

**Single-layer 2D supramolecular-organic-frameworks supported polyoxometalates:
efficient selective oxidation of toluene in seawater under sunlight**

Yan Fan, Yi Luo, Xu Luo and Xin-Long Ni*

Key Laboratory of Chemical Biology and Traditional Chinese Medicine, Ministry of Educational of China, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China.

General instrumentation and methods

^1H and COSY NMR (500 MHz) spectra were taken on a Bruker AVANCE-500 spectrometer, and chemical shifts were reported as the delta scale in ppm. The residual peak of D_2O was used as internal reference for ^1H NMR ($\delta = 4.79$ ppm). UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Dynamic light scattering (DLS) experiments were performed on a Malvern Zetasizer Nano ZS90. X-ray photoelectron spectra (XPS) were detected using an Thermo Scientific K-Alpha instrument with $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) radiation. Electron paramagnetic resonance (ESR) spectra were recorded on a JES-FA200 spectrometer. Natural seawater was obtained from the South Sea of China.

Scanning electron microscopy (SEM)

SEM images were obtained with a ZEISS Sigma 300 instrument. For sample preparation, 10 μL the solution of **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** (**TPE-MV⁸⁺**: 2-furaldehyde: Q[10]: POMs = 1:2:2:1, [**TPE-MV⁸⁺**] = 40 μM) was dropped onto a mica wafer and then dried at room temperature in air.

Transmission electron microscopy (TEM)

TEM images were performed on a JEOL JEM-F200 instrument with an accelerating voltage of 200 kV. The samples for TEM measurement were prepared by dropping 5 μL the solution of **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** (**TPE-MV⁸⁺**: 2-furaldehyde: Q[10]: POMs = 1:2:2:1, [**TPE-MV⁸⁺**] = 2 μM) onto copper grid coated with a carbon support film and then dried at room temperature in air.

The photocatalytic selective oxidation of toluene to benzaldehyde:

The aqueous solution of 4.0 mM toluene was added with 40 μM **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** and 40 mg NaCl. After purging with O_2 for 15 min, the solution was irradiated by white LED light source (10 W, 400-830 nm). The conversion and selectivity were determined by the integral of the ^1H NMR signals.

The generation of $\text{O}_2^{\cdot-}$ detected by dihydroethidium (HE):

When $\text{O}_2^{\cdot-}$ is generated in the system, the HE will be oxidized and emit strong fluorescence centered at 590 nm. The aqueous solutions of 50 μM HE with 1.0 μM **K-PTA**, **D-PTA**, **Q[10]-SOFs**, **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** were irradiated by white LED light source (10 W, 400-830 nm), respectively. The fluorescence change of the mixed solution at 590 nm were recorded by the fluorescence spectrometer.

The generation of H_2O_2 detected by I^- :

K-PTA@Q[10]-SOFs or **D-PTA@Q[10]-SOFs** (1 mg) was added into deionized water (2 mL), which irradiated by white LED light source (10 W, 400-830 nm) for 30 min. The transparent reaction solution was collected by centrifugation for the H_2O_2 detection.

1 mL of $\text{C}_8\text{H}_5\text{KO}_4$ aqueous solution (0.1 M) and 1 mL of KI aqueous solution (0.4 M) were added into the above transparent reaction liquid (1 mL), which was then kept for 30 min. In the presence of H^+ , the reaction between H_2O_2 with I^- occurs to generate triiodide anions (I_3^-), which shows a characteristic absorption peak at about 350 nm.

The generation of •OH detected by coumarin:

The aqueous solutions of 0.1 mM coumarin with 4 μ M **K-PTA**, **D-PTA**, **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** irradiated by white LED light source (10 W, 400-830 nm) for 10 min in O₂ atmosphere, respectively. After the reaction, the fluorescence emission of 7-hydroxycoumarin was measured at 460 nm under the excitation at 330 nm.

Photoelectrochemical measurements:

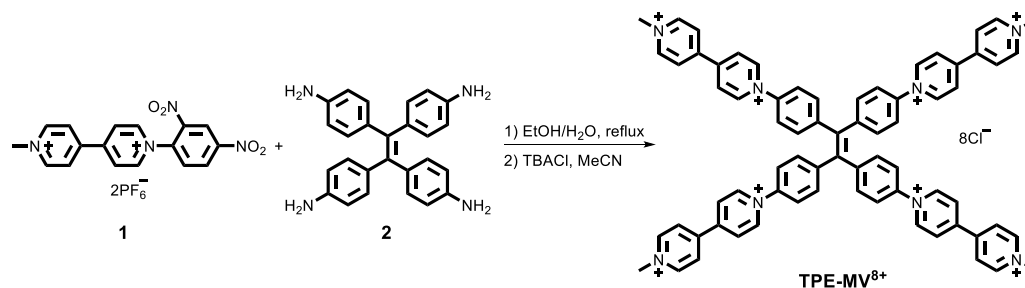
All electrochemical measurements (photocurrent, electrochemical impedance spectroscopy (EIS) and Mott Schottky) were made in 0.5 M sodium sulfate solution (pH=6.8) through the traditional three electrode system in the CHI 760E electrochemical workstation. The working electrode is ITO glass plate coated with catalyst slurry, the counter electrode is platinum foil, and saturated Ag/AgCl as reference electrode. The photocurrent was detected by using the visible-light ($\lambda > 400$ nm, 300 W Xe lamp) on-off process with a pulse of 30 s on-off cycle at potential of 0.5 V versus Ag/AgCl electrode. Electrochemical impedance spectra (EIS) measurements were carried out in the range of 1000 KHz \sim 0.1 Hz. Mott Schottky plots were measured at alternating current (AC) frequencies of 1500 Hz, 2000 Hz and 2500 Hz.

Preparation of working electrode: 2 mg catalyst, 1 mL ethanol and 10 μ L Nafion D-520 were mixed and ultrasound for 30 min. Then, 200 μ L of slurry was deposited evenly on the ITO glass plate (1 \times 1 cm²) and left in the air to dry.

Detection of •OH and •Cl:

A solution containing N-tert-butyl- α -phenylnitron (PBN) as •Cl radicals spin trapping agent was used to directly observe the generation of •OH and •Cl.

Synthesis of TPE-MV⁸⁺ guest:



A mixture of 1 (314.2 mg, 0.5 mmol) and 2 (39.2 mg, 0.1 mmol) in EtOH (10 mL) and H₂O (10 mL), the solution was refluxed for 96 h. The reaction mixture was cooled to room temperature, the precipitate was filtered, washed with acetone, EtOH, dichloromethane and dried in vacuo to obtain an orange solid (70 mg, 32%). Then, the solid (70 mg, 0.032 mmol) was dissolved in 10.0 mL absolute MeCN, and tetrabutylammonium chloride (TBACl) (177.8 mg, 0.64 mmol) was added to the solution and stirred at room temperature for 12 h, the obtained solid was filtered and washed with MeCN to afford TPE-MV⁸⁺ (37.4 mg, 90%). ¹H NMR (500 MHz, D₂O), δ = 9.31 (d, J = 6.5 Hz, 8H), 9.03 (d, J = 6.5 Hz, 8H), 8.66 (d, J = 6.5 Hz, 8H), 8.54 (d, J = 6.5 Hz, 8H), 7.70 (d, J = 8.5 Hz, 8H), 7.62 (d, J = 8.5 Hz, 8H), 4.45 (s, 12H). ¹³C NMR (126 MHz, D₂O), δ = 150.9, 149.5, 146.4, 145.4, 145.2, 141.3, 140.9, 133.5, 127.0, 126.8, 124.2, 48.4.

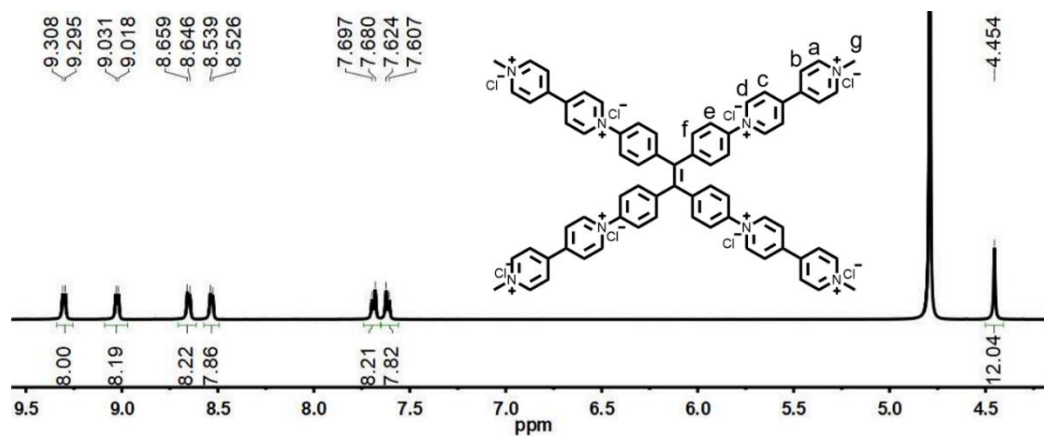


Figure S1. ¹H NMR spectra of TPE-MV⁸⁺ in D₂O.

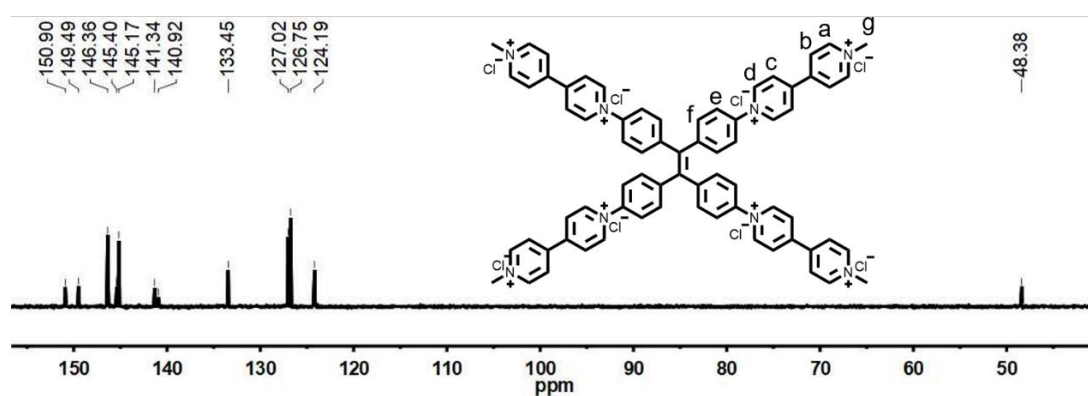


Figure S2. ¹³C NMR spectra of TPE-MV⁸⁺ in D₂O.

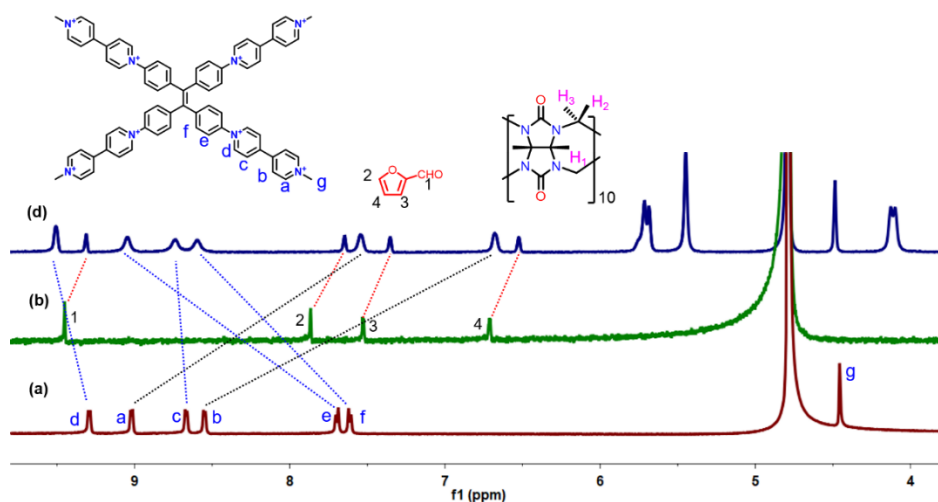


Figure S3. ¹H NMR spectra obtained for (a) TPE-MV⁸⁺, (b) 2-furaldehyde and (c) Q[10]-SOFs in D₂O.

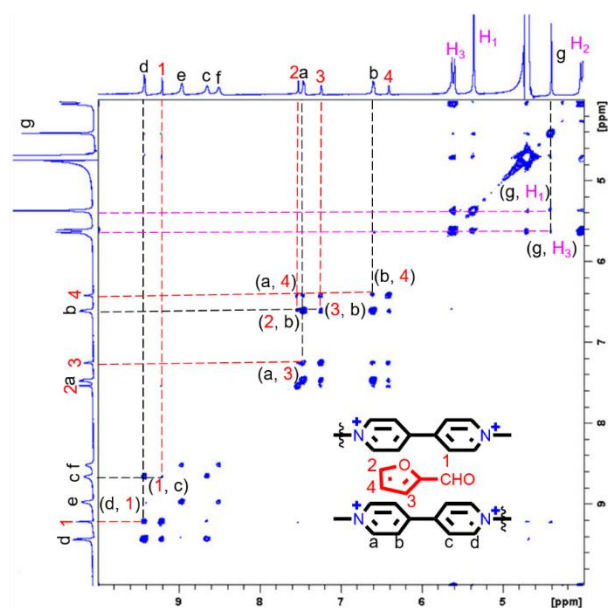


Figure S4. COSY ^1H NMR spectrum (500 MHz, D_2O , 298 K) recorded for Q[10]-SOFs.

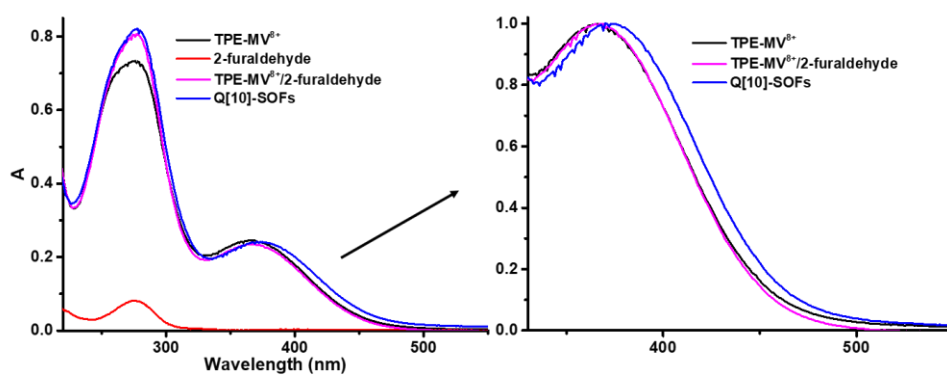


Figure S5. UV-vis absorption spectra obtained for TPE-MV $^{8+}$, 2-furaldehyde and Q[10]-SOFs in water (each of 10.0 μM).

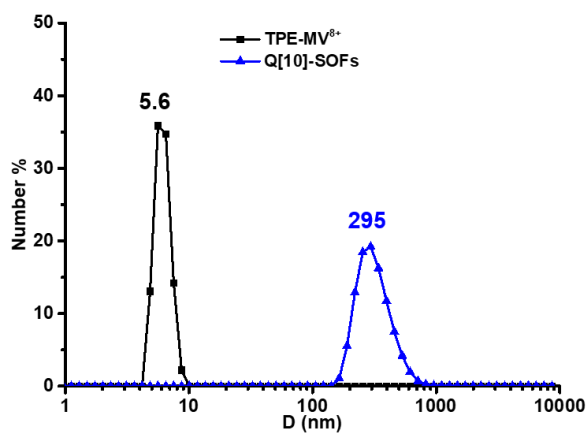


Figure S6. DLS data of TPE-MV $^{8+}$ and Q[10]-SOFs (TPE-MV $^{8+}$ = 0.04 mM).

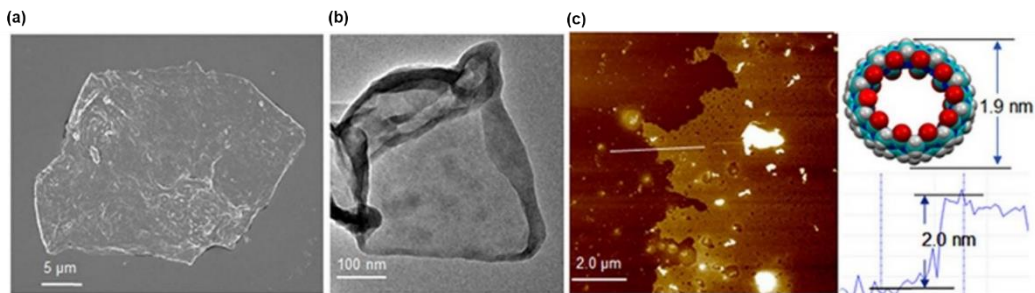


Figure S7. (a) SEM, (b) TEM and (c) AFM images of the Q[10]-SOFs upon slowly evaporating the aqueous solution.

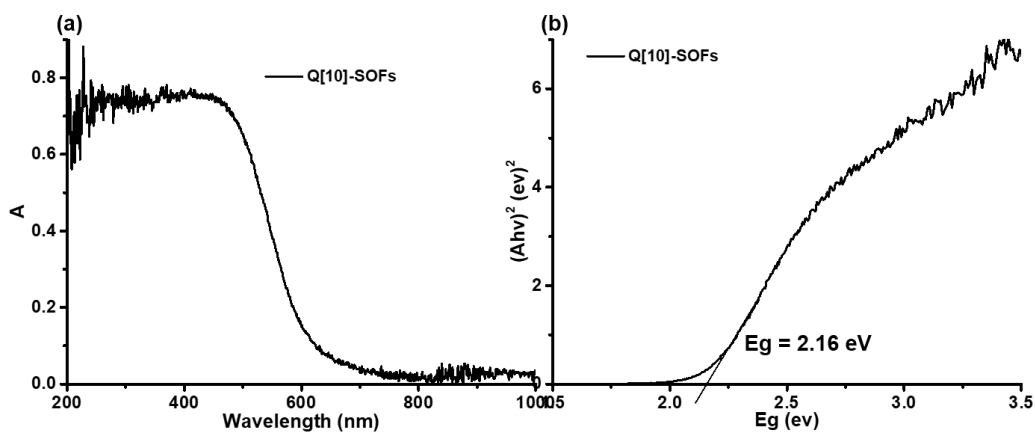


Figure S8. (a) UV-DRS spectra and (b) Tauc plots of Q[10]-SOFs.

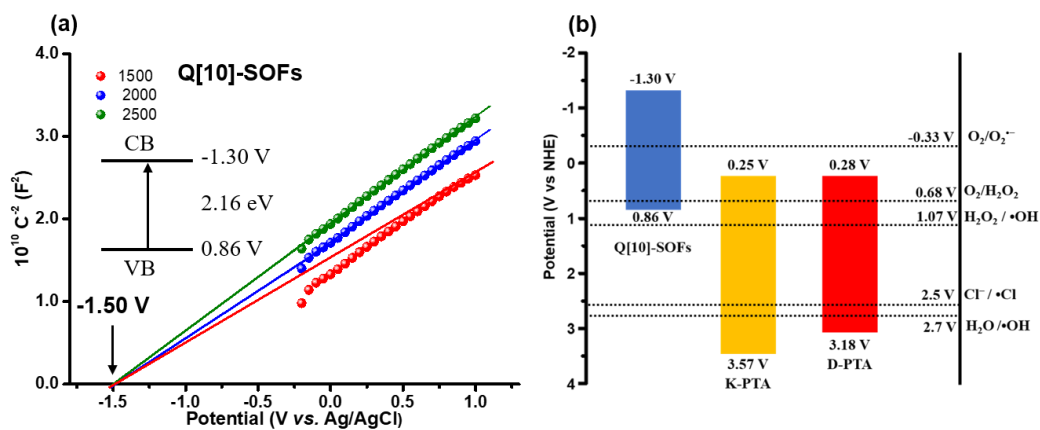


Figure S9. (a) Mott-Schottky plots of Q[10]-SOFs, (b) band structure diagram of Q[10]-SOFs, K-PTA and D-PTA.

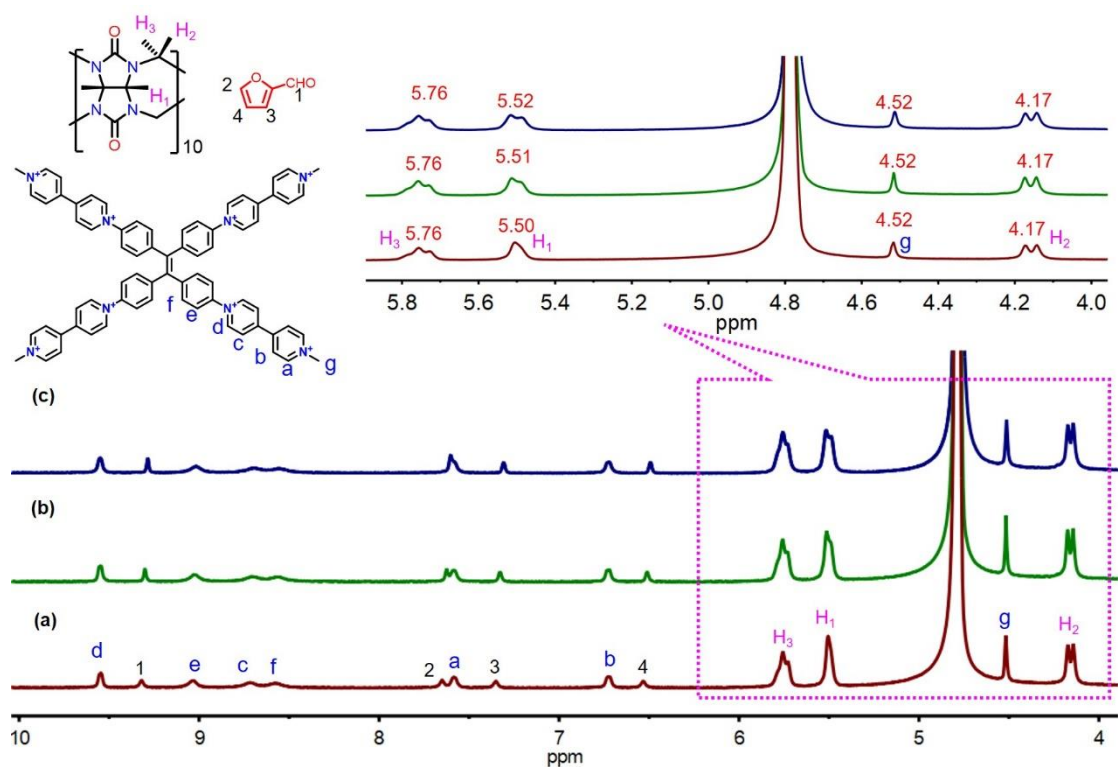


Figure S10. ^1H NMR spectra obtained for (a) Q[10]-SOFs, Q[10]-SOFs in the presence of (b) 0.5 eq., (c) 1.0 eq. **K-PTA**.

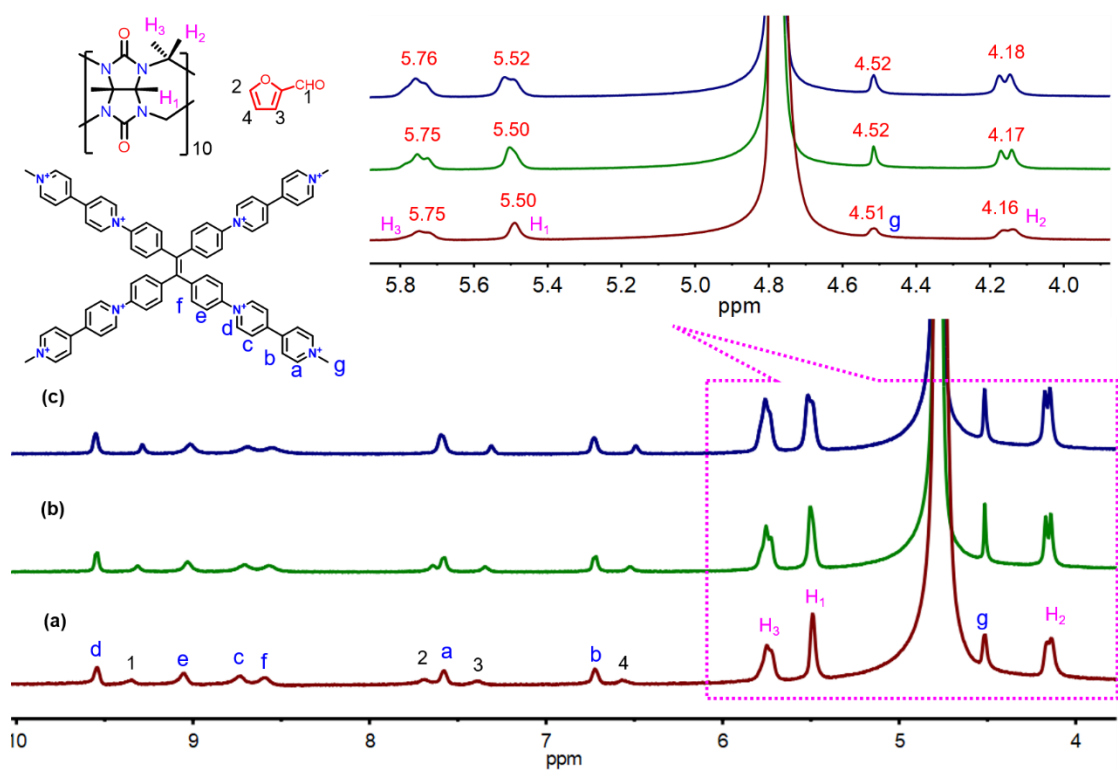


Figure S11. ^1H NMR spectra obtained for (a) Q[10]-SOFs, Q[10]-SOFs in the presence of (b) 0.5 eq., (c) 1.0 eq. **D-PTA**.

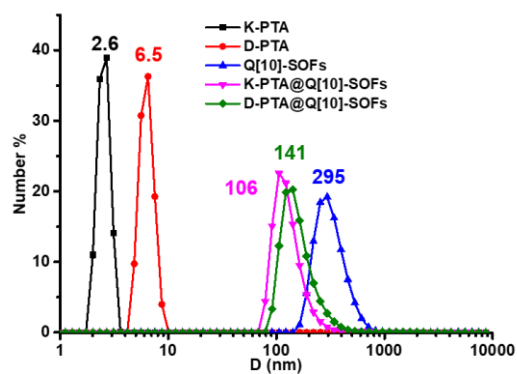


Figure S12. DLS data of K-PTA, D-PTA, Q[10]-SOFs, K-PTA@Q[10]-SOFs and D-PTA@Q[10]-SOFs (TPE-MV⁸⁺ = 0.04 mM).

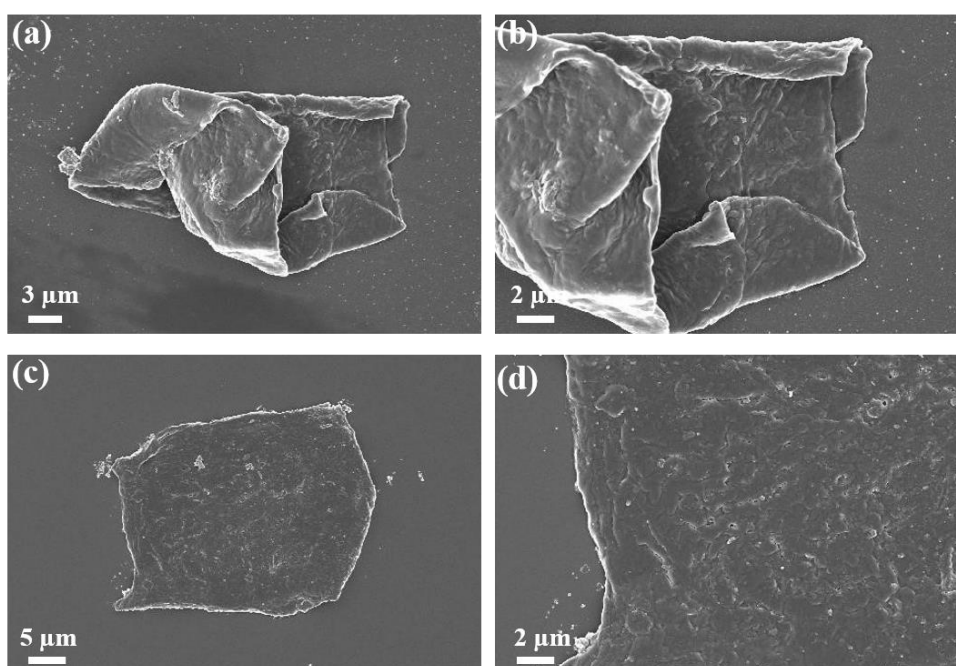


Figure S13. SEM images of the samples from (a, b) K-PTA@Q[10]-SOFs; (c, d) D-PTA@Q[10]-SOFs.

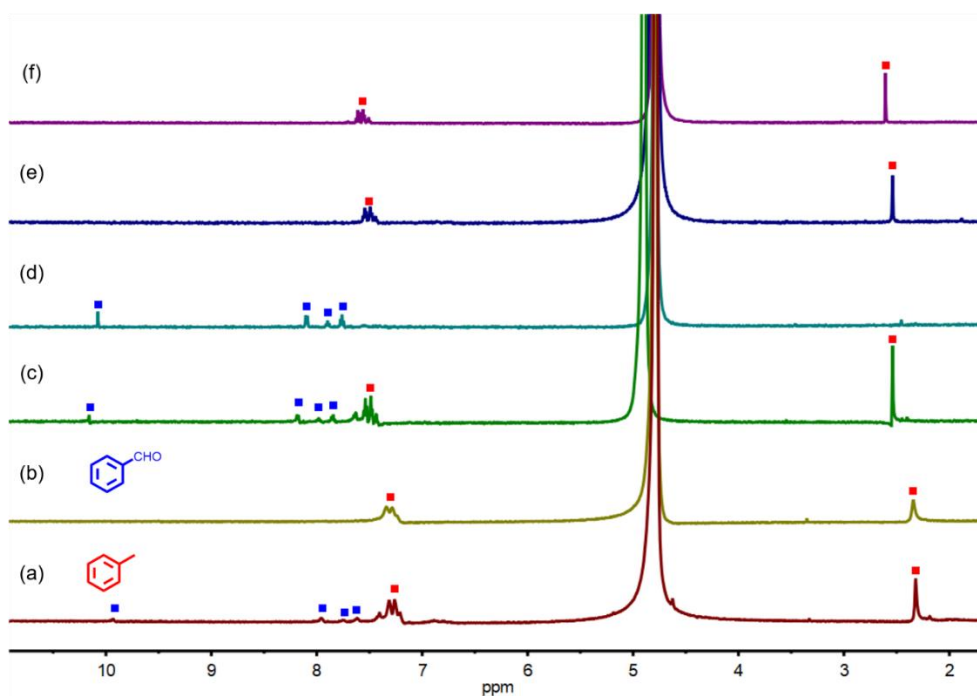


Figure S14. The ^1H NMR spectra of toluene after oxidation catalyzed by (a) **D-PTA@Q[10]-SOFs** in O_2 atmosphere; (b) **D-PTA@Q[10]-SOFs** in Ar atmosphere; (c) **D-PTA@Q[10]-SOFs+NaCl** in Ar atmosphere; (d) **D-PTA@Q[10]-SOFs+NaCl** in O_2 atmosphere; (e) **D-PTA+NaCl** in O_2 atmosphere (f) **Q[10]-SOFs+NaCl** in O_2 atmosphere.

Table S1. Substrate Scope on **K-PTA@Q[10]-SOFs** and **D-PTA@Q[10]-SOFs** under white LED light source (10 W, 400-830 nm) irradiation.

Entry	Catalyst	Substrate	Time (h)	Conversion (%)	Selectivity (%)
1	K-PTA@Q[10]-SOFs	toluene	1 or 2	40 or 98	96 or 99
2	K-PTA@Q[10]-SOFs	<i>o</i> -xylene	2	92	84
3	K-PTA@Q[10]-SOFs	<i>m</i> -xylene	2	98	99
4	K-PTA@Q[10]-SOFs	<i>p</i> -xylene	2	99	99
5	D-PTA@Q[10]-SOFs	toluene	1	98	99
6	D-PTA@Q[10]-SOFs	<i>o</i> -xylene	1	99	99
7	D-PTA@Q[10]-SOFs	<i>m</i> -xylene	1	97	99
8	D-PTA@Q[10]-SOFs	<i>p</i> -xylene	1	99	99

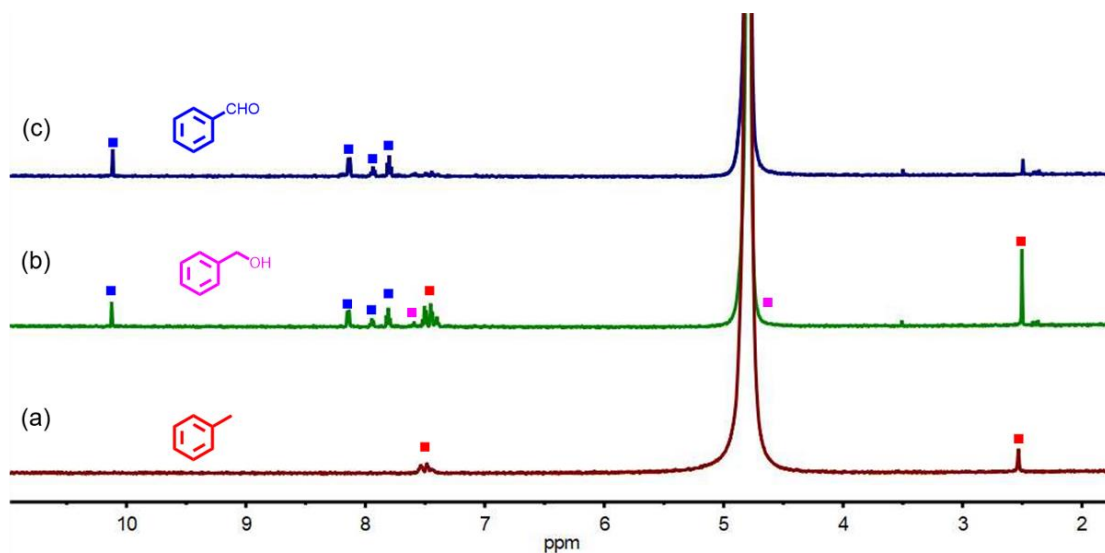


Figure S15. (a) The ^1H NMR spectra of toluene in the presence of $\text{K-PTA@Q[10]-SOFs+NaCl}$ (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h; (c) 2 h in D_2O .

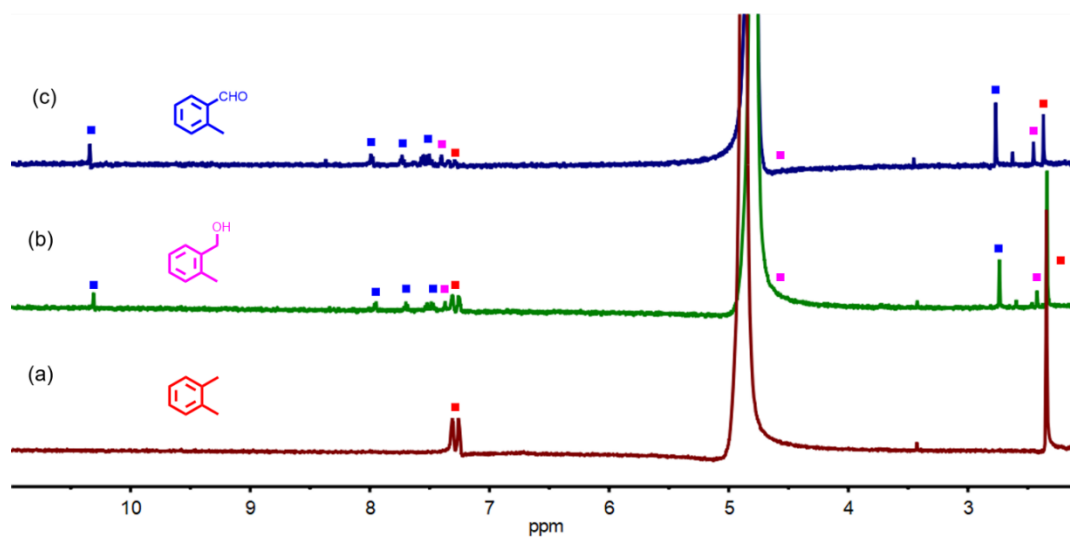


Figure S16. (a) The ^1H NMR spectra of *o*-xylene in the presence of $\text{K-PTA@Q[10]-SOFs+NaCl}$ (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h; (c) 2 h in D_2O .

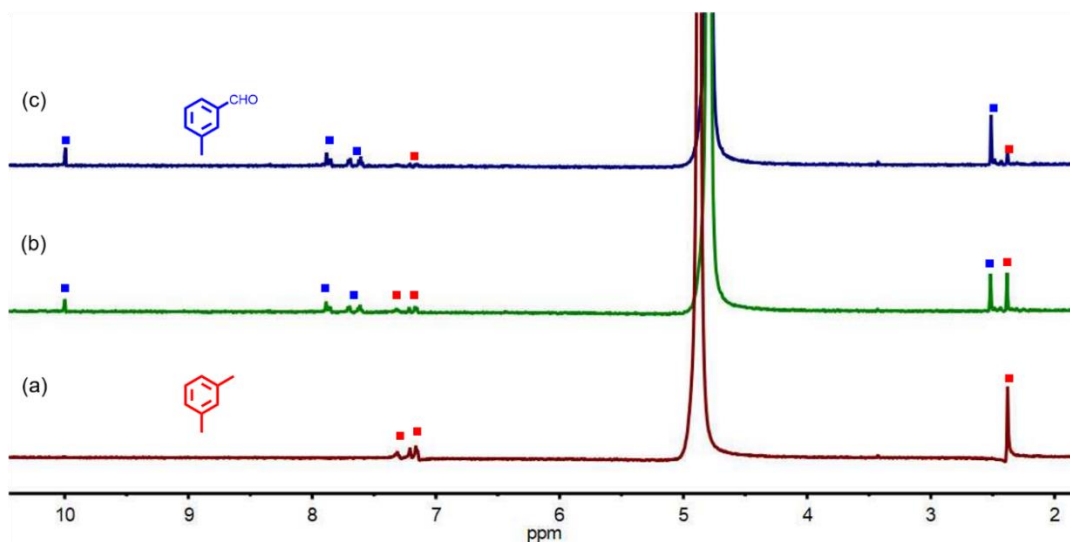


Figure S17. The ^1H NMR spectra of *m*-xylene in the presence of K-PTA@Q[10]-SOFs+NaCl (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h; (c) 2 h in D_2O .

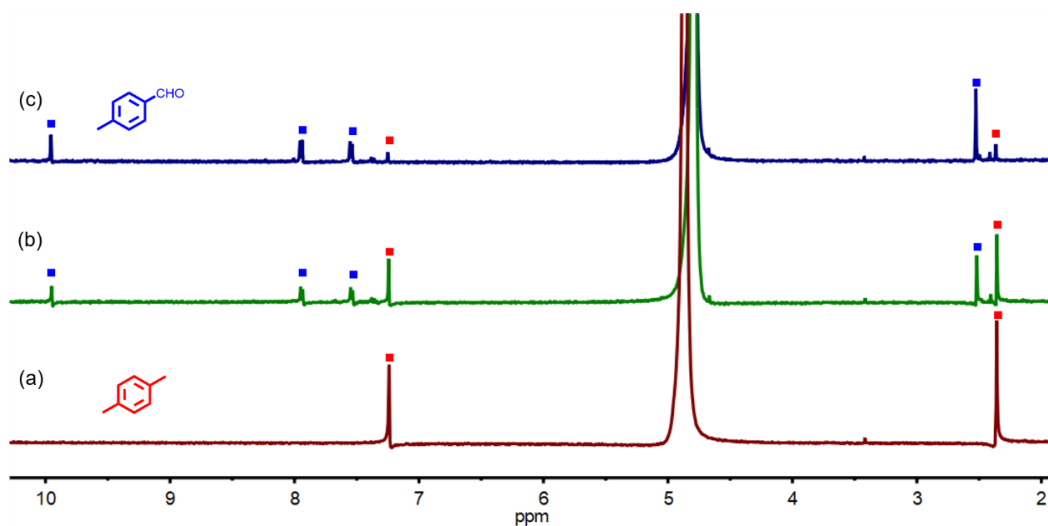


Figure S18. The ^1H NMR spectra of *p*-xylene in the presence of K-PTA@Q[10]-SOFs+NaCl (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h; (c) 2 h in D_2O .

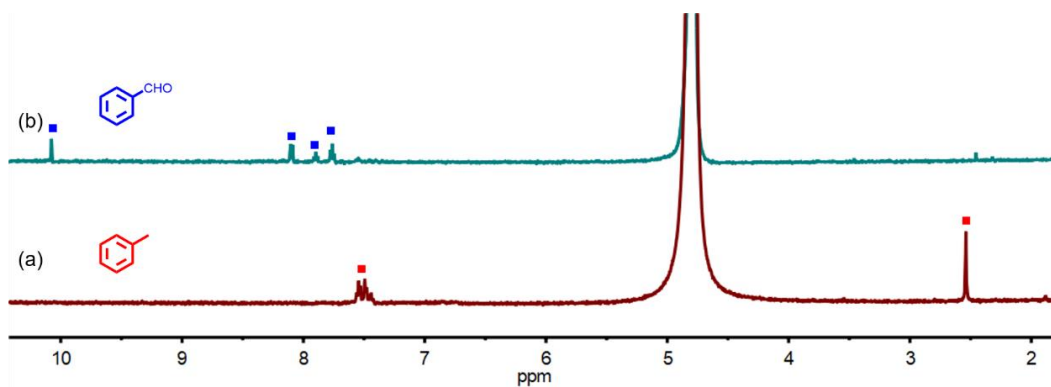


Figure S19. (a) The ^1H NMR spectra of toluene in the presence of D-PTA@Q[10]-SOFs+NaCl (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h in D_2O .

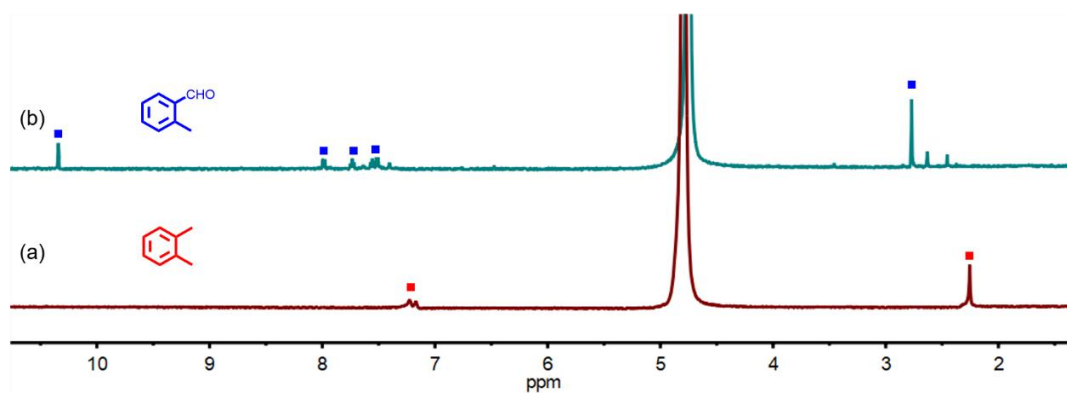


Figure S20. (a) The ^1H NMR spectra of *o*-xylene in the presence of **D-PTA@Q[10]-SOFs**+NaCl (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h in D_2O .

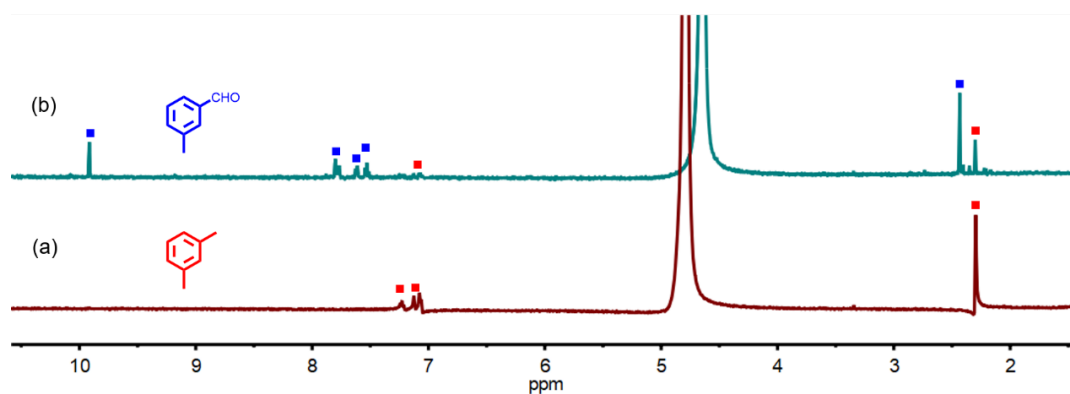


Figure S21. The ^1H NMR spectra of *m*-xylene in the presence of **D-PTA@Q[10]-SOFs**+NaCl (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h in D_2O .

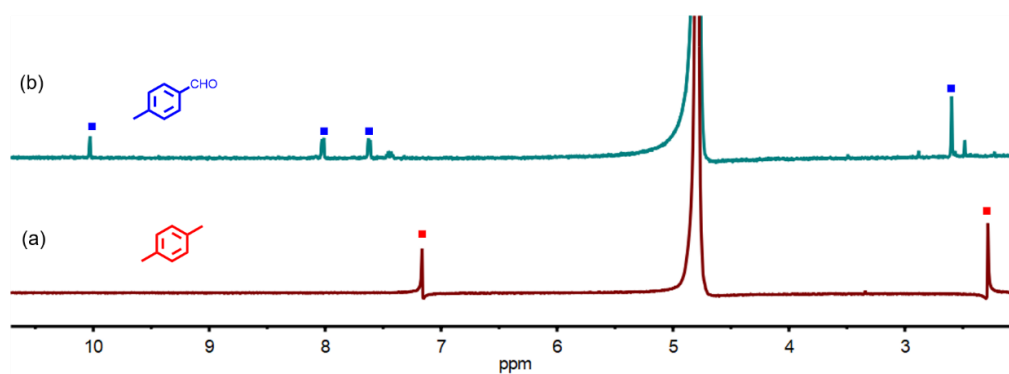


Figure S22. The ^1H NMR spectra of *p*-xylene in the presence of **D-PTA@Q[10]-SOFs**+NaCl (40 mg) after irradiation of white LED light source (400-830 nm) for (a) 0 h; (b) 1 h in D_2O .

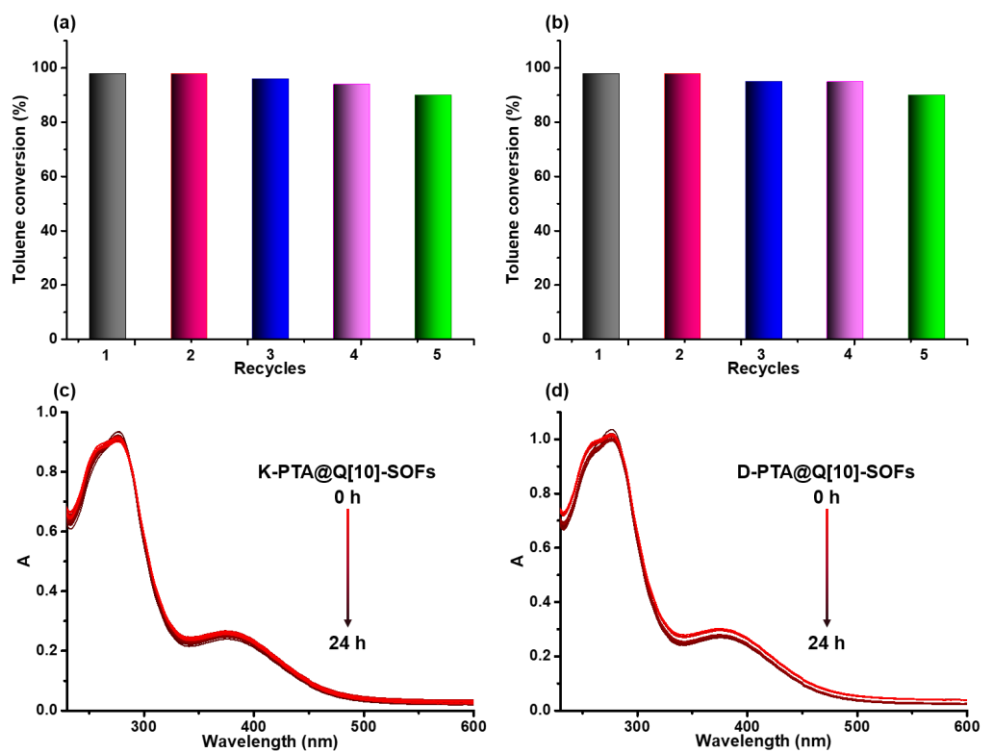


Figure S23. (a) White LED light source (10 W, 400-830 nm) activities for selective oxidation of toluene of recycle test of (a) **K-PTA@Q[10]-SOFs** (2 h), (b) **D-PTA@Q[10]-SOFs** (1 h) for four runs; UV-vis absorption spectra of (c) **K-PTA@Q[10]-SOFs** and (d) **D-PTA@Q[10]-SOFs** under white LED light source during the selective oxidation of toluene within 24 h.

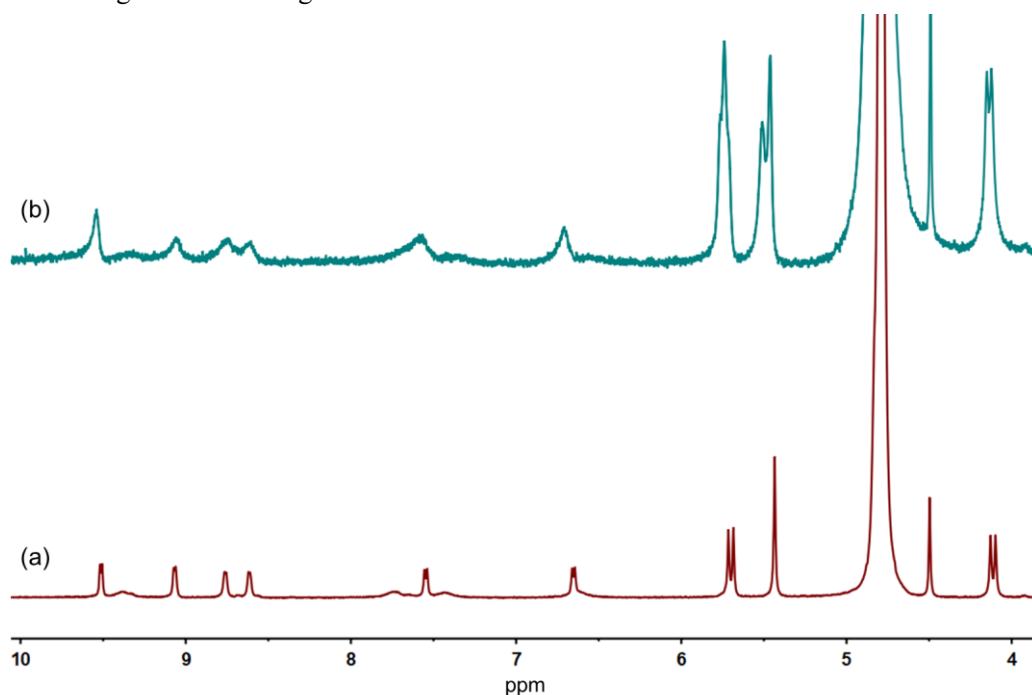


Figure S24. The ¹H NMR spectra of (a) **K-PTA@Q[10]-SOFs**, (b) **K-PTA@Q[10]-SOFs** after the photocatalytic reaction in D₂O.

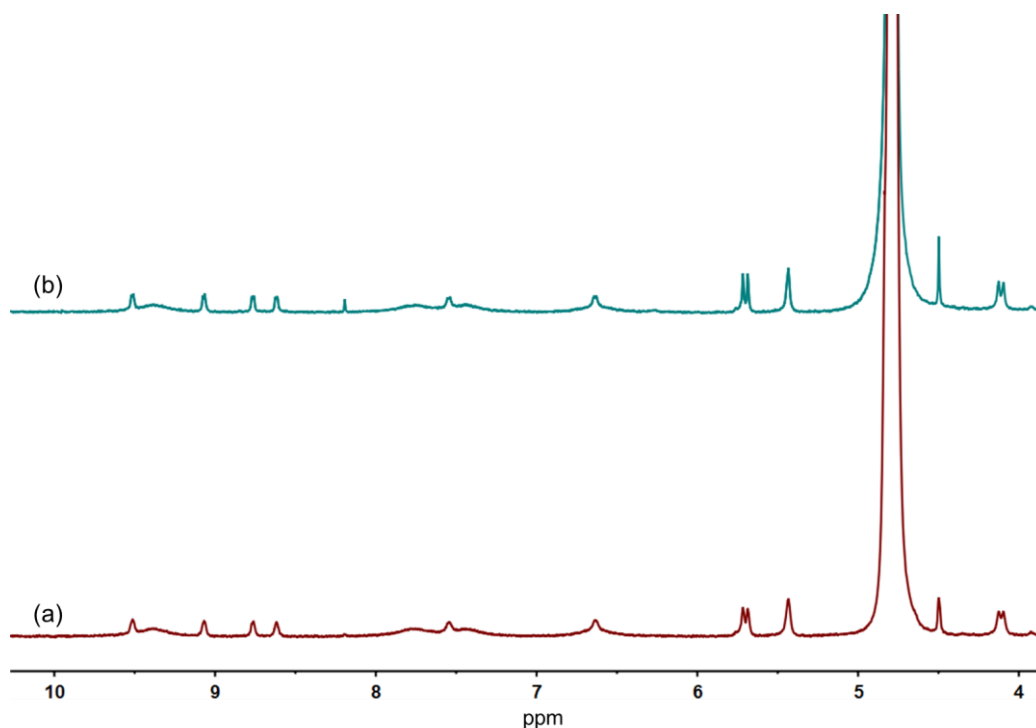


Figure S25. The ^1H NMR spectra of (a) **D-PTA@Q[10]-SOFs**, (b) **D-PTA@Q[10]-SOFs** after the photocatalytic reaction in D_2O .

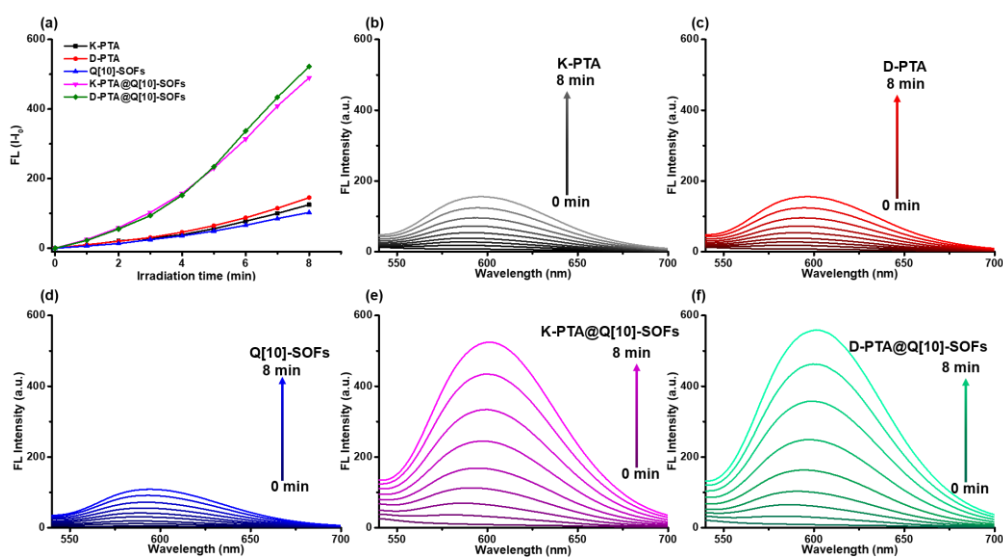


Figure S26. (a) Degradation rates of HE using **K-PTA**, **D-PTA**, **Q[10]-SOFs**, **K-PTA@Q[10]-SOFs** and **D-PTA@Q[10]-SOFs**, I_0 and I are the intensity of HE in the presence of the different species before and after irradiation with white light, respectively. The fluorescence spectra of HE solution with (b) **K-PTA**, (c) **D-PTA** (d) **Q[10]-SOFs**; (e) **K-PTA@Q[10]-SOFs** and (f) **D-PTA@Q[10]-SOFs** upon light irradiation at white LED light source (10 W, 400-830 nm).

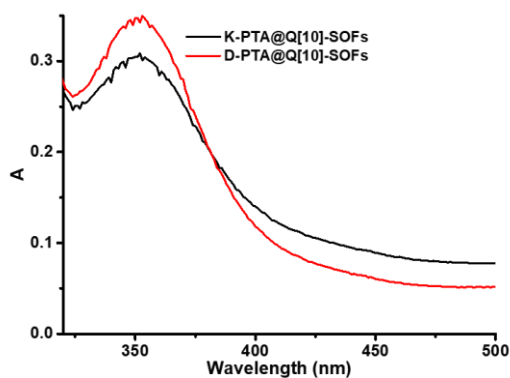


Figure S27. UV-vis absorption spectra of I_3^- in the presence of the **K-PTA@Q[10]-SOFs** and **D-PTA@Q[10]-SOFs** after photoirradiation.

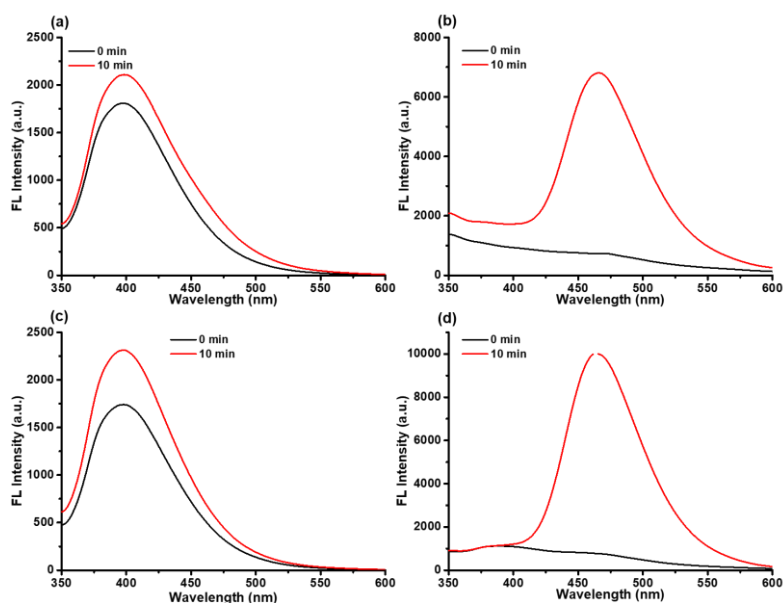


Figure S28. The detection of 7-hydroxycoumarin fluorescence peak (460 nm) with (a) **K-PTA**, (b) **K-PTA@Q[10]-SOFs**, (c) **D-PTA** and (d) **D-PTA@Q[10]-SOFs** in O_2 atmosphere upon light irradiation at white LED light source (400-830 nm).

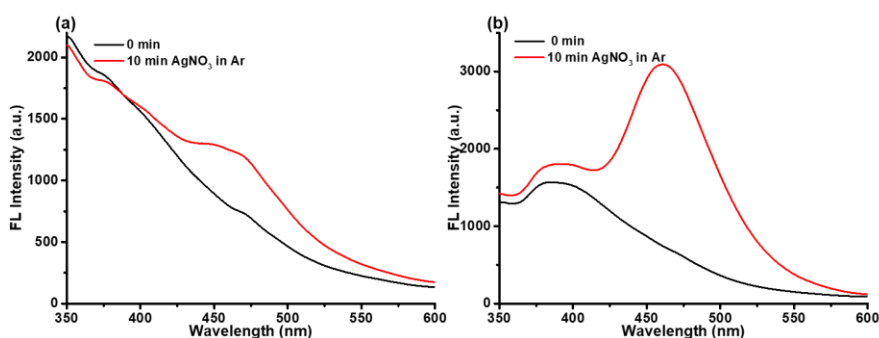


Figure S29. The detection of 7-hydroxycoumarin fluorescence peak (452 nm) intensity (a) **K-PTA@Q[10]-SOFs** and (b) **D-PTA@Q[10]-SOFs** with $AgNO_3$ as sacrificial oxidant under Ar (please see ref. *Angew. Chem. Int. Ed.* 2023, e202304699). The increased fluorescence intensity indicated $\bullet OH$ can be generated by the oxidation of water.

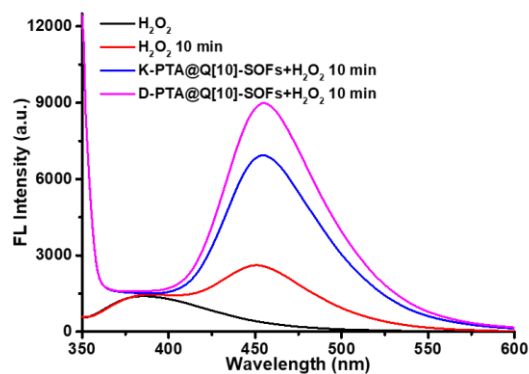


Figure S30. The detection of 7-hydroxycoumarin fluorescence peak (452 nm) intensity in existence of **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** containing 5 mM H_2O_2 under Ar.

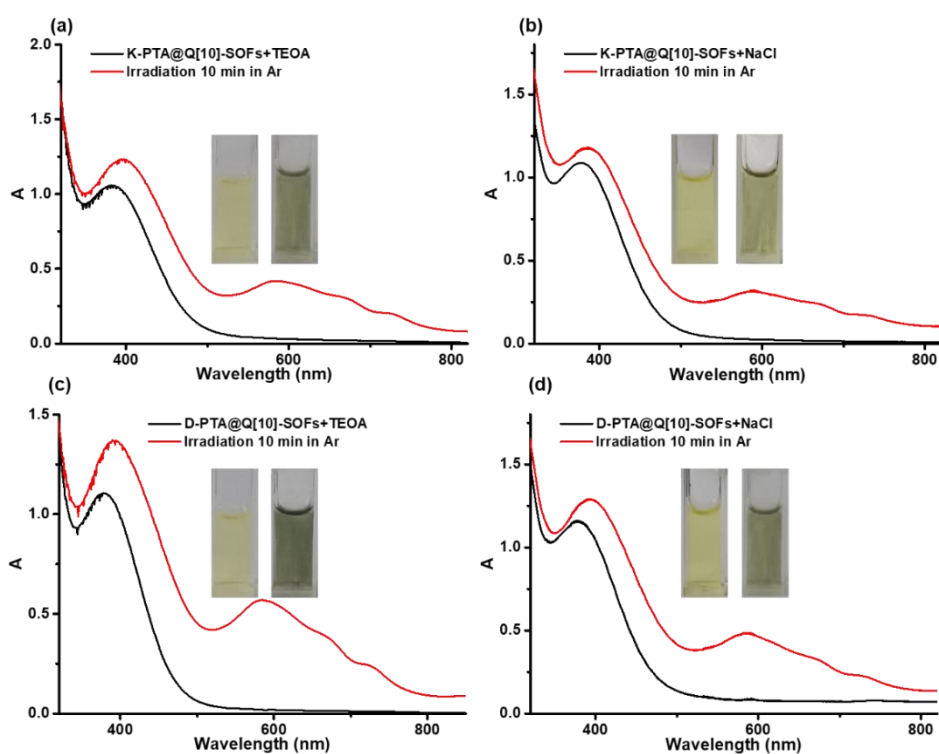


Figure S31. UV-vis absorption spectra (a) **K-PTA@Q[10]-SOFs+TEOA**; (b) **K-PTA@Q[10]-SOFs+NaCl**; (c) **D-PTA@Q[10]-SOFs+TEOA** and (d) **D-PTA@Q[10]-SOFs+NaCl** under white light with increasing irradiation times in Ar in water.

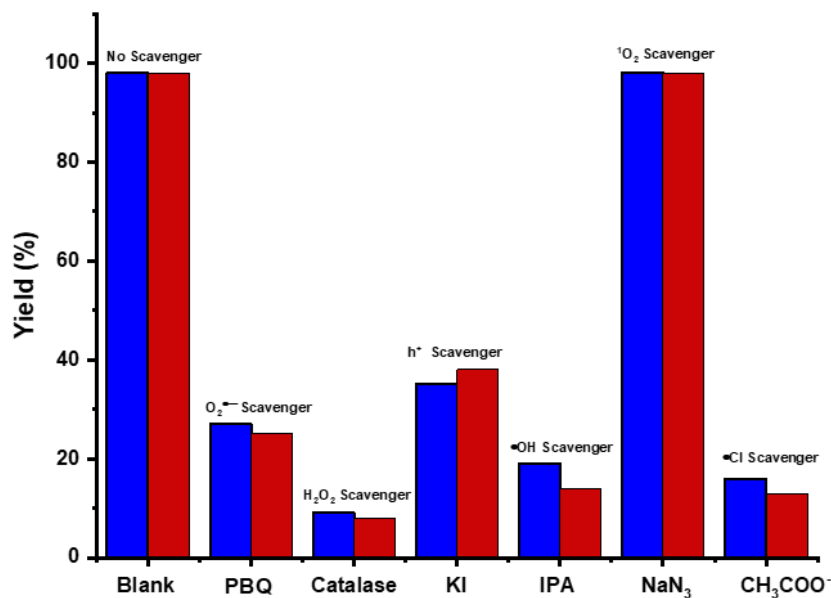


Figure S32. Under white LED light source (400-830 nm) irradiation, the conversion of toluene after adding different scavengers in the presence of **K-PTA@Q[10]-SOFs** (red) and **D-PTA@Q[10]-SOFs** (Blue).

X-ray photoelectron spectroscopy (XPS) spectra under light irradiation

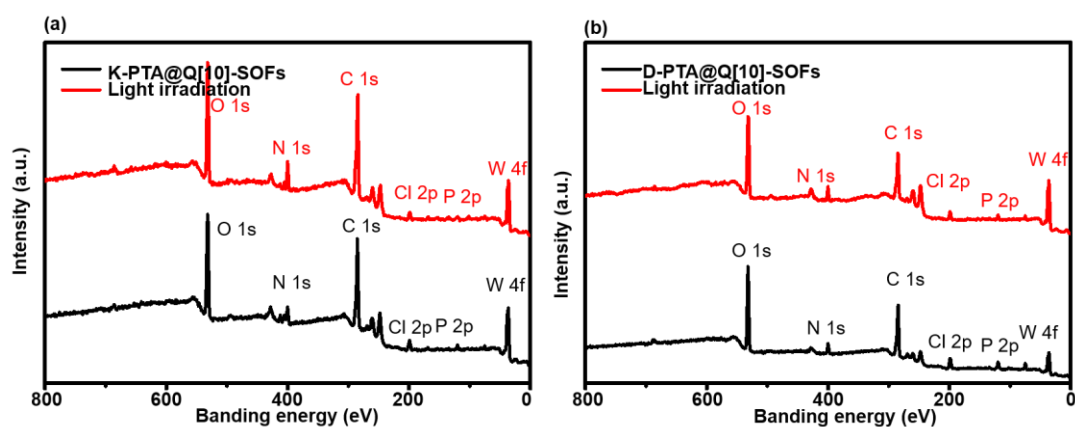


Figure S33. The full-scan X-ray photoelectron spectroscopy (XPS) spectra of C 1s, N 1s, W 4f, Cl 2p, P 2p and O 1s of **K-PTA@Q[10]SOFs** and **D-PTA@Q[10]-SOFs** before and after light irradiation.

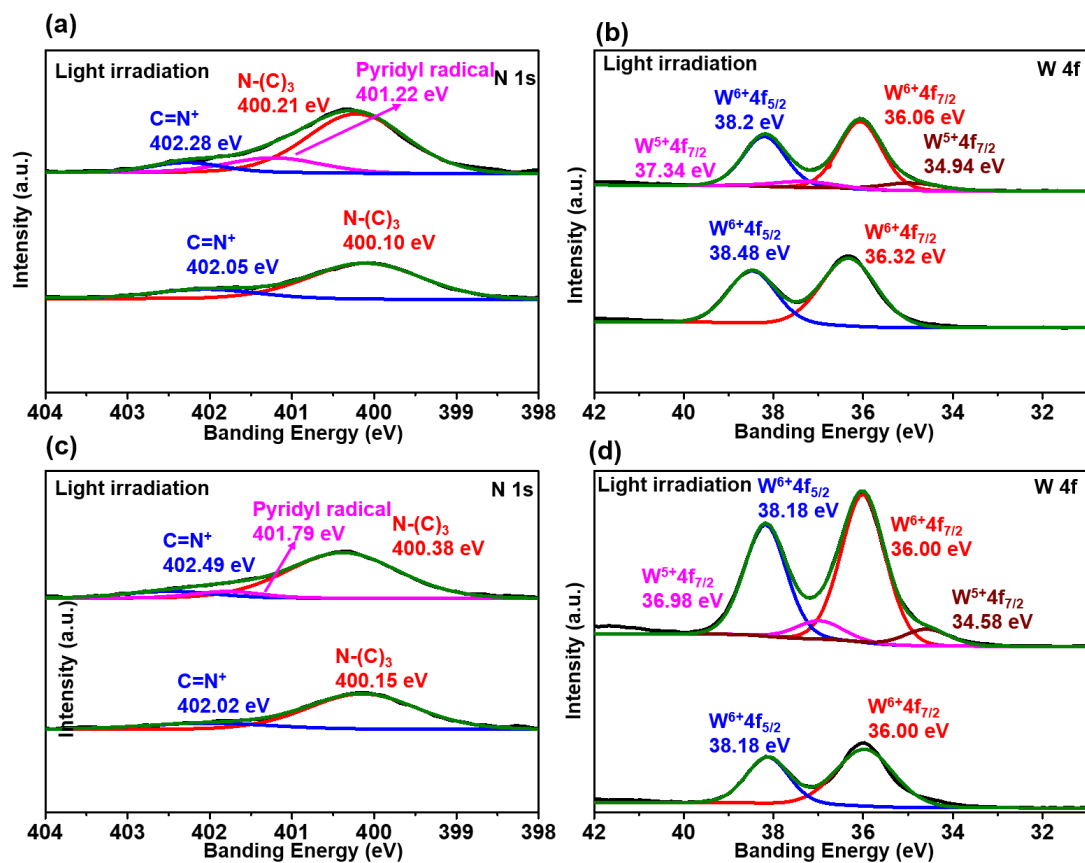


Figure S34. XPS spectra corresponding to (a) N 1s, (b) W 4f in the **K-PTA@Q[10]-SOFs**, (c) N 1s, (d) W 4f in the **D-PTA@Q[10]-SOFs** before and after irradiation with white LED light source.

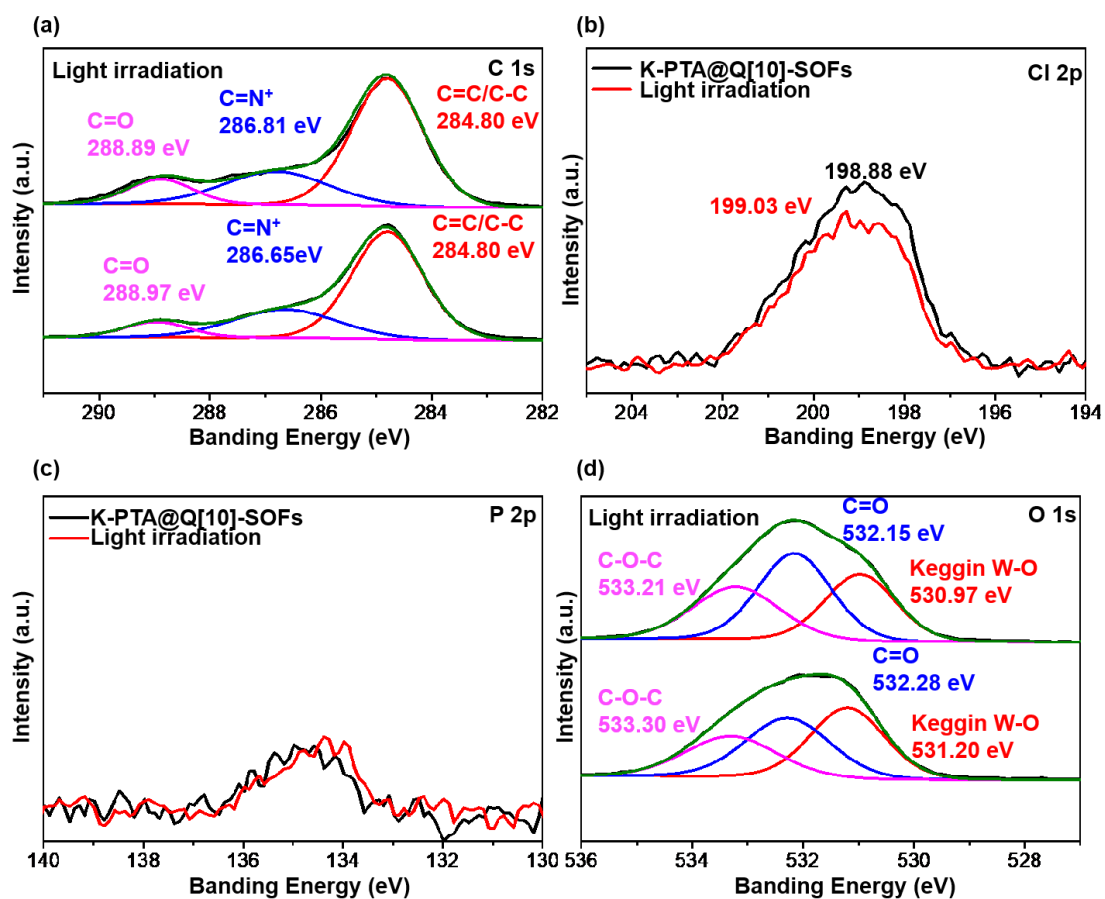


Figure S35. The high resolution XPS spectra of (a) C 1s, (b) Cl 2p, (c) P 2p and O 1s of K-PTA@Q[10]SOFs before and after light irradiation.

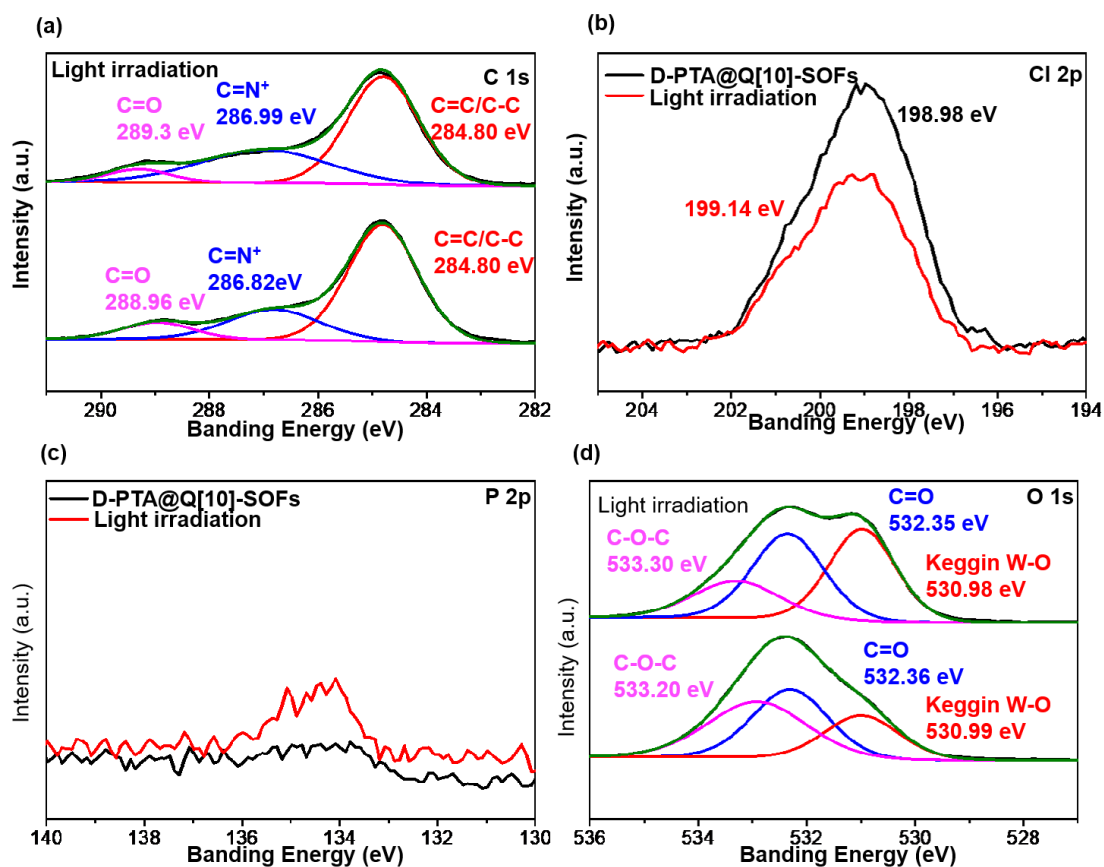


Figure S36. The high resolution XPS spectra of (a) C 1s, (b) Cl 2p, (c) P 2p and O 1s of D-PTA@Q[10]SOFs before and after light irradiation.

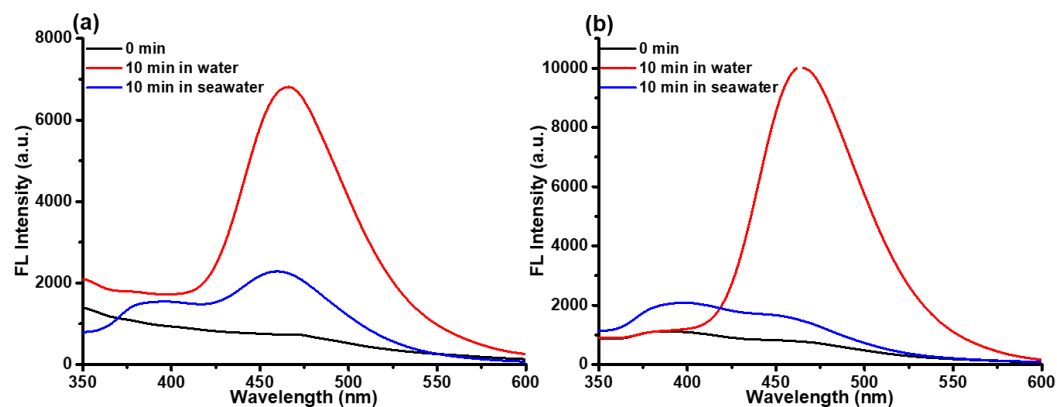


Figure S37. The detection of 7-hydroxycoumarin fluorescence peak (460 nm) intensity (a) K-PTA@Q[10]SOFs, (b) D-PTA@Q[10]SOFs in seawater.

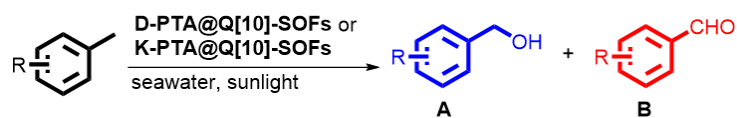


Table S2. Substrate Scope on **K-PTA@Q[10]-SOFs** or **D-PTA@Q[10]-SOFs** under sunlight after 1 h in seawater.

Entry	Catalyst	R	Conversion (%)	Selectivity (A/B)(%)
1	K-PTA@Q[10]-SOFs	H	85	36/64
2	K-PTA@Q[10]-SOFs	<i>o</i> -CH ₃	81	22/78
3	K-PTA@Q[10]-SOFs	<i>m</i> -CH ₃	76	17/83
4	K-PTA@Q[10]-SOFs	<i>p</i> -CH ₃	69	2/98
5	D-PTA@Q[10]-SOFs	H	98	99
6	D-PTA@Q[10]-SOFs	<i>o</i> -CH ₃	99	99
7	D-PTA@Q[10]-SOFs	<i>m</i> -CH ₃	99	99
8	D-PTA@Q[10]-SOFs	<i>p</i> -CH ₃	99	99

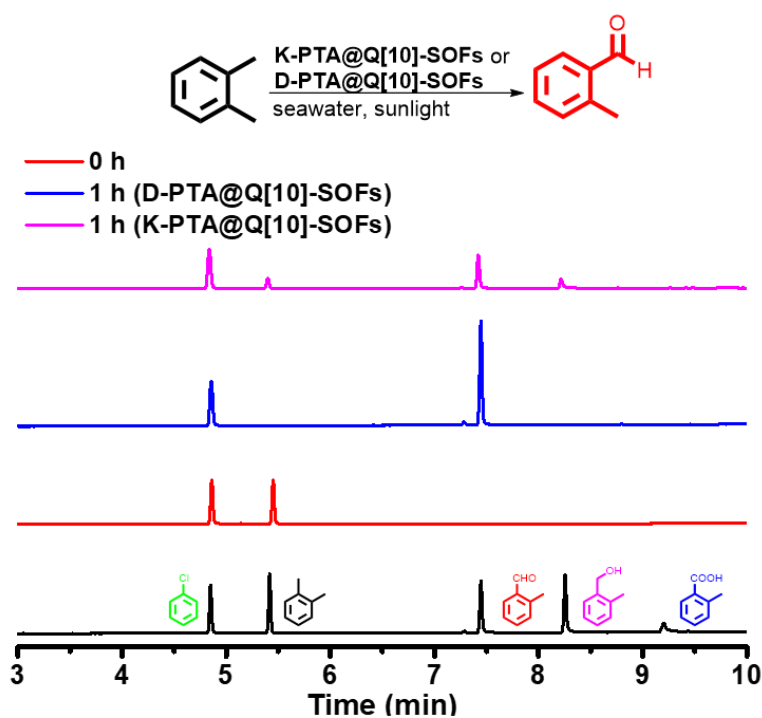


Figure S38. The GC chromatogram of *o*-xylene in the presence of **D-PTA@Q[10]-SOFs** or **K-PTA@Q[10]-SOFs** after irradiation of sunlight for 1 h in seawater. Determined by GC using a standard curve with chlorobenzene internal reference.

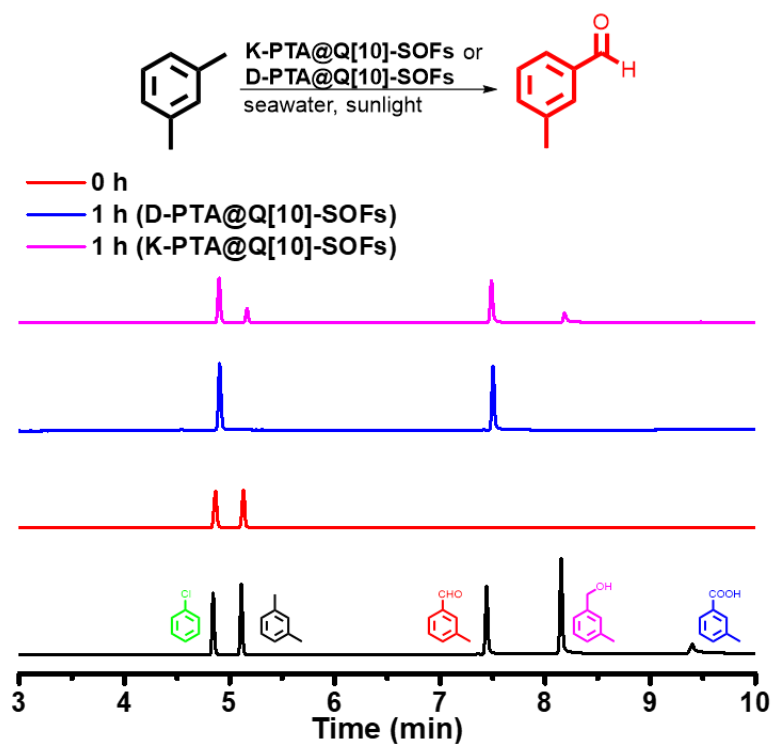


Figure S39. The GC chromatogram of *m*-xylene in the presence of D-PTA@Q[10]-SOFs or K-PTA@Q[10]-SOFs after irradiation of sunlight for 1 h in seawater. Determined by GC using a standard curve with chlorobenzene internal reference.

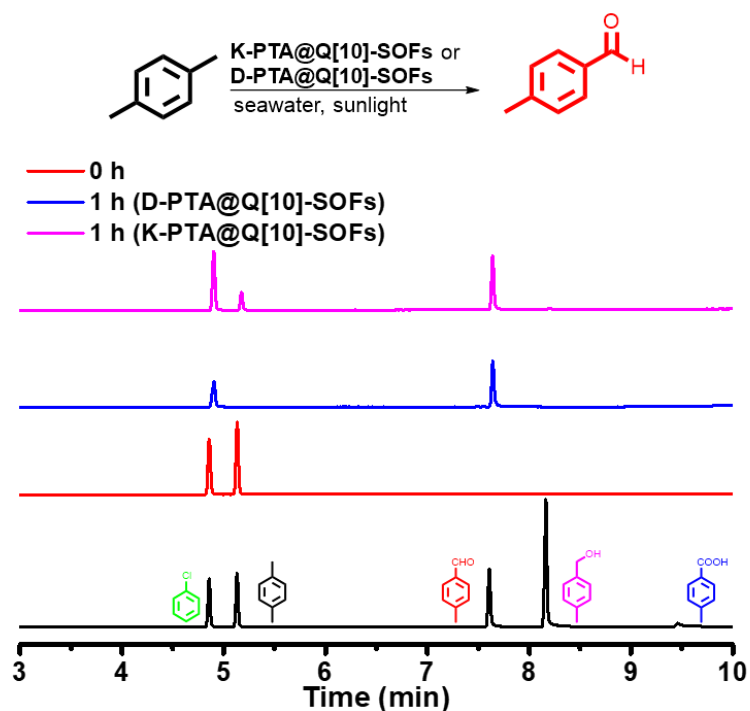


Figure S40. The GC chromatogram of *p*-xylene in the presence of D-PTA@Q[10]-SOFs or K-PTA@Q[10]-SOFs after irradiation of sunlight for 1 h in seawater. Determined by GC using a standard curve with chlorobenzene internal reference.