intervals.

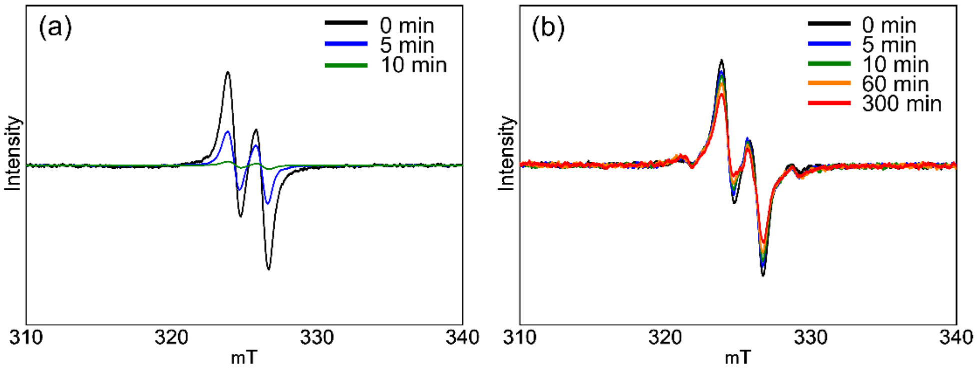

Fig. S12 ESR spectra of (a) H_2lip, (b) **Znlip** recorded at 90 K under O_2 atmosphere.

<Gas Adsorption Measurement>

100 mg of **Znlip** was put on the Φ2.5×2.5 cm sample cell and desolvated at 393 K for 6 h *in vacuo* by cryostat. After cooling to the room temperature, the sample was cooled down to boiling point (O_2: 90 K, N_2: 77 K) and measured gas adsorption.

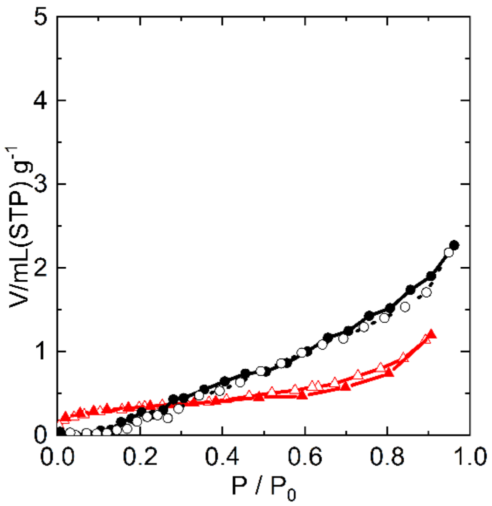

Fig. S13 Gas adsorption isotherm of **Znlip**. Black: N_2, 77 K; Red: O_2, 90 K.

<Theoretical Calculation>

DFT calculations were carried out with ub3lyp functional using the Gaussian 09.[4] The model structures (phenoxy radical and alkyl radical) were constructed with gaussview. Then these models were optimized by 6-311G+(d, p)[5] for all the elements. After these calculation, the formation energy of phenoxy radical were calculated using the equation below.

$$E = (E_{phenoxy\,radical} + E_{ethylene}) - E_{alkyl\,radical}$$

which $E_{pheoxy\ radical}$, $E_{ethylene}$ and $E_{alkyl\ radical}$ is the potential energy of phenoxy radical, ethylene and alkyl radical calculated by Gaussian 09.

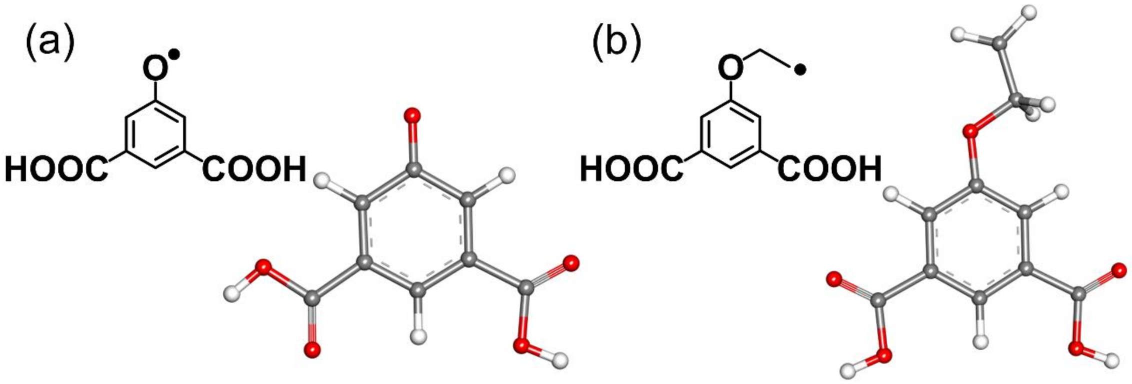

Fig. S14 The optimized structure of (a) phenoxy radical, (b) alkyl radical.

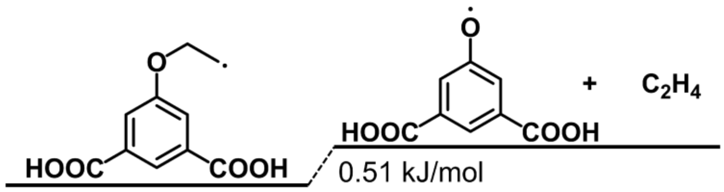

Fig. S15 The reaction energy of alkyl radical to phenoxy radical calculated by Gaussian 09.

<ESR Simulation>

ESR spectrum simulation was done by an EasySpin program.[6]

The simulated spectrum of the alkyl radical with g = 2.0030 and hyperfine coupling structures (HFSs) with two equal α- and β-protons is shown in Fig. S16, S17. HFS due to two equal β-protons in the alkyl radical makes triplet lines with isotropic hyperfine coupling constant (HFCC) of 3.7 mT. Equal HFCC of two β-protons, *i.e.* the angle between the axis of the 2pπ orbital on the α-carbon where the unpaired electron exists and the C-H bonds between the β-carbon and the two β-hydrogens is symmetric, is supported by *ab-initio* calculation of optimizing molecular structure with ub3lyp/EPR-III basis set level. The first and third lines due to the two equal β-protons at 321.6 and 329 mT, respectively, are easily detectable in the experimental one but centerline at *ca.* 325.4 mT is not due to overlapping with the large doublet lines at 324.4 and 326.3 mT. Anisotropic HFCC of –1.76, –1.96, and –2.90 mT for two α-protons of the alkyl radical is applied to the simulation.[7,8] The HFCC of two α-protons does not affect to the line position of the triplet lines due to the two β-protons.

The ESR peaks at 324 mT and 327 mT could not be fit as phenoxy radicals using the reported values.[9] The radical might be formed by the photoexcitation of organic ligands as reported in several MOFs.[10,11] So far, we assume that a phenoxy radical might easily abstract a hydrogen atom from other species to form 5-hydroxyisophthalic acid, thus were not observed.

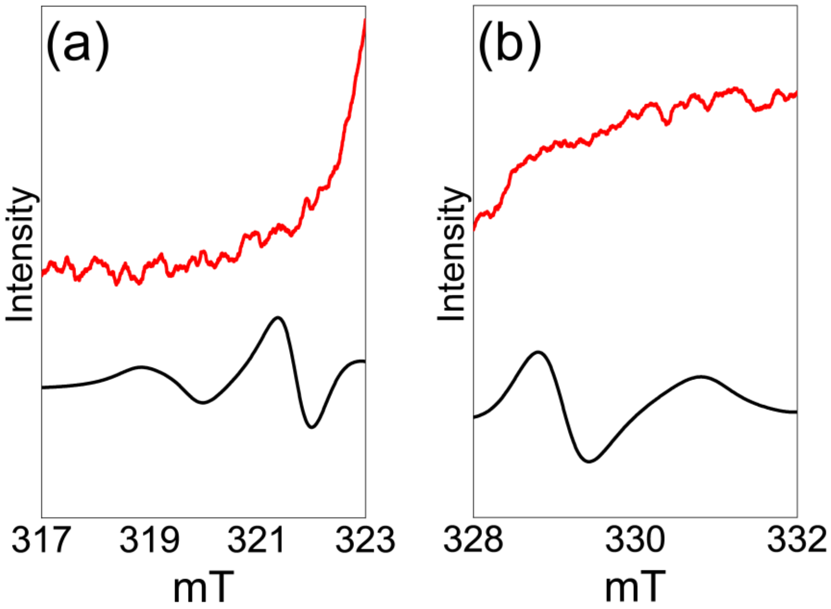

Fig. S16 ESR spectrum of H_2lip measured at 80 K after irradiating the light for 30 min. (a) 317 mT~323 mT, (b) 328 mT~332 mT. Black line is the simulated spectrum of alkyl radical with *g* = 2.003.

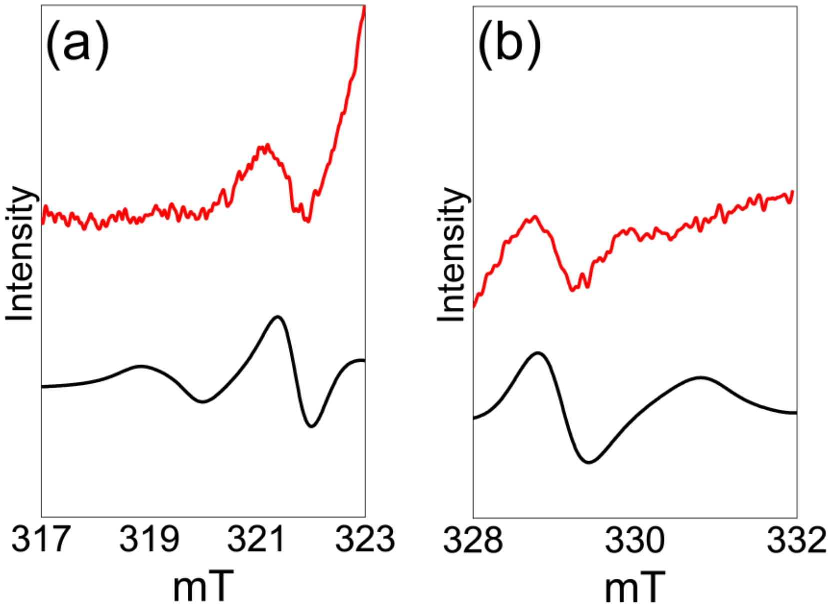

Fig. S17 ESR spectrum of **Znlip** measured at 80 K after irradiating the light for 30 min from (a) 317 mT~323 mT, (b) 328 mT~332 mT. Black line is the simulated spectrum of alkyl radical with *g* = 2.003.

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