Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Conjugated microporous polymers as visible light driven platform for photo-redox conversion of biomass derived chemicals

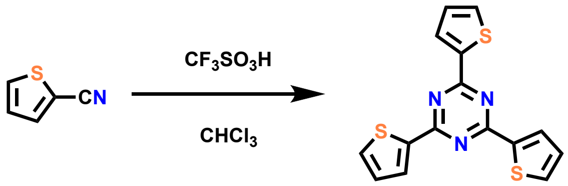
Bo Chen, Lang Chen, Zijun Yan, Jinyang Kang, Shanyong Chen, Yongdong Jin, Lijian Ma, Hongjian Yan,* Chuanqin Xia*

College of Chemistry, Sichuan University, Chengdu 610064, P.R. China.

*Corresponding author: hjyan@scu.edu.cn; xiachqin@163.com

Experimental section

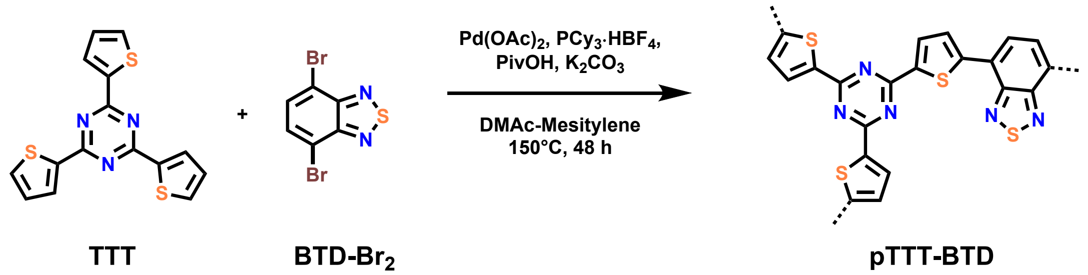
Synthesis of the TTT monomer



2,4,6-(tri-2-thienyl)-1,3,5-triazine (TTT) was synthesized as colorless needle-like crystals with an 81% yield according to literature procedure with an additional purification procedure.[1]

Thiophene-2-carbonitrile (8.0 g, 73.2 mmol) was dissolved in 100 mL $CHCl_3$ and cooled to 0°C by an ice-water bath. Then CF_3SO_3H (19.5 g, 130.0 mmol) was added drop wise to the reaction mixture under nitrogen atmosphere. The ice-water bath was removed and the resulting mixture was stirred at room temperature for 24 h. After neutralized by concentrated $NaHCO_3$ solution, the organic layer was then washed with water and saturated NaCl solution. The organic layer was separated and dried over anhydrous Na_2SO_4. After evaporation of solvent, the crude product was obtained as a light green solid. To get pure product, column chromatography (petroleum ether – dichloromethane, 5:1) and recrystallization (hexane - trichloromethane) were conducted. The final product was colorless needle crystals (6.5 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, 3H), 7.62 (d, 3H), 7.21 (t, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): 167.76, 141.47, 132.35, 131.72, 128.45 ppm. ESI-MS: C15H9N3S3, m/z (cal.) = 328.0031 ($[M+H]^+$), m/z (exp.) = 328.0037 ($[M+H]^+$).

Synthesis procedure of TTT-based CMPs



In a Schlenk tube, DMAc/Mesitylene (1 mL/3 mL) was added to a mixture of TTT (0.60 mmol, 196.5 mg), BTD-Br_2 (0.90 mmol, 264.6 mg), $Pd(OAc)_2$ (0.04 mmol, 8.8 mg), $PCy_3 \cdot HBF_4$ (0.08 mmol, 29.6 mg), PivOH (0.20 mmol, 20.4 mg) and K_2CO_3 (3.0 mmol, 414.6 mg). After nitrogen replacement and protection, the mixture was stirred at 150°C in an oil bath for 48 h. The reaction was cooled to room temperature and then diluted with ethanol. The powder was collected by filtration and washed with 2 M HCl solution, water and THF. Then it was transferred into 2 M HCl solution and stirred overnight. The solid was filtered again and washed with 2 M HCl solution, water, THF, toluene, ethyl acetate. Subsequently it was subjected to Soxhlet extraction with methanol and THF sequentially for 24 h with each solvent. A black-red solid was obtained after dried at 80°C in vacuum overnight with 96% isolated yield.

The yellow pTTT-Ben and orange pTTT-DMOB were obtained by a similar procedure with yield of 94% and 89%, respectively.

Material characterizations

^{1}H and ^{13}C NMR experiments were carried out on a Bruker AVANCE III HD spectrometer operating at resonance frequencies of 400 MHz.

Solid-state ^{13}C CP/MAS NMR experiments were carried out on a Bruker AVANCEIII/WB-400.

Fourier transform infrared (FT-IR) spectra was measured in the range of 4000−400 cm^{-1} using reflection mode on an infrared spectrometer (Bruker INVENIO R).

Organic elemental analysis (C, H, N, S) were performed on a CARLO ERBA 1106.

Powder X-ray diffraction (PXRD) data were collected on a Panalytical EMPYREAN diffractometer using Cu Kα radiation with 2θ range of 2° to 45°.

Brunauer–Emmett–Teller (BET) surface areas were measured according to **nitrogen adsorption and desorption** at 77 K on a Quantachrome Autosorb-iQ. The samples were degassed at 100°C for 12 h under high vacuum before analysis.

Scanning electron microscopy (SEM) images and **energy-dispersive X-ray spectroscopy (EDX)** were carried out on a JEOLA JSM-7500F).

Transmission electron microscopy (TEM) images were carried out using a FEI Tecnai G2 F20 S-TWIN.

Thermogravimetric analysis (TGA) spectrum was recorded from 30 to 800°C on a Shimadzu DTG-60(H) at a rate of 10°C/min under nitrogen.

UV−vis diffuse reflectance spectra (UV−vis DRS) was recorded on a Shimadzu UV-3600.

Fluorescence spectra was recorded on a fluorescence spectrophotometer (Shimadzu RF-5301) with the exciting wavelength fixted to 470 nm.

Fluorescence lifetime was measured on a Fluorolog-3 spectrofluorometer (Horiba JobinYvon) with a DeltaDiode (406 nm, DD-405L) as the excitation source.

Inductively coupled plasma atomic emission spectrometry (**ICP-AES**) data was collected with an spectrometer (Optima 8000, PerkinElmer). Samples were prepared by digesting 10 mg CMPs in a solution of HNO_3 (70%)/HCl (37%) (2.5/0.5, v/v) at 120°C for 48 h.[2]

Electrochemical analysis

The Mott-Schottky analysis was performed on a CHI660E electrochemical workstation at room temperature in the dark. Fluorine-doped tine oxide (FTO) conductive glass (working electrode), platinum plate electrode (counter electrode) and silver-silver chloride electrode (reference electrode) are used. The samples was prepared by mixing CMPs and 5 wt% Nafion, then the mixture was droped cast on the top of a FTO conductive glass within a confined area ($1*1$ cm^2). The conductive glass was dried at 65°C for 5 h before using. The potentiostatic impedance was measured between -1.4 V and 0.10 V versus Ag-AgCl electrode in the dark at the modulation frequency of 300 Hz, 500 Hz and 700 Hz in 0.2 M Na_2SO_4. The obtained flat band potentials were calculated to values versus saturated calomel electrode (SCE) using $E_{SCE} = E_{Ag\text{-}AgCl} + 0.04$ V.[3] The photocurrent of the CMPs was performed under irradiation 300 W Xe lamp using the same electrochemical workstation, electrodes and electrolyte.

Photocatalytic reaction of maleic acid

Experiments were conducted in a 15 mL test tube cooled by an ethanol bath (< 30°C). During each experiment, 10 mg catalysts and 880.6 mg (5 mmol) ascorbic acid were added to 10 mL 0.1 M solution of maleic acid. After sealed with a rubber plug, the tube was replaced and protected by nitrogen, then it was sonicated to obtain a fine dispersion. The mixture was irradiated under a 40W 460 nm LED lamp for 5 h.

To analysis the product, 100 μL reaction solution filtered by a syringe filter (0.22 μm) was mixed with 100 μL 0.1 M HCOONa solution and 400 μL D_2O. The product, succinic acid, was quantified by the variation of integration of its peak in nuclear magnetic resonance (NMR) spectra using HCOONa as an internal standard. The production rates are calculated using the following formula:

$$v = \frac{I_t - I_0}{4} * 100 \quad (mM) \quad * 0.01(L) * \frac{1}{0.01(g) * 5(h)}$$

in which I_t and I_0 are the final and initial integral of succinic acid with the integral of HCOONa fixed to 1.000, v is the production rate (mmol g^{-1} h^{-1}).

For time-dependent experiment, a 300 μL suspension was taken out by a syringe at a given time and filtered. The following processes were the same as discussed above.

For experiment of recyclability, after a cycle, the suspension was centrifuged and the supernatant was discarded. Afte washed with water, the solid was mixed with fresh ascorbic acid and maleic acid solution for the next cycle.

For pH-dependent experiment, the initial pH of reaction systems were adjusted to 0.51, 1.01, 1.52, 2.05, 4.00, 7.06, 9.96 and 12.02 with HCl and NaOH solutions. The following processes were the same as discussed above.

Photocatalytic reaction HMF

Similarly, experiments were conducted in an open test tube (15 mL) cooled by an ethanol bath (< 30°C). During each experiment, 10 mg catalysts and were added to 10 mL 0.1 M aqueous solution of HMF. After sonification, the reaction mixture was irradiated under an LED lamp for 10 h.

To analysis the product, 300 μL suspension was taken out from the stirring reaction mixture and extracted with 700 μL $CDCl_3$. The organic layer was collected and tested for NMR spectra. DFF yield was calculated by the integration ratio of C**H**O signals in DFF and HMF. The extraction process is indispensable because DFF has a very low solubility in water. The production rates are calculated using the following formula:

$$v = \frac{\frac{I_t - I_0}{2}}{\frac{I_t - I_0}{2} + 1} * 1 \quad (mmol) \quad * \frac{1}{0.01(g) * 10(h)}$$

in which I_t and I_0 are the final and initial integral of CHO in DFF with the integral of CHO in HMF fixed to 1.000, v is the production rate (mmol g^{-1} h^{-1}).

For time-dependent experiment, a 300 μL suspension was taken out by a pipette at a given time. The following processes were the same as discussed above.

For pH-dependent experiment, the initial pH of reaction systems were adjusted to 1.97, 3.98, 7.04, 10.09, and 11.99 with HCl and NaOH solutions. The following processes were the same as discussed above.

Photocatalytic reaction with natural sunlight

Experiments were conducted in a 15 mL test tube half-submerged in a water bath. The temparature was keeped below 30°C during the experiment. Compared with photocatalytic experiments mentioned above, the only difference is that the experiment was conducted directly under the sunshine for 5 h (10:50 to 15:50). Sunlight intensity was recorded at half-hour intervals using a sunlight power meter. This work was carried out in Chengdu on a sunny day at 11/Jan./2021.

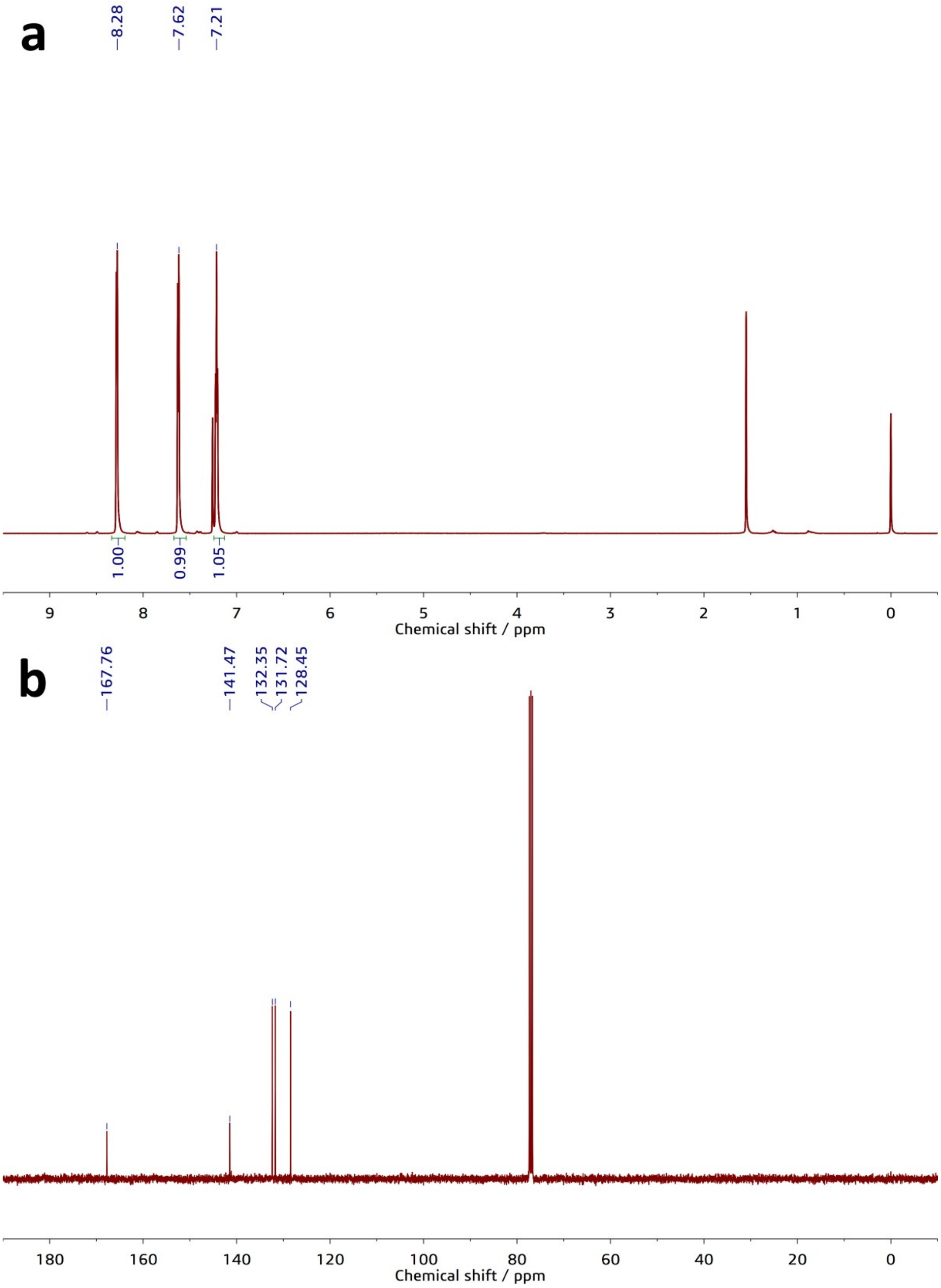


Figure S1. a) ^{1}H NMR and b) ^{13}C NMR spectra of TTT.

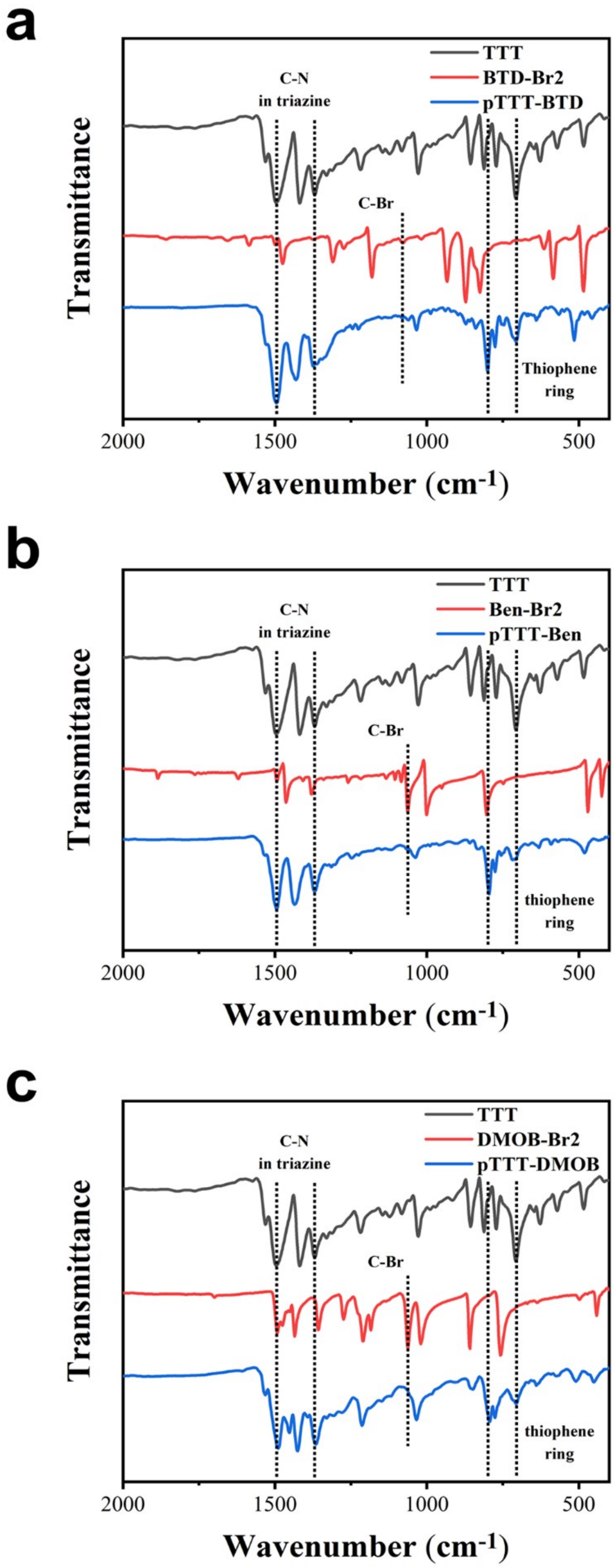


Figure S2. FT-IR spectra of a) pTTT-BTD, b) pTTT-Ben and c) pTTT-DMOB and comparison with their monomers.

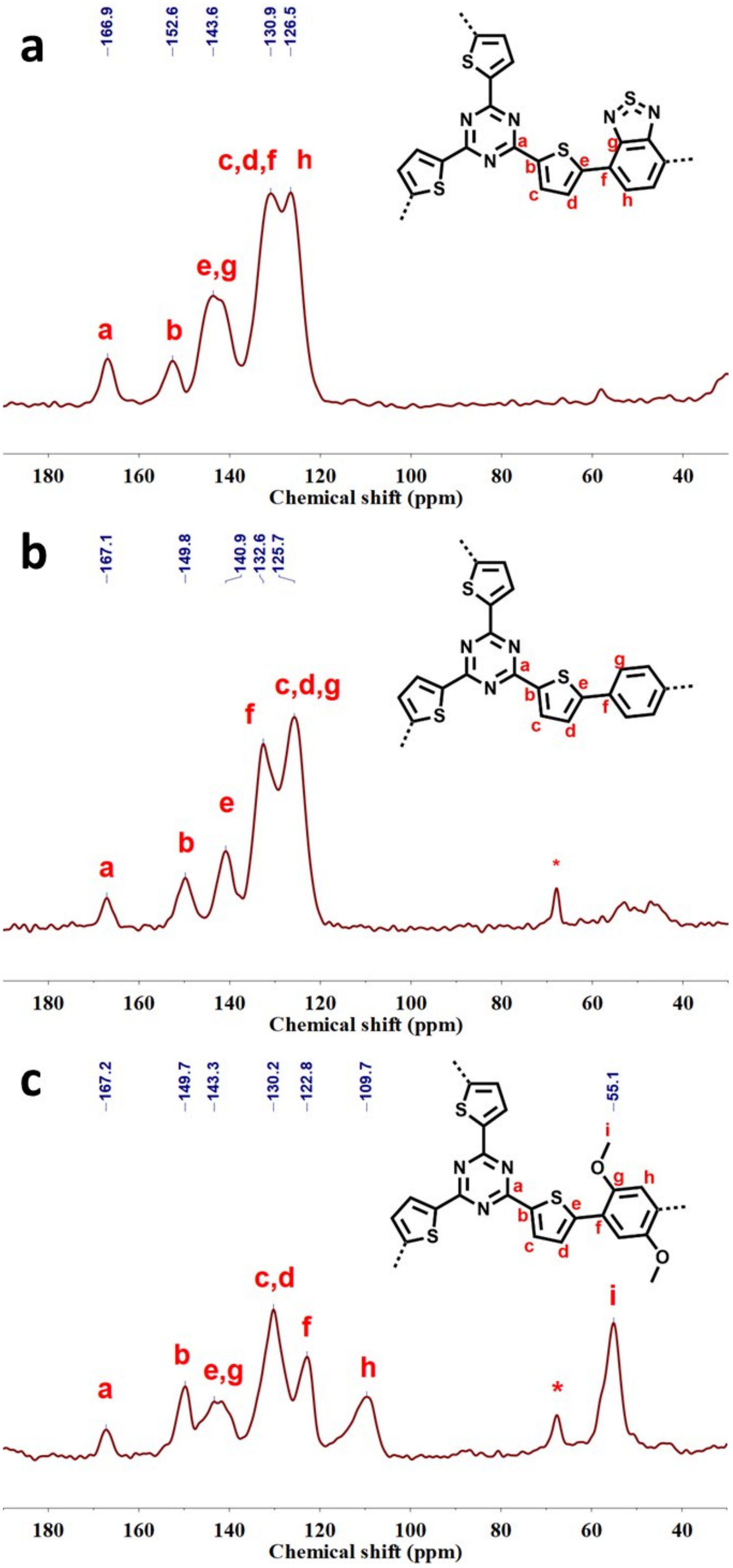


Figure S3. Solid state ^{13}C NMR spectra of a) pTTT-BTD, b) pTTT-Ben and c) pTTT-DMOB.

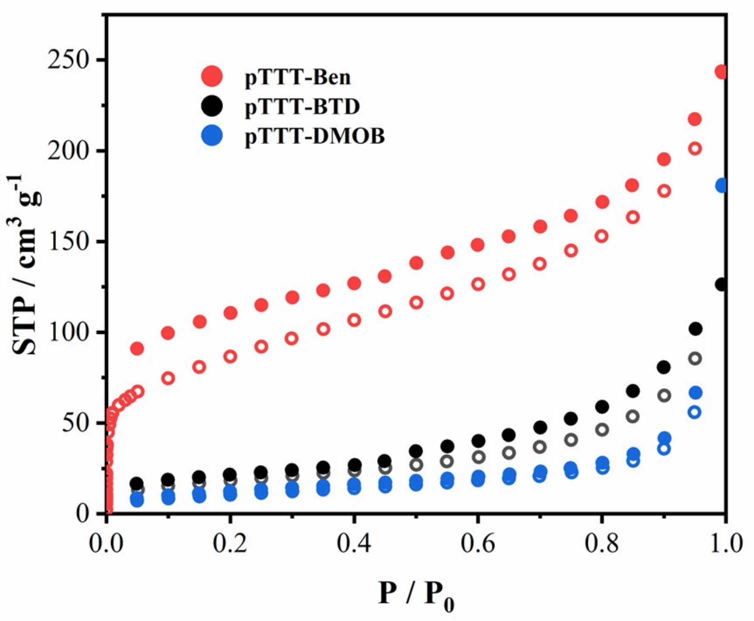


Figure S4. N2 isotherms of TTT-based CMPs.

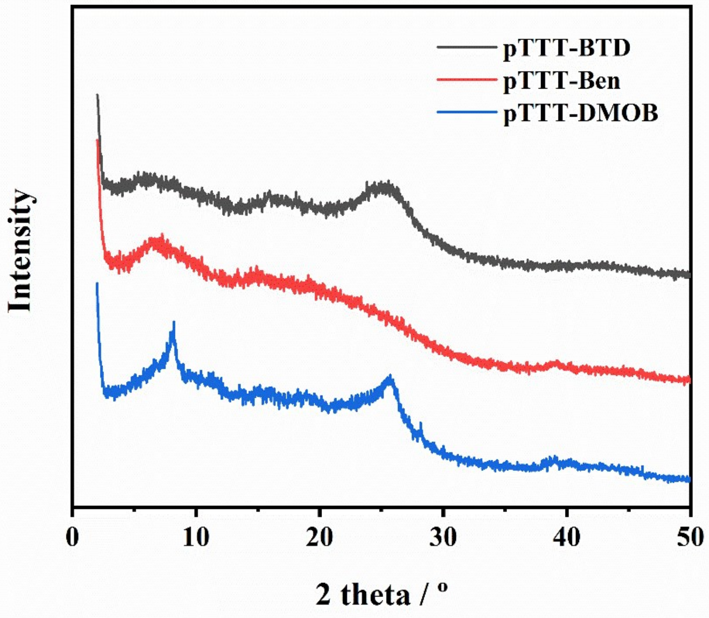


Figure S5. Powder X-ray Diffraction patterns of TTT-based CMPs.

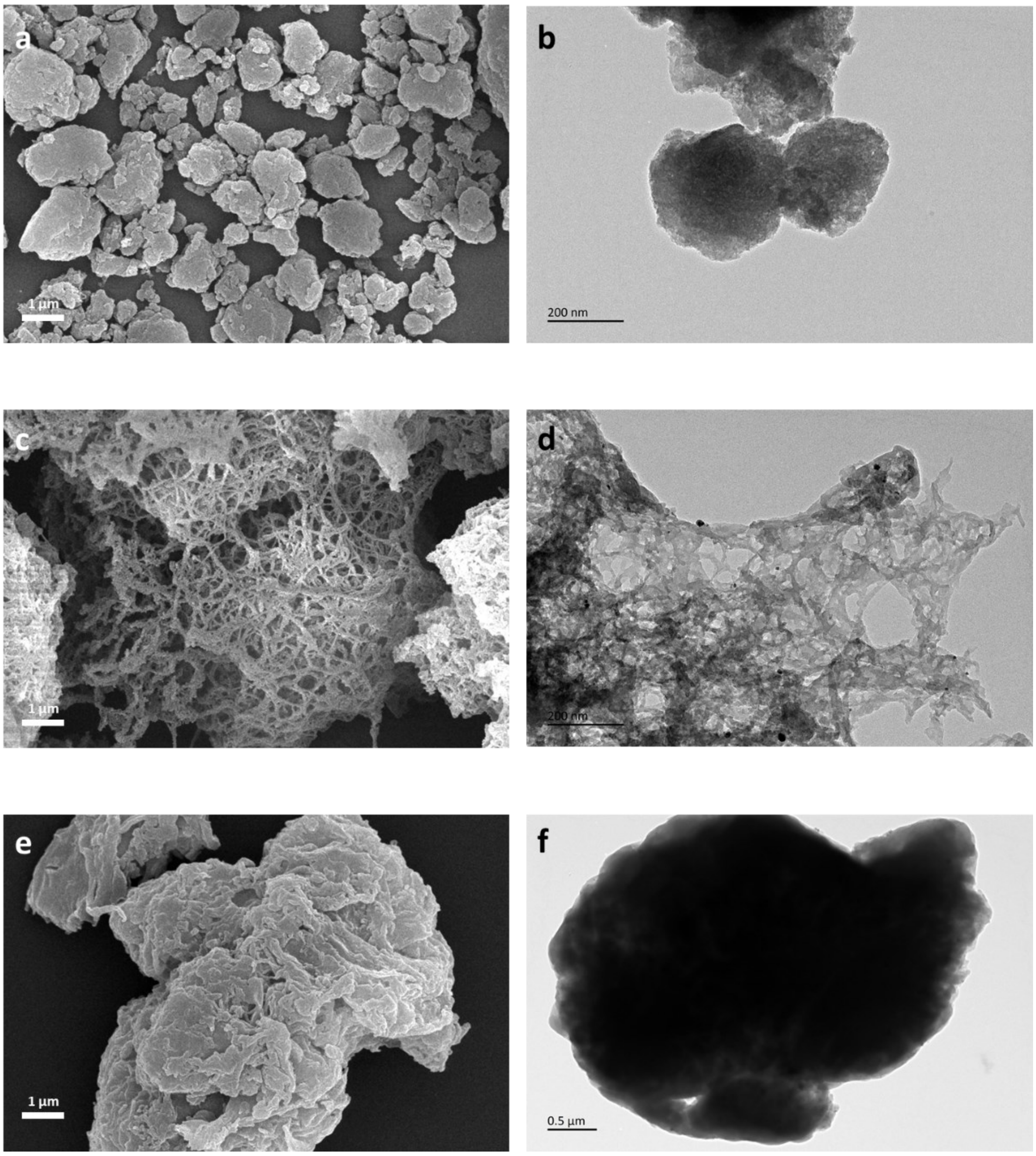


Figure S6. SEM (a, c and e) and TEM (b, d and f) images of pTTT-BTD (a, b), pTTT-Ben (c, d) and pTTT-DMOB (e, f).

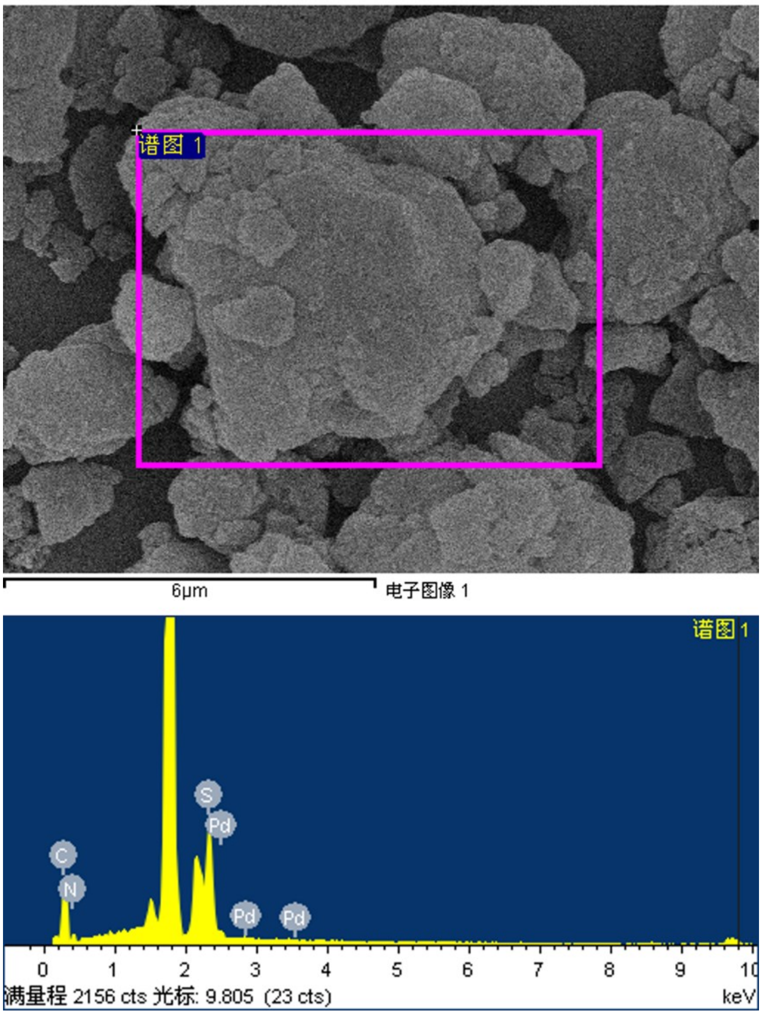


Figure S7. The selected area on SEM image and EDX spectra of pTTT-BTD.

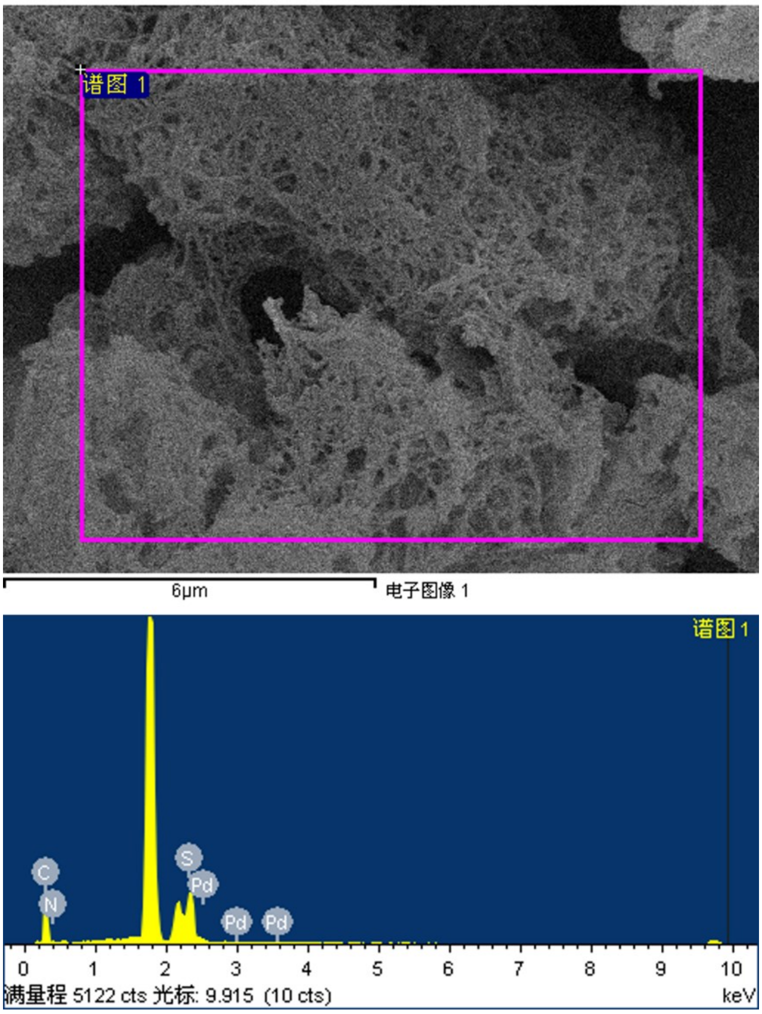


Figure S8. The selected area on SEM image and EDX spectra of pTTT-Ben.

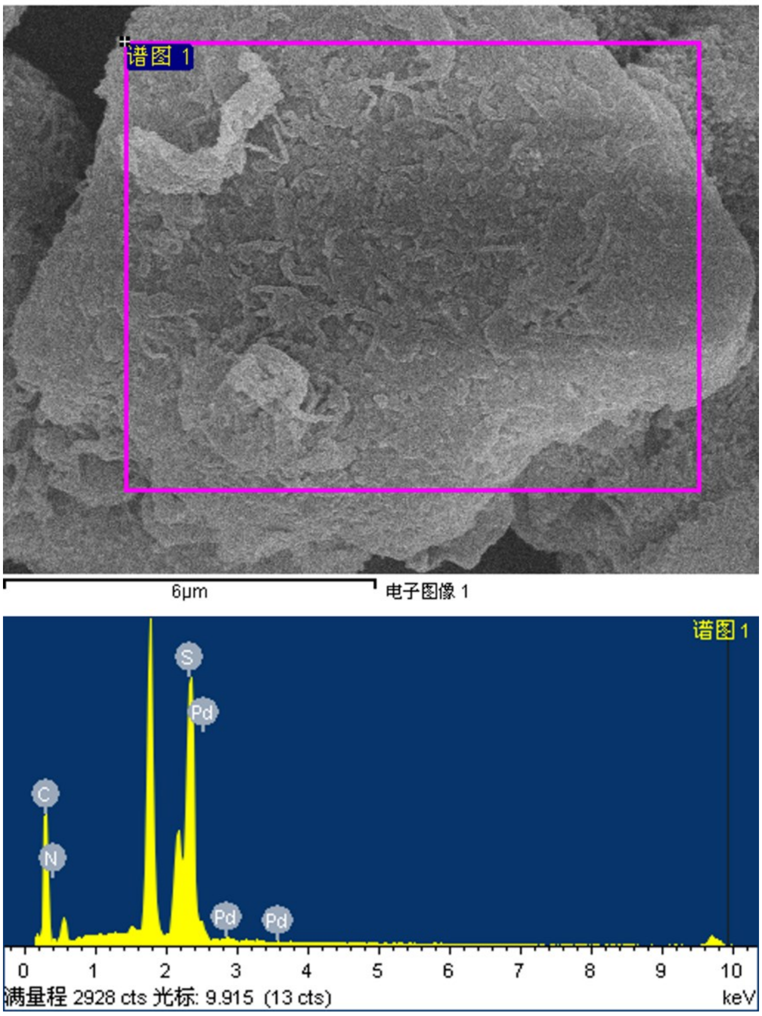


Figure S9. The selected area on SEM image and EDX spectra of pTTT-DMOB.

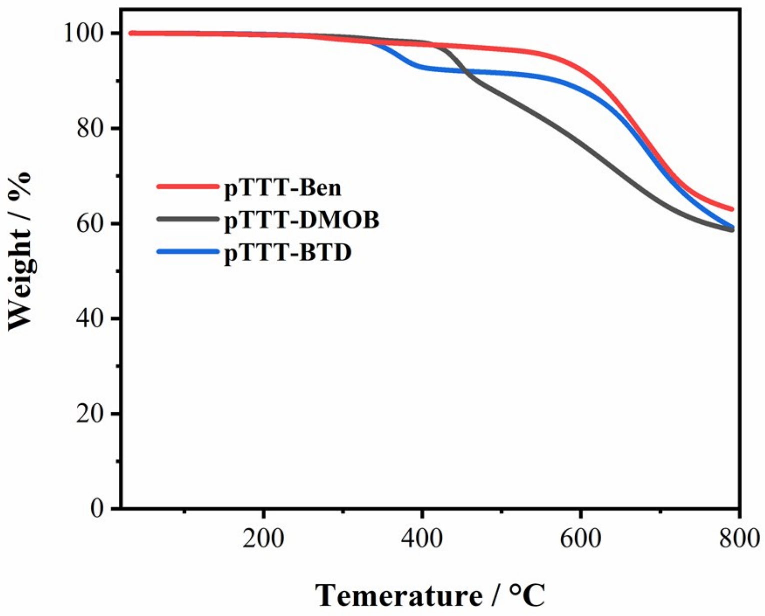


Figure S10. TGA curves of TTT-based CMPs.

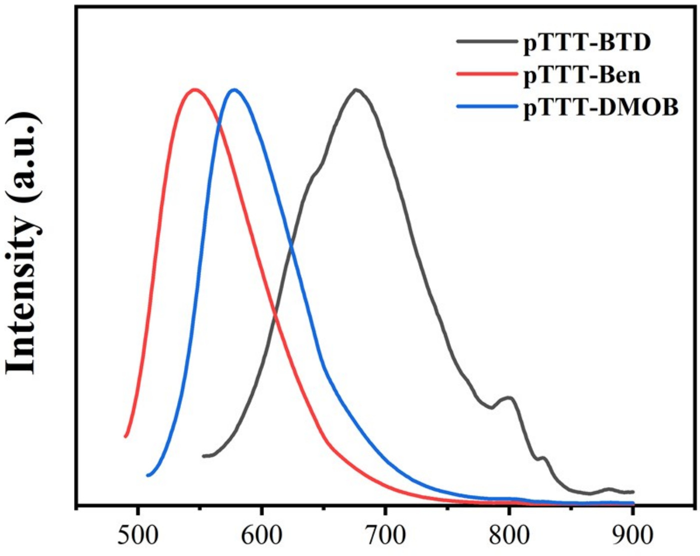


Figure S11. Solid-state fluorescent spectra of TTT-based CMPs.

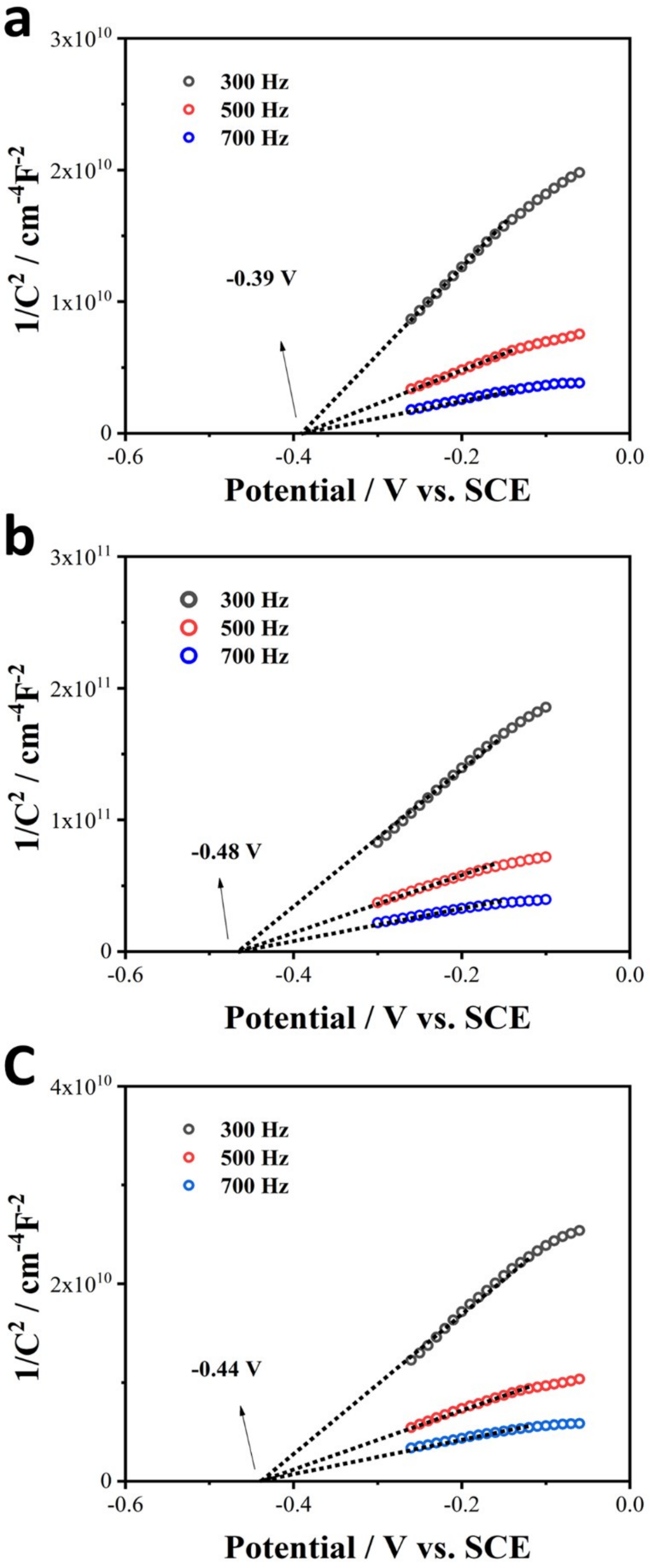


Figure S12. Mott-Schottky plots of a) pTTT-BTD, b) pTTT-Ben and c) pTTT-DMOB.

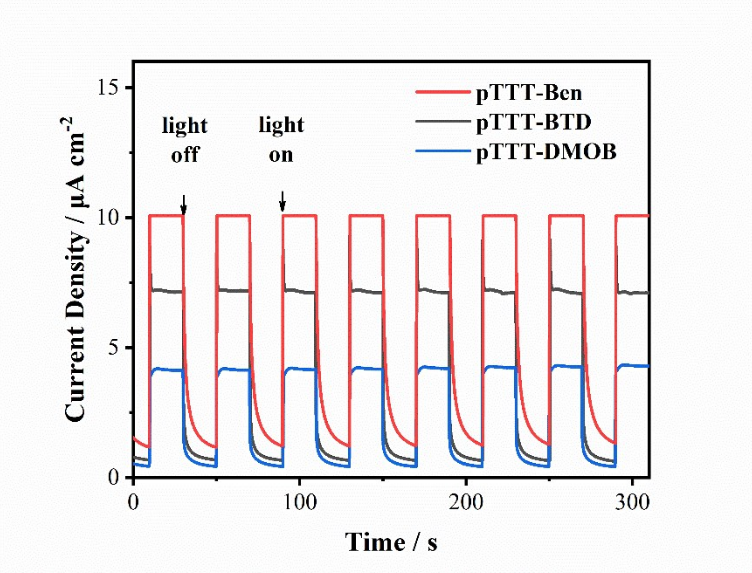


Figure S13. Time-resolved photoluminescence spectroscopy of three CMPs.

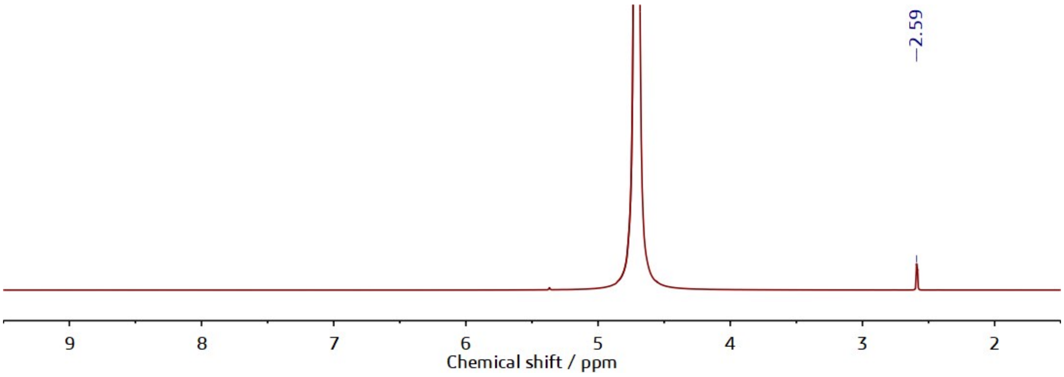


Figure S14. ^{1}H-NMR spectra of pure succinic acid in D_2O.

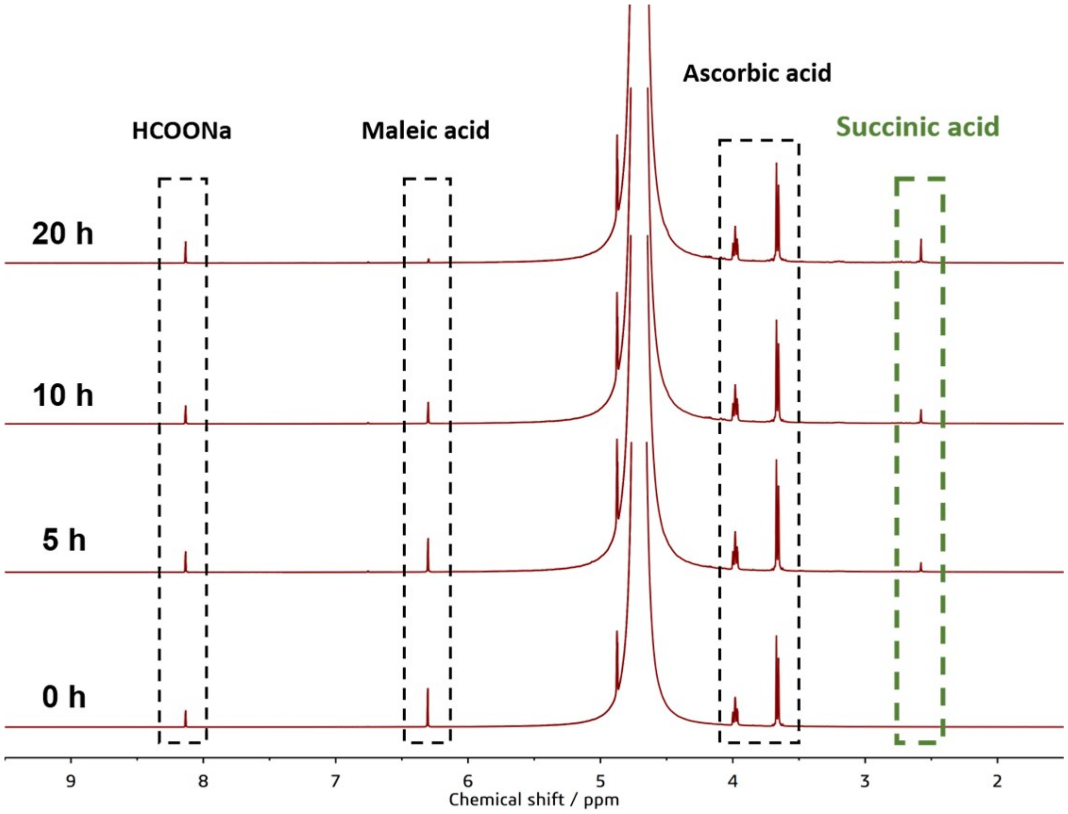


Figure S15. ^{1}H-NMR spectra of photocatalytic hydrogenation of maleic acid with different reaction time (D_2O).

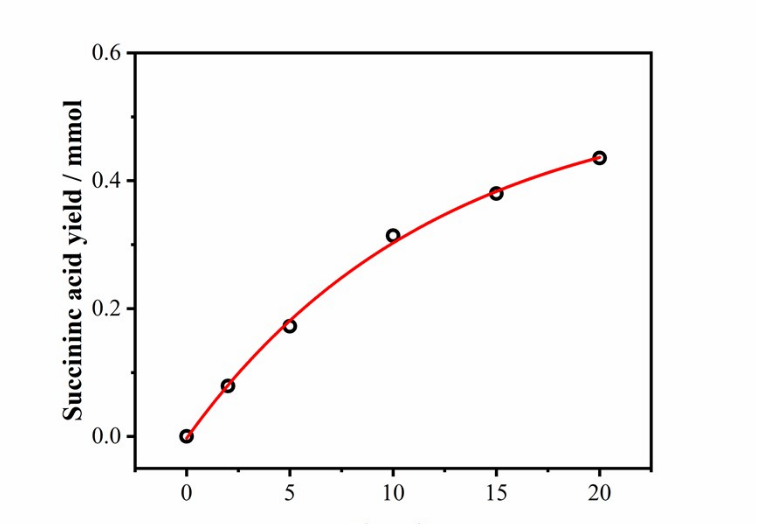


Figure S16. Photocatalytic production rates of succinic acid over reaction time with pTTT-Ben.

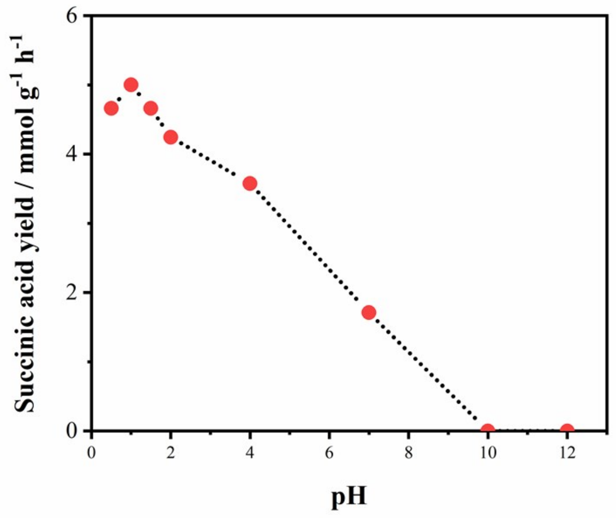


Figure S17. Photocatalytic production rates of succinic acid over different initial pH with pTTT-Ben.

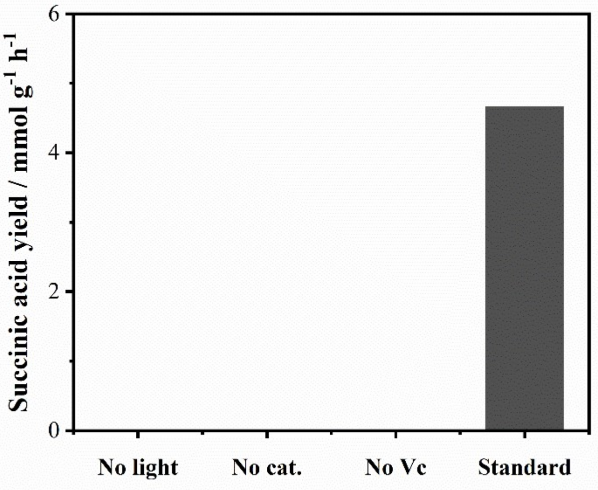


Figure S18. Control experiments conducted in the absence of light, pTTT-Ben or ascorbic acid in photocatalytic hydrogenation of maleic acid.

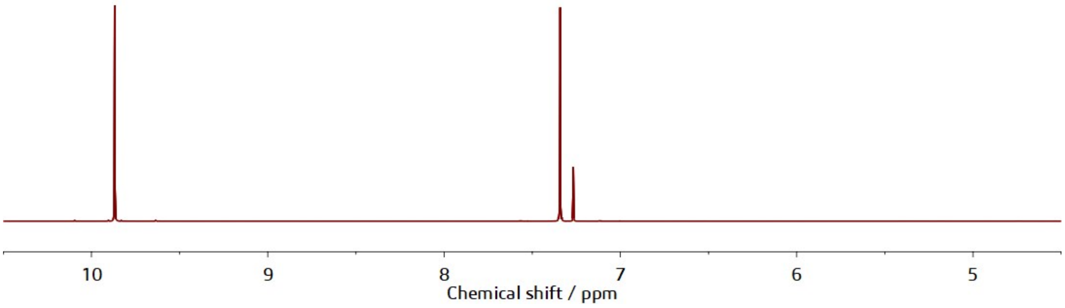


Figure S19. ^{1}H-NMR spectra of pure DFF in $CDCl_3$.

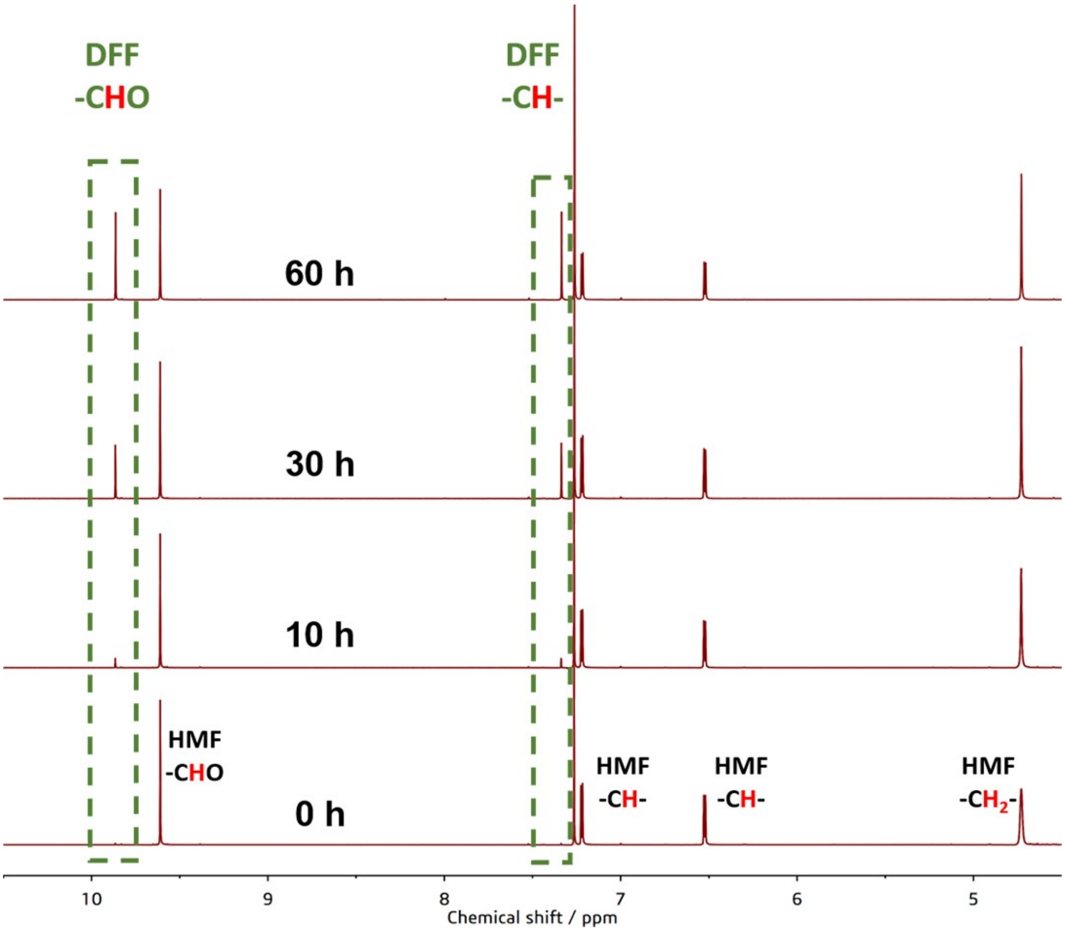


Figure S20. ^{1}H-NMR spectra of photocatalytic oxidation of maleic acid with different reaction time ($CDCl_3$).

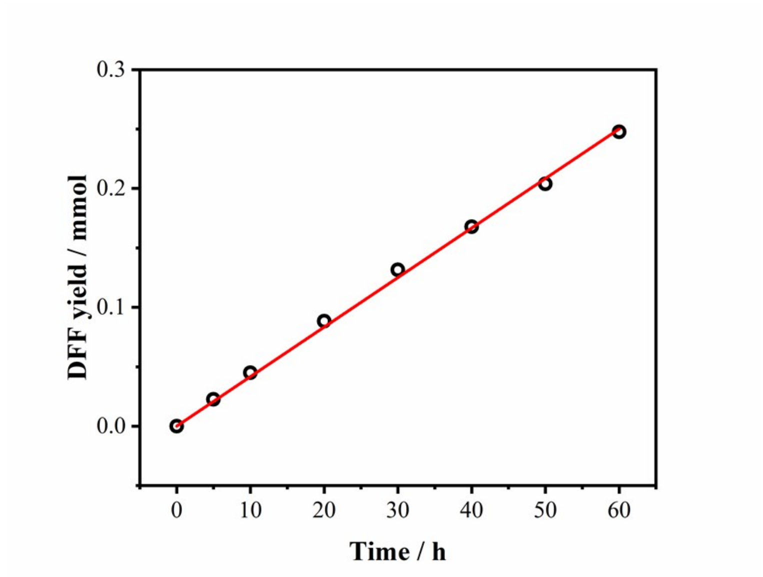


Figure S21. Photocatalytic production rates of DFF over reaction time with pTTT-Ben.

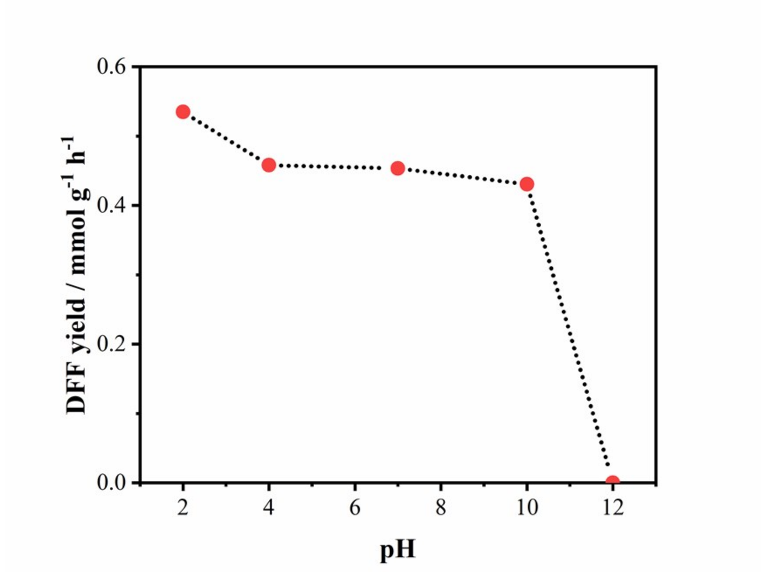


Figure S22. Photocatalytic production rates of DFF over different initial pH with pTTT-Ben.

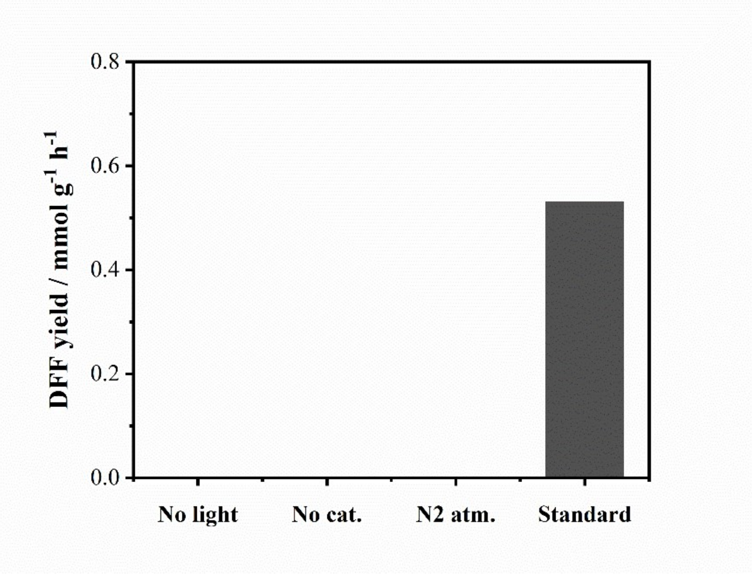


Figure S23. Control experiments conducted in the absence of light, pTTT-Ben or oxygen in photocatalytic oxidation of HMF.

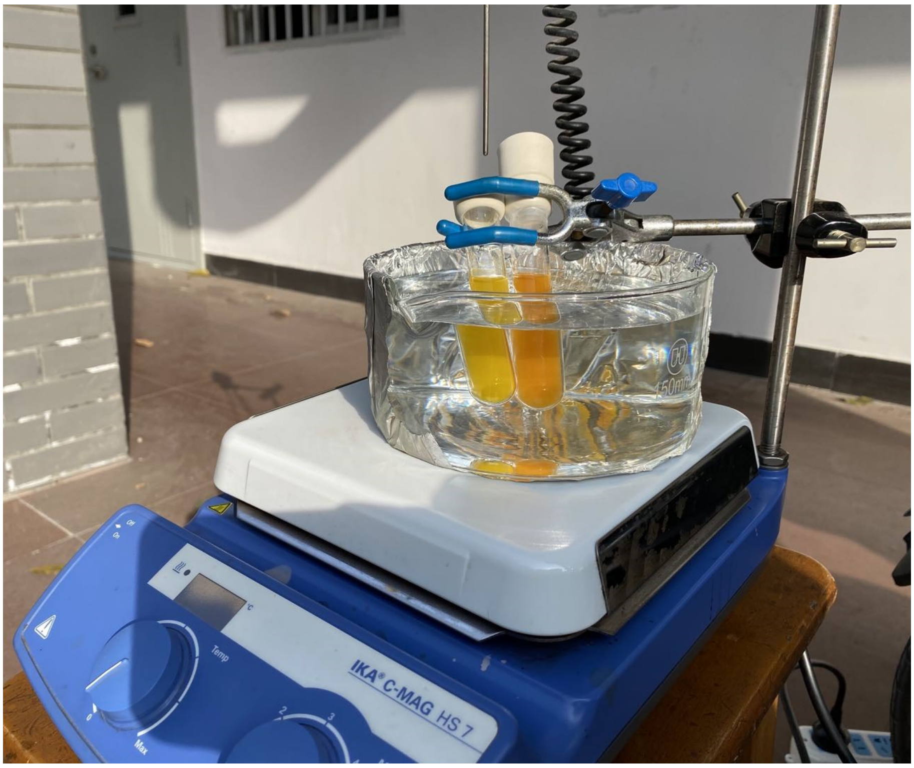


Figure S24. Picture of sunlight-driven photocatalytic reaction. This photo was taken by Bo Chen.

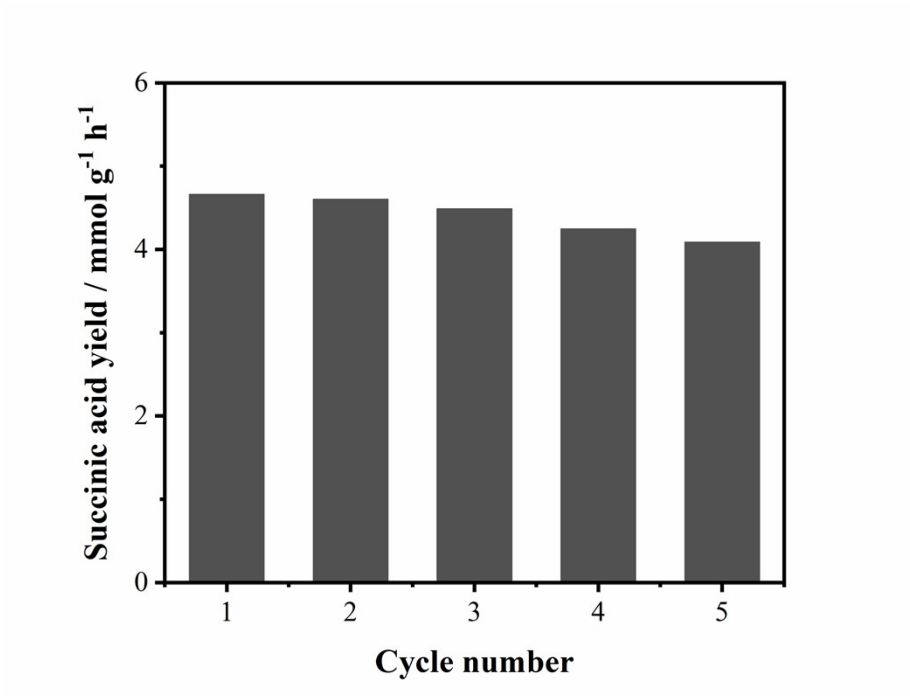


Figure S25. Recyclability of photocatalyst for hydrogenation of maleic acid with pTTT-Ben.

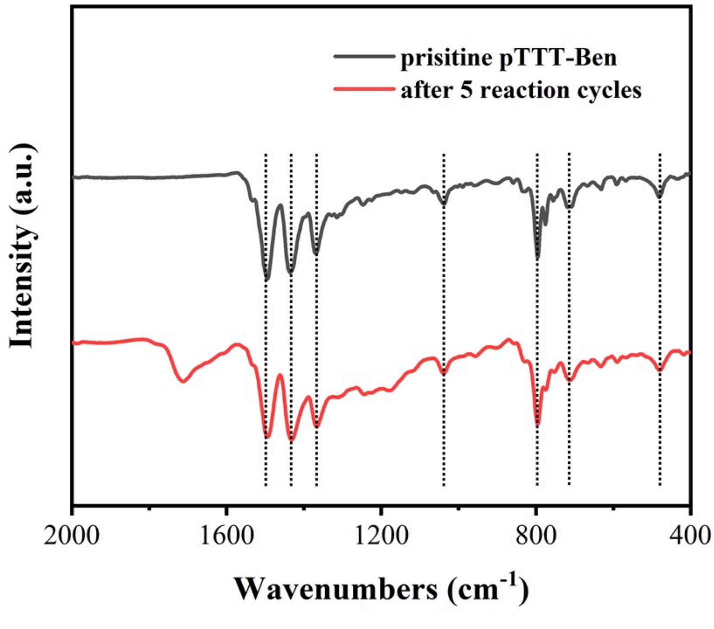


Figure S26. FT-IR spectra of pristine pTTT-Ben and after 5 reaction cycles.

Table S1. Organic elemental analysis (in weight %) for TTT-based CMPs

CMPs	C		H		N		S		O	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
pTTT-BTD	54.84	**51.87**	1.73	**2.10**	15.99	**13.98**	27.45	**24.26**		
pTTT-Ben	65.73	**64.77**	2.76	**3.26**	9.58	**8.86**	21.93	**20.04**		
pTTT-DMOB	61.35	**60.32**	3.43	**3.63**	7.95	**8.01**	18.19	**18.31**	9.08	

Table S2. Elemental composition (in weight %) of TTT-based CMPs detected by EDX

CMPs	C		N		S		Pd
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Exp.
pTTT-BTD	54.84	55.55	15.99	29.02	27.45	15.43	**0.00**
pTTT-Ben	65.73	66.29	9.58	19.81	21.93	13.91	**0.00**
pTTT-DMOB	61.35	63.21	7.95	21.47	18.19	15.32	**0.00**

Table S3. Pd contents detected by ICP-AES

CMPs	Pd (ppm)
pTTT-BTD	＜**0.1**
pTTT-Ben	**0.19**
pTTT-DMOB	＜**0.1**

Table S4. The sunlight intensity during photocatalysis

No.	Time	Sunlight intensity (W/m^2)
1	10:50	744.1
2	11:20	830.4
3	11:50	867.5
4	12:20	903.7
5	12:50	978.4
6	13:20	1013.2
7	13:50	980.7
8	14:20	764.4
9	14:50	832.6
10	15:20	791.4
11	15:50	249.6

Substrate	Catalyst	Reaction condition	Product yield	Ref.
Maleic acid	CTP-Th	300 W Xe lamp, r.t.,, H_2O	Succinic acid 2.05 mmol g^{-1} h^{-1}	4
Maleic acid	pTTT-Ben	40 W 460 nm LED, r.t., H_2O	succinic acid 4.66 mmol g^{-1} h^{-1}	This work
Maleic acid	pTTT-Ben	sunlight, r.t., H_2O	succinic acid 0.57 mmol g^{-1} h^{-1}	This work
HMF	Nb_2O_5	O_2, 300 W Xe lamp, r.t., benzotrifluoride	DFF 0.29 μmol g^{-1} h^{-1}	5
HMF	g-C_3N_4	O_2, 300 W Xe lamp, 80℃, H_2O	DFF 0.19 mmol g^{-1} h^{-1}	6
HMF	CTF-Th@SBA-15	O_2, Xe lamp, r.t., H_2O	DFF 0.19 mmol g^{-1} h^{-1}	7
HMF	pTTT-Ben	air, 40 W 460 nm LED, r.t., H_2O	DFF 0.53 mmol g^{-1} h^{-1}	This work
HMF	pTTT-Ben	air, sunlight, r.t., H_2O	DFF 0.28 mmol g^{-1} h^{-1}	This work

Table S5. Photocatalytic activities of maleic acid and HMF by heterogeneous catalysts

References

1. M. E. Bhosale, R. Illathvalappil, S. Kurungot and K. Krishnamoorthy, *Chem. Commun.*, 2016, **52**, 316-318.
2. S. Ashoka, B. M. Peake, G. Bremner, K. J. Hageman and M. R. Reid, *Anal. Chim. Acta.*, 2009, **653**, 191-199.
3. D. T. Sawyer, A. Sobkowiak and J. L. Roberts, *Electrochemistry for Chemists, 2nd Edition*, Wiley, 1995.
4. Y. Hu, W. Huang, H. Wang, Q. He, Y. Zhou, P. Yang, Y. Li and Y. Li, *Angew. Chem. Int. Ed.*, 2020, **59**, 14378-14382.
5. H. Zhang, Q. Wu, C. Guo, Y. Wu and T. Wu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 3517-3523.
6. Q. Wu, Y. He, H. Zhang, Z. Feng, Y. Wu and T. Wu, *Mol. Catal.*, 2017, **436**, 10-18.
7. C. Ayed, W. Huang, G. Kizilsavas, K. Landfester and K. A. I. Zhang, *ChemPhotoChem*, 2020, **4**, 571-576.