

## **Electronic Supplementary Information (ESI†)**

### **Triphenylamine-Anthraquinone based Donor-Acceptor Conjugated Microporous Polymers for Photocatalytic Hydroxylation of Phenylboronic Acids**

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# 1. Experimental Section

## 1.1. Materials and Methods

All the chemicals and reagents were purchased from commercial sources. Solvents were dried as per literature procedure prior to use according to the requirements. Monomer **1** was synthesized following a reported procedure with slight modification.<sup>[1] [2]</sup> Monomer **2** was purchased from commercial sources. Monomer **3** was synthesized from monomer **2** following a reported procedure with minor modification (Scheme S1).<sup>[3]</sup> Thin layer chromatography (TLC) on silica gel GF<sub>254</sub> was used for the determination of R<sub>f</sub> values, and the visualization was performed by irradiation with UV lamp at 254 nm. Column chromatography was performed on Merck silica gel (100-200 mesh) with eluent as mentioned. <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectra were recorded in a Bruker advance-500 NMR spectrometer in deuterated solvent at ambient temperature (300 K). Chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) as the internal standard (CDCl<sub>3</sub>  $\delta$  7.26 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C). Solid state <sup>13</sup>C CPMAS NMR spectra were recorded in a Bruker Ultrashield-500 NMR spectrometer. Mass spectra were recorded on Agilent 6500 Series Q-TOF spectrometer. Fourier transform infrared spectra (FTIR, 4000-600 cm<sup>-1</sup>) were performed on Nicolet 6700 FT-IR spectrometer (Thermo Fischer) instrument, the wave numbers of recorded IR-signals are reported in cm<sup>-1</sup>. XPS measurements were carried out using the PHI 5000 Versa Probe II, ULVAC-PHI, Inc. instrument. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond TG DTA (PerkinElmer) instrument. The BINOL based porous organic polymers were observed under scanning electron microscope (SEM) model ZEISS SUPRA 40. The samples were prepared on gold stubs by adding powder polymers mounting on top of double-sided tapes. TEM measurements were carried out in a JEOL-2010EX machine operating at an accelerating voltage of 200 V. TEM samples were prepared by mounting on the copper grid for analysis. UV-Vis-NIR diffuse reflection spectrum (DRS) was acquired with UV-Vis-NIR spectrophotometer (Cary 5000, Agilent). X-Ray diffraction patterns of the powder organic polymer samples were obtained using a Bruker AXS D-8Advanced SWAX diffractometer using Cu-K $\alpha$  (0.15406 nm) radiation. The N<sub>2</sub> adsorption/desorption isotherms of the sample was recorded on a Micromeritics 3-Flex Surface Characterization Analyzer at 77 K. UV-visible adsorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer. The specific measurement details regarding reactive oxygen species (ROS) trapping are as follows: In 3 ml air-saturated CH<sub>3</sub>CN, 5 mg photocatalyst and 5 mg of N,N,N',N'-tetramethyl-p-phenylenediamine (NTPD) were added. Then O<sub>2</sub> was purged into that mixture and stirred the whole mixture under white light irradiation (18 W white LED) for 45 min. Then the polymer was filtered out and the filtrate portion was submitted for UV. Bruker ELEXSYS 580 spectrometer was used to record the EPR spectra. The specific measurement details regarding reactive oxygen species (ROS) trapping are as follows: the modulation frequency = 100.00 kHz, modulation amplitude = 5.000 G. The samples were prepared by adding 1 mg of photocatalyst to a 1 ml 0.1 M air-saturated acetonitrile solution of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO).

## 1.2. Electrochemical measurements

Cyclic voltammetry (CV) measurement was carried out by using a CH instrument with a three electrode-cell [CMPs-coated glassy carbon electrode as a working electrode, platinum wire as a counter electrode, and Ag/AgCl (KCl, 3M) as a reference electrode]. Ferrocene-ferrocenium (Fc/Fc<sup>+</sup>) was used as an internal standard. A scan rate of 0.1 V/s was used. A solution of 0.1 (M) tetrabutylammonium perchlorate in acetonitrile was used as the supporting electrolyte. 2 mg of well-dried CMPs was well-dispersed in a binder solution of 25 wt% of polyvinylidene fluoride (PVDF) and 500  $\mu$ L of ethanol through ultrasonication for 1 h to obtain a stable suspension. Then the pre-polished glassy carbon electrode was coated by 20  $\mu$ L of the prepared polymeric dispersion. The electrode was dried for 1 day at room temperature and then prior to CV experiment. The electrode potential values are given with respect to  $E_{\text{Ag/AgCl}} = 0.197$  vs NHE. The LUMO energy levels of the CMPs were determined by using the empirical equations,  $E_{\text{LUMO}} = (E_{\text{onset/red}} + 0.49 - 0.197)$  eV (vs Ag/AgCl).<sup>[4]</sup> EIS is determined over the frequency range of  $10^2$ – $10^6$  Hz with an ac amplitude of 10 mV at the open circuit voltage under room-light illumination by using 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as supporting electrolyte.

## 1.3. Photocurrent measurements

Photoelectrochemical measurements were conducted in a three-electrode system with a potentiostat (CH instruments 660D potentiostat) under simulated AM 1.5G solar light illumination, where a Newport Xe lamp with a light intensity of 10 Mw/cm<sup>2</sup> was used as the visible light source. The working electrodes are prepared as follows: 2.5 mg of DA-CMPs is separately ground with 2  $\mu$ L of a Nafion aqueous solution and 50  $\mu$ L of ethanol to make slurry. The slurry is then coated onto FTO glass electrodes with an active area of 1.3 cm<sup>2</sup>, and these electrolytes are dried at 100 °C for 1 h to evaporate the solvent. An aqueous solution of 0.5 M KOH was used as the supporting electrolyte. The photocurrent intensity of as-prepared electrodes is measured at 0 V versus s-Ag/AgCl with the light on and off.

## 2. Chemical Synthesis and Procedure

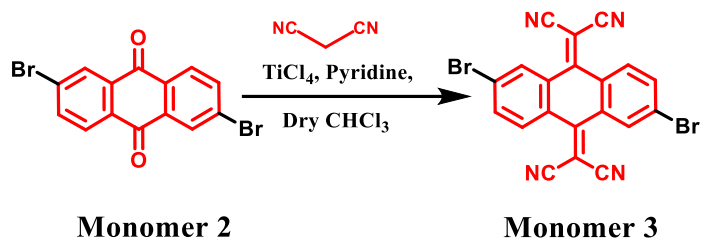
### 2.1 Synthesis

**2.1.1. Synthesis of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-amine (Monomer 1):** Monomer **1** was synthesized following a published procedure with slight modification.<sup>[1] [2]</sup>

### 2.1.2. Synthesis of 2,2'-(2,6- dibromoanthracene-9,10-diyldene)dimalononitrile (Monomer 3)

Monomer **3** was synthesized from monomer **2** following a reported procedure with minor modification (Scheme S1).<sup>[3]</sup> Malononitrile (59.4 mg, 0.9 mmol), TiCl<sub>4</sub> (0.18 mL, 0.9 mmol) and pyridine (0.15 mL, 1.8 mmol) was added to an anthracene-9,10-dione derivative (200 mg, 0.55 mmol) in dry CHCl<sub>3</sub> (50 mL). The mixture was heated to reflux for 36 hours. Identical amounts of malononitrile, TiCl<sub>4</sub> and pyridine were added to the reaction mixture for every 12 hours. The mixture was then poured in ice/water and extracted with CHCl<sub>3</sub> (3x100 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under

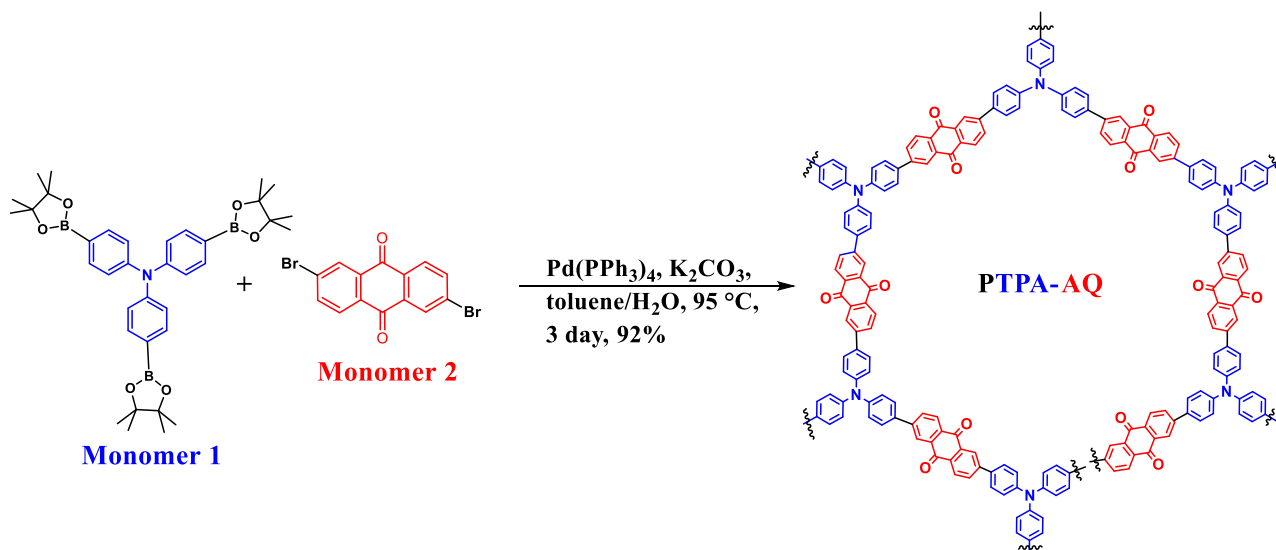
vacuo. Then the residue was purified by column chromatography to obtain 2,2'-(2,6-dibromoanthracene-9,10-diyldiene)dimalononitrile. Yield 61%,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.89$  (dd,  $^3J_{\text{H,H}} = 9.0$  Hz,  $^4J_{\text{H,H}} = 2.0$  Hz, 2H, AQ), 8.09 (d,  $^3J_{\text{H,H}} = 9.0$  Hz, 2H, AQ), 8.37 (d,  $^4J_{\text{H,H}} = 2.0$  Hz, 2H, AQ) ppm.



**Scheme S1.** Synthesis of Monomer 3

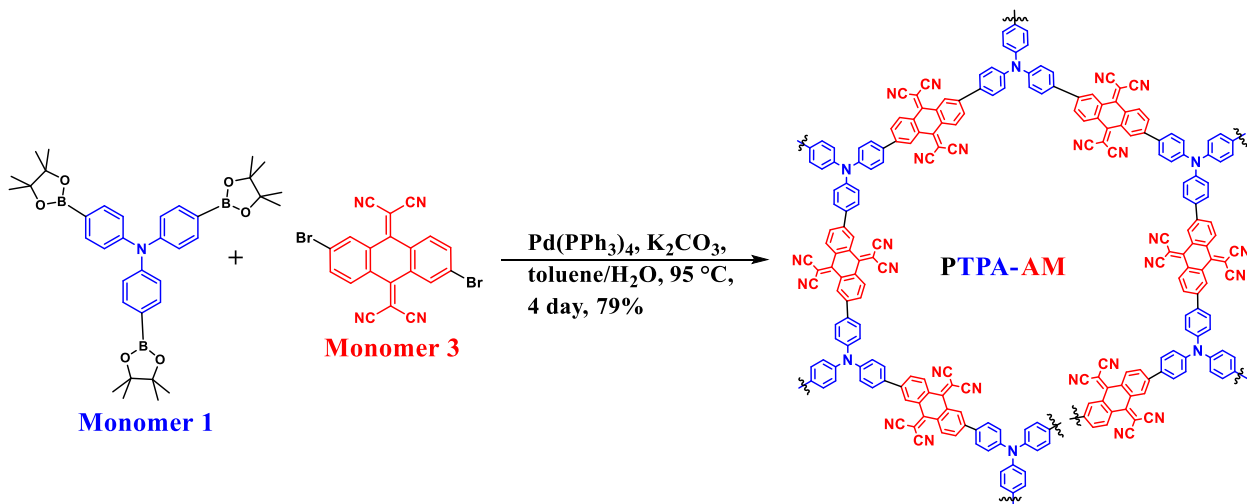
### 2.1.3. Synthesis of PTPA-AQ and PTPA-AM

**a) Synthesis of PTPA-AQ:** A 50 ml two neck round bottom flask was charged with monomer 1 (374 mg, 0.6 mmol), monomer 2 (329.2 mg, 0.9 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (35 mg, 5 mol%), and  $\text{K}_2\text{CO}_3$  (1.38 g, 10 mmol) under  $\text{N}_2$  atmosphere. Previously degassed toluene/water (9ml:3ml) solvent was injected into the reaction mixture and bubbled with  $\text{N}_2$  for 45 minutes. Then the mixture was stirred vigorously at 95 °C for 3 day. After 3 day, the precipitate was collected through filtration and thoroughly washed with water, MeOH and  $\text{CHCl}_3$ . Then the precipitate was further washed with MeOH, acetone and  $\text{CHCl}_3$  in Soxhlet apparatus. For every solvent, the Soxhlet purification was done for 1 day. Then the obtained polymer was dried under vacuum. The polymer was obtained as deep brown polymer (305 mg) and the yield was 92%. FT-IR: 1680, 1575, 1505, 1309, 826  $\text{cm}^{-1}$ ,  $^{13}\text{C}$  CPMAS NMR:  $\sim 183$ ,  $\sim 145$ , 115-140 ppm, TGA: 5% weight loss at 374 °C.



**Scheme S2.** Synthesis of PTPA-AQ

**b) Synthesis of PTPA-AM:** A 50 ml two neck round bottom flask was charged with monomer **1** (374 mg, 0.6 mmol), monomer **3** (415.8 mg, 0.9 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 5 mol%), and K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol) under N<sub>2</sub> atmosphere. Previously degassed toluene/water (9ml:3ml) solvent was injected into the reaction mixture. The reaction mixture was bubbled with N<sub>2</sub> for 45 minutes. Then the mixture was stirred vigorously at 95 °C for 4 day. After 4 day, the precipitate was collected through filtration and thoroughly washed with water, MeOH and CHCl<sub>3</sub>. Then the precipitate was further washed with MeOH, acetone and CHCl<sub>3</sub> in Soxhlet apparatus. For every solvent, the Soxhlet purification was done for 1 day. Then the obtained polymer was dried under vacuum. The polymer was obtained as blackish brown polymer (332 mg) and the yield was 79%. FT-IR: 2218, 1575, 1503, 1317, 825 cm<sup>-1</sup>. <sup>13</sup>C CPMAS NMR: ~145, 115-140 ppm, TGA: 5% weight loss at 340 °C.



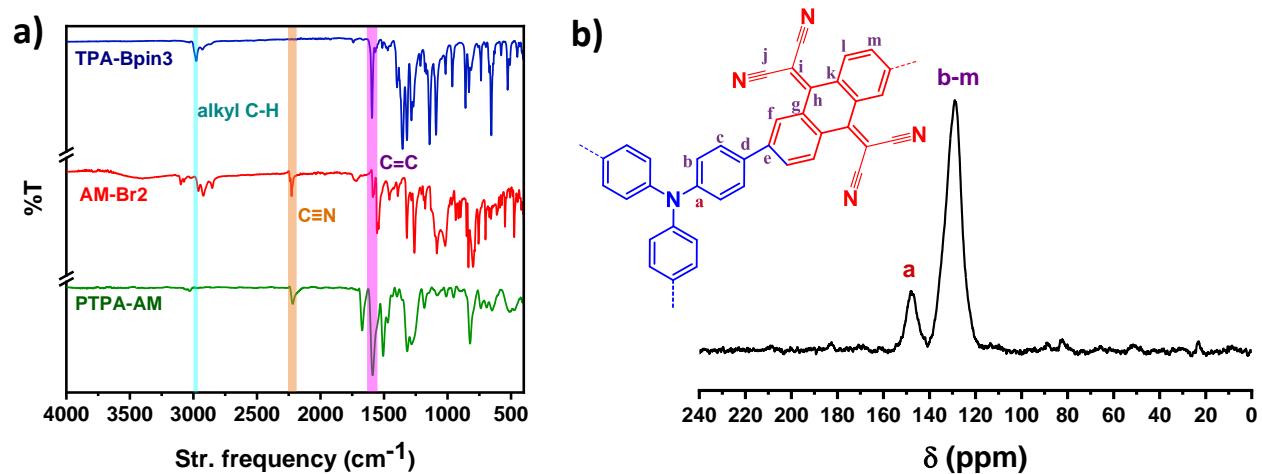
## 2.2 Procedures

### 2.2.1 General Procedure for the photocatalytic oxidative hydroxylation of arylboronic acids

A 20 ml glass tube was charged with phenylboronic acid (30.5 mg, 0.25 mmol), photocatalyst (5 mg), trimethylamine (38 mg, 0.375 mmol) and acetonitrile (3 ml). The mixture was ultra-sonicated for few minutes to make a stable dispersion of photocatalyst. Then the mixture was saturated with O<sub>2</sub> in an oxygen flow for 15 minutes. A oxygen containing balloon was installed in that tube. A white LED (18 W) light was irradiated into that tube throughout the reaction period and the mixture was stirred at room temperature for 14 h. After reaction, photocatalyst was isolated by filtration and washed with ethanol and DCM. The filtrated part was concentrated by rotavapor and the crude was subjected to column chromatography. The Product was isolated from silica gel column chromatography by using chloroform as an eluent. For recycling experiment, the photocatalyst was filtered out by filtration and washed thoroughly with MeOH, EtOH, CHCl<sub>3</sub> and DCM. Then the washed photocatalyst was dried under vacuum for 12 h and used for next cycle.

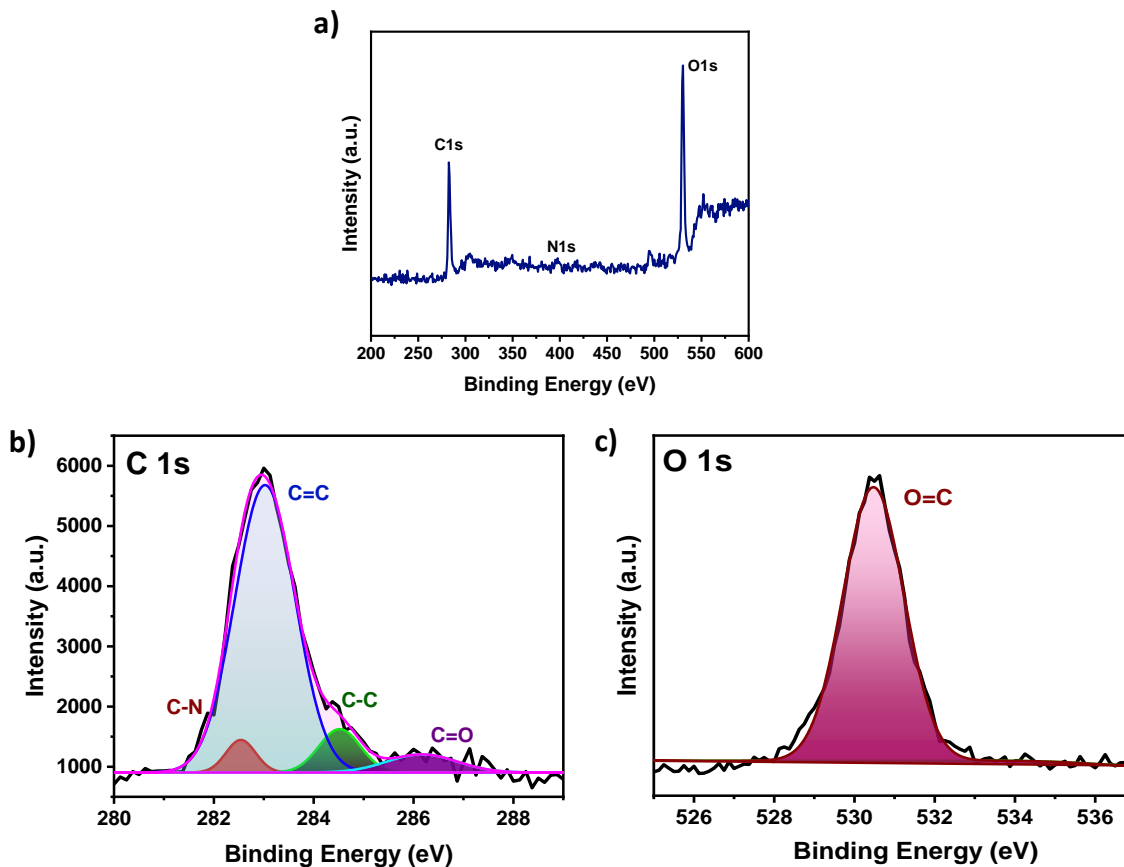
### 3. Characterization

#### 3.1 FTIR and Solid State $^{13}\text{C}$ NMR



**Fig. S1.** (a) Fourier transform infrared spectroscopy (FTIR) spectra of monomers monomer **1** (TPA-Bpin3, blue), monomer **2** (AM-Br2, red) and PTPA-AM polymer (green). (b) Solid-state  $^{13}\text{C}$  CPMAS NMR spectrum of PTPA-AM.

### 3.2. XPS



**Fig. S2.** X-ray photoelectron spectroscopy (XPS) a) survey scan, b) C 1s spectra and c) O 1s spectra of PTPA-AQ. The survey scan of PTPA-AQ exhibited three main characteristics peaks at  $\sim 283$ ,  $\sim 398$  and  $\sim 530$  eV, which are assigned to C 1s, N 1s and O 1s, respectively. The C 1s spectra showed four peaks centered at 282.9, 284.4, 282.5 and 286.5 eV after deconvolution, which corresponds to C=C, C-C, C-N and C=O, respectively. In O 1s spectra only one peak was observed at 530 eV corresponding to C=O of anthraquinone moiety.



### 3.3. TGA

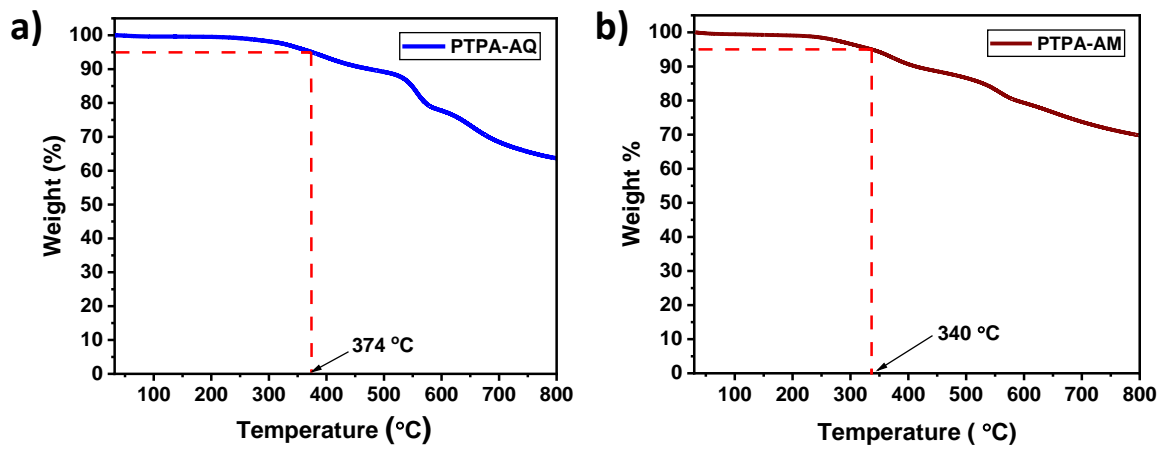


Fig. S3. TGA curves for the D-A CMPs: a) PTPA-AQ, and b) PTPA-AM under nitrogen atmosphere.

### 3.4. SEM and TEM:

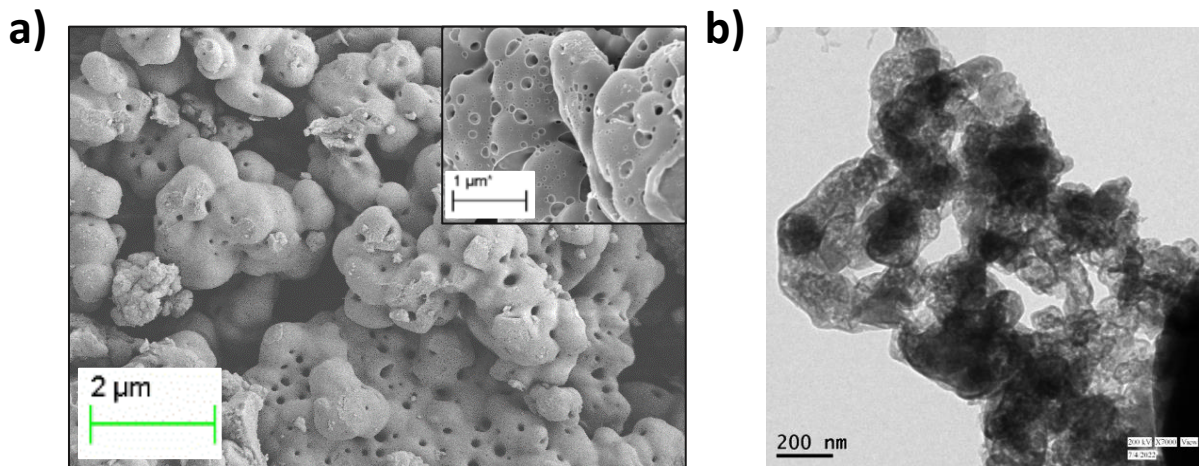
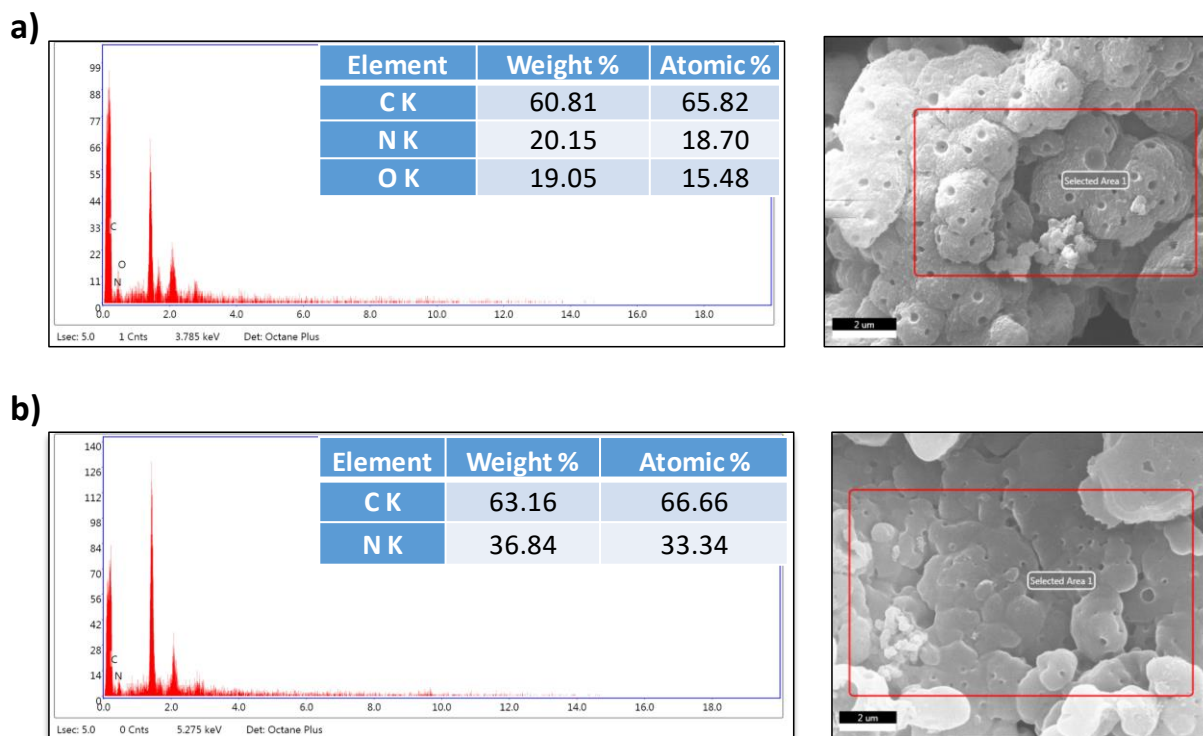
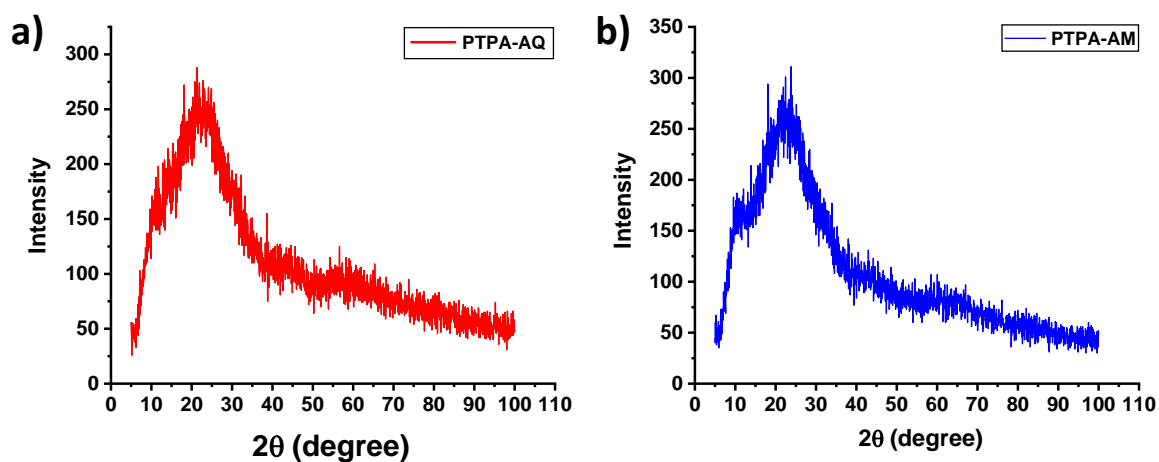


Fig. S4. (a) SEM image and (b)TEM image of PTPA-AM.



**Fig. S5.** Energy dispersive X-ray (EDX) analysis of a) PTPA-AQ and b) PTPA-AM coupled with Scanning Electron Microscopy; inset: tabular representation of different elements in atomic% and weight% present in the polymer.

### 3.5. PXRD



**Fig. S6.** PXRD patterns of a) PTPA-AQ, and b) PTPA-AM.

### 3.6. Nitrogen adsorption-desorption isotherm

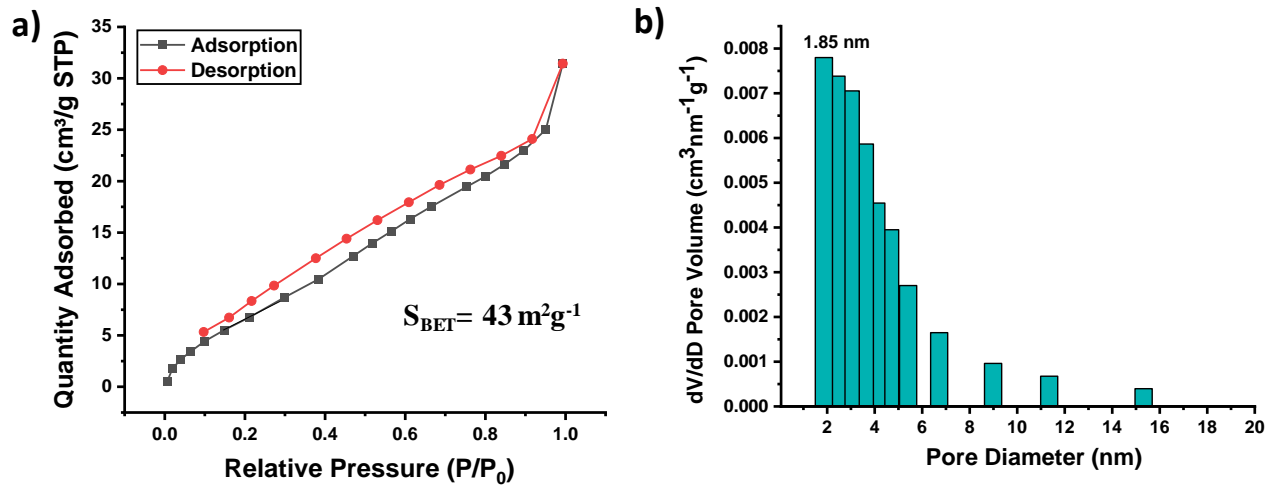


Fig. S7. a) Nitrogen sorption isotherm at 77 K (adsorption: black squares; desorption: red dots), and b) pore size distribution of PTPA-AM.

### 3.7. CV analysis and DFT study:

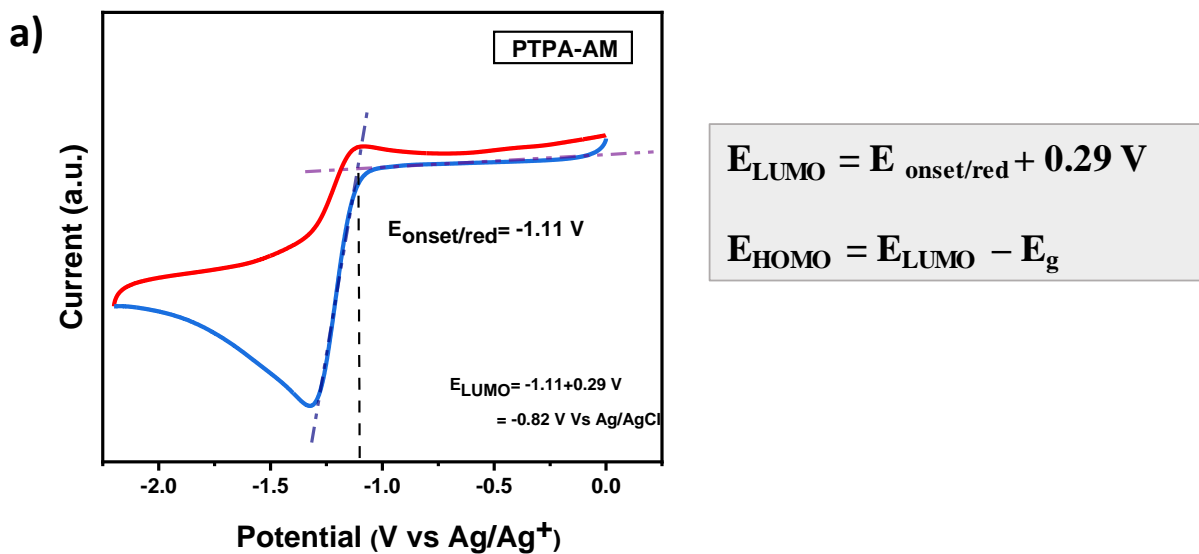
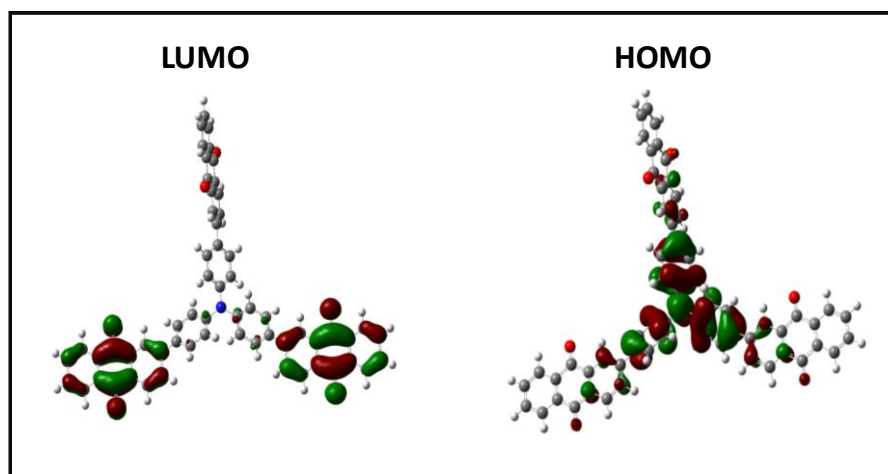
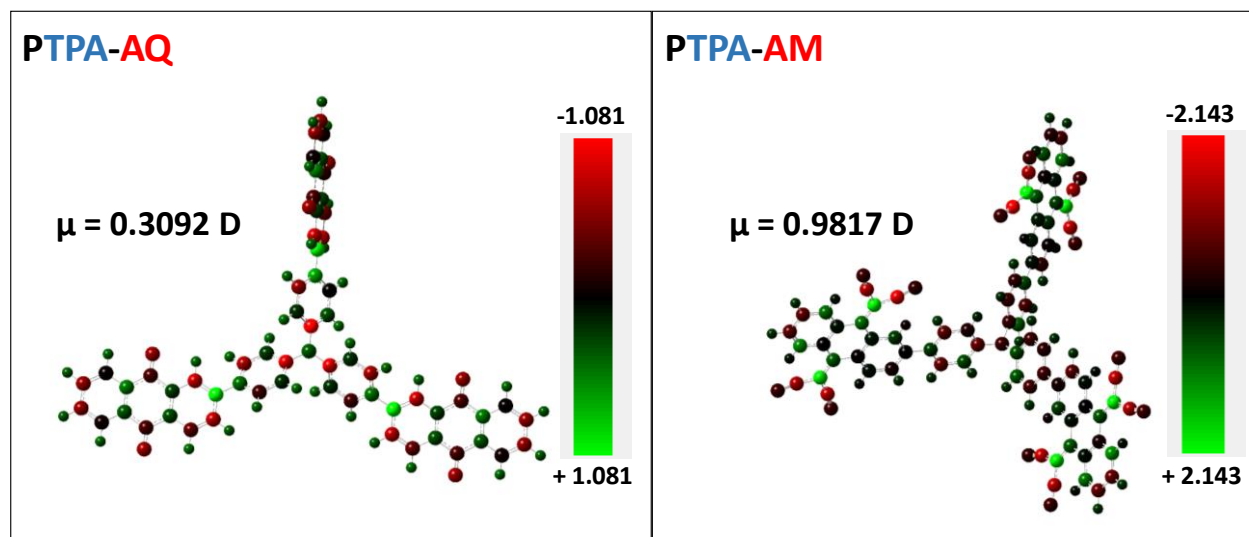


Fig. S8. a) CV diagram of PTPA-AM.

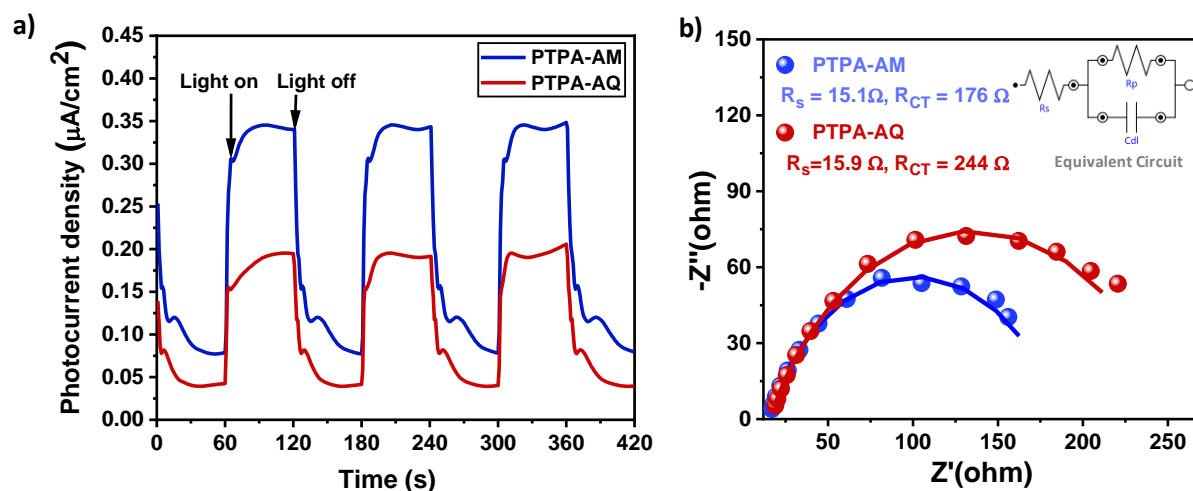


**Fig. S9.** Density functional theory (DFT, Gaussian 16, 6-31G<sup>+</sup>) calculation of the molecular orbital diagrams of PTPA-AQ. The highest occupied molecular orbitals (HOMO) are mainly delocalized on the electron donor unit, triphenylamine while the lowest unoccupied molecular orbitals (LUMO) move towards the anthraquinone unit, suggesting that anthraquinone serves as an electron acceptor and indicating the D-A characteristics of the as-prepared DA-CMPs.



**Fig. S10.** The Mulliken atomic charges of every atom in PTPA-AQ and PTPA-AM, and the corresponding dipole moments ( $\mu$ : the unit of dipole moment is Debye) of PTPA-AQ and PTPA-AM. PTPA-AM has higher dipole-moment (0.9817 D) as compared to PTPA-AQ (0.3092 D). Due to higher dipole moment, PTPA-AM should have stronger exciton separation efficiency and efficient intramolecular charge transfer (ICT) ability.

### 3.8. Photocurrent measurement and EIS:



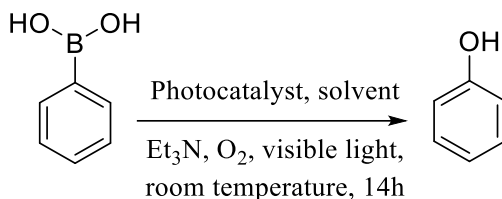
**Fig. S11.** (a) Transient photocurrent response of PTPA-AQ and PTPA-AM under visible-light irradiation. (b) EIS Nyquist plots of PTPA-AQ and PTPA-AM at open circuit voltage.

The transient photocurrent responses ( $I-t$ ) and electrochemical impedance spectra (EIS) are monitored to evaluate the separation and transfer rate of photogenerated electron-hole pairs. It can be seen from the  $I-t$  curve that the PTPA-AM ( $0.34 \mu\text{A}/\text{cm}^2$ ) displayed higher photocurrent density than that of PTPA-AQ ( $0.20 \mu\text{A}/\text{cm}^2$ ), proclaiming that much photoinduced electrons can be generated in case of PTPA-AM. The Nyquist plot also revealed that the arc radius of PTPA-AM is smaller than that of PTPA-AQ, further demonstrating better interfacial charge transfer kinetics for PTPA-AM.

## 4. Photocatalytic Application

### 4.1. Oxidative hydroxylation of phenyl boronic acid

**Table S1.** Photocatalyst screening and optimization of reaction conditions<sup>a</sup>



Entry	Catalyst	Solvent	Amine	Reaction time (h)	Yield <sup>b</sup>
1	PTPA-AQ	CH <sub>3</sub> CN	Et <sub>3</sub> N	10	77%
2	PTPA-AQ	CH <sub>3</sub> CN	Et <sub>3</sub> N	14	94%
3	PTPA-AQ	DCM	Et <sub>3</sub> N	14	91%
4	PTPA-AM	CH <sub>3</sub> CN	Et <sub>3</sub> N	14	56%

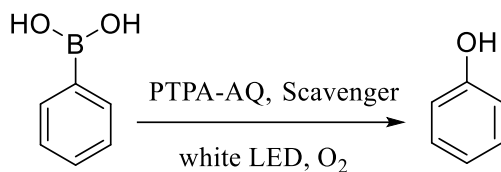
<sup>a</sup>Reaction conditions: Phenylboronic acid (0.25 mmol), photocatalyst (5 mg), Et<sub>3</sub>N (0.375 mmol), solvent (2 mL), white LED (18 W), O<sub>2</sub>, room temperature, 14 h. <sup>b</sup>The yield was determined after the isolation of the product.

**Table S2.** Control experiments for the photocatalytic oxidative hydroxylation of phenylboronic acid<sup>a</sup>

Entry	Catalyst	Solvent	Reaction condition	Yield
1	PTPA-AQ	CH <sub>3</sub> CN	In absence of O <sub>2</sub>	Trace
2	PTPA-AQ	CH <sub>3</sub> CN	In absence of catalyst	No conversion
3	PTPA-AQ	CH <sub>3</sub> CN	In open air	92%
4	PTPA-AQ	CH <sub>3</sub> CN	In absence of light	No conversion
5	PTPA-AQ	CH <sub>3</sub> CN	In absence of Et <sub>3</sub> N	Trace

<sup>a</sup>Reaction conditions: Phenylboronic acid (0.25 mmol), PTPA-AQ (5 mg), Et<sub>3</sub>N (0.375 mmol), CH<sub>3</sub>CN (2 mL), white LED (18 W), O<sub>2</sub>, room temperature, reaction time: 14 h.

**Table S3.** Control experiments for the photocatalytic oxidative hydroxylation of phenyl boronic acid<sup>a</sup>

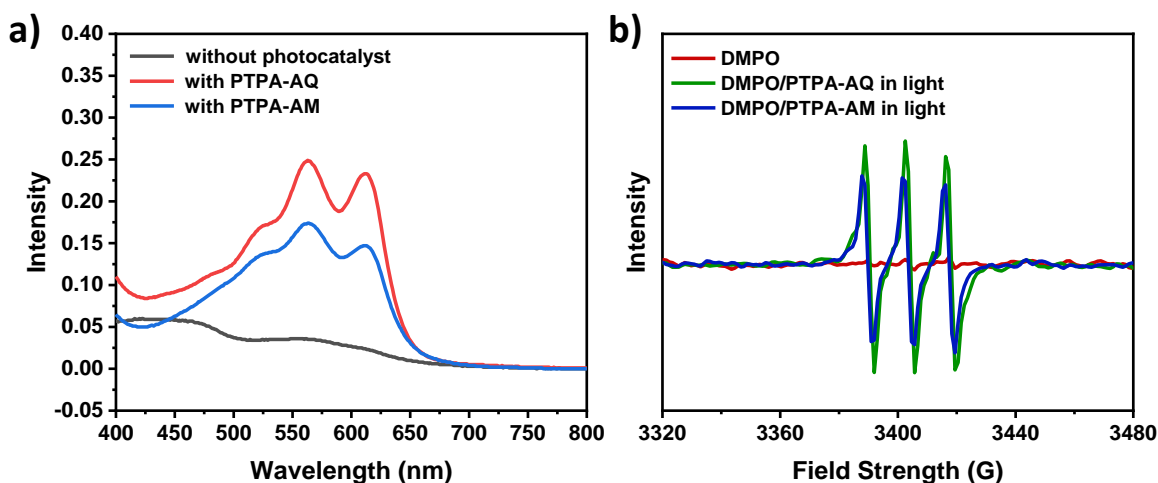


Entry	Scavenger	Yield <sup>b</sup>
1	p-benzoquinone	48%
2	CuCl <sub>2</sub>	43%
3	KI	68%
4	NaN <sub>3</sub>	94%

<sup>a</sup> Reaction conditions: Phenylboronic acid (0.25 mmol), PTPPA-AQ (5 mg), scavenger (5 mg), Et<sub>3</sub>N (0.375 mmol), CH<sub>3</sub>CN (2 mL), white LED (18 W), O<sub>2</sub>, room temperature, reaction time: 14 h.

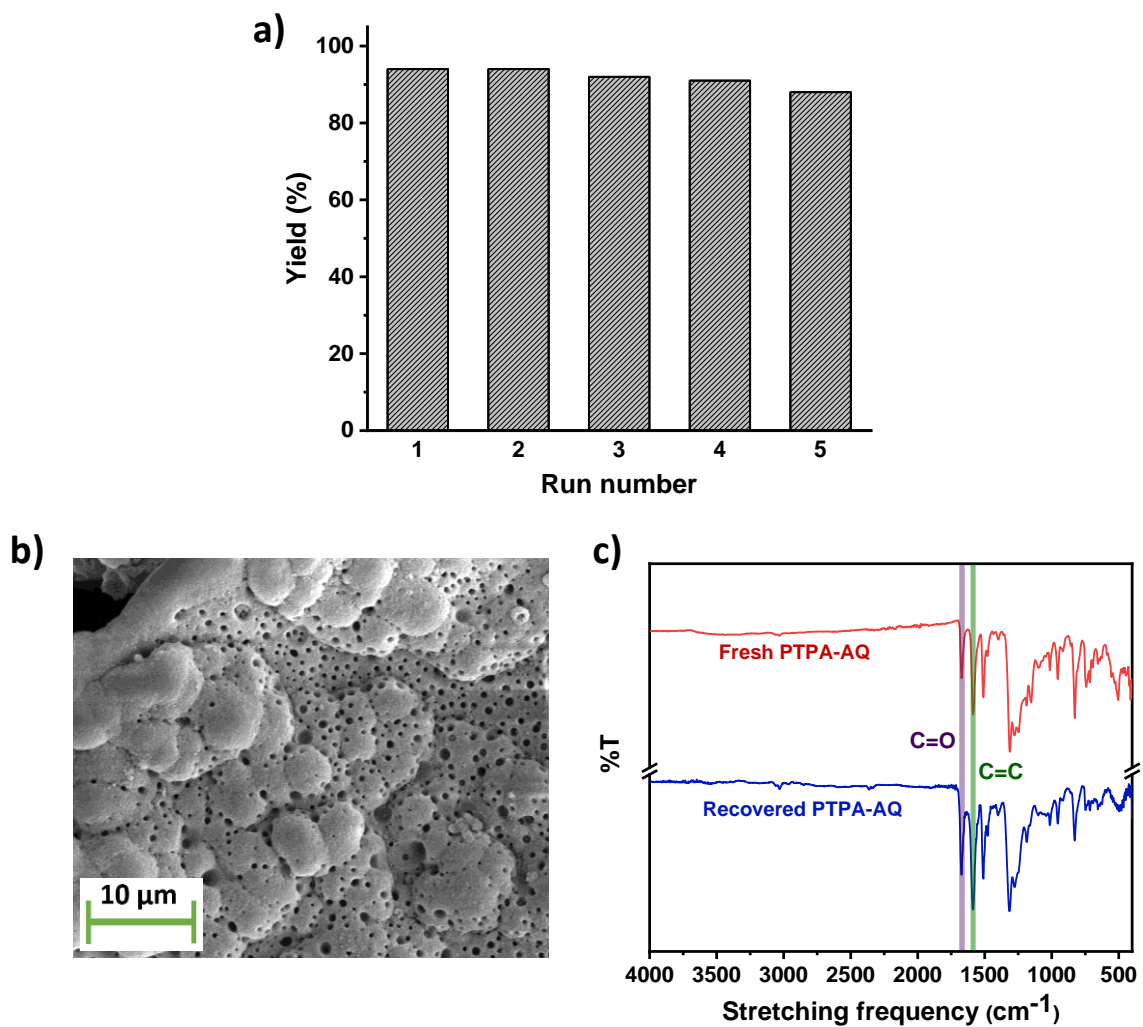
<sup>b</sup> The yield was determined after the isolation of the product.

**4.2. Generation of reactive oxygen species:** The generation of reactive oxygen species was confirmed by UV-Vis and EPR studies.



**Fig. S12.** a) Absorption spectra of the acetonitrile solution of N,N,N',N'-tetramethyl-*p*-phenylenediamine (NTPD) in the presence and absence of photocatalysts. b) Electron paramagnetic resonance (EPR) signals of DMPO in absence (red) and presence of PTPA-AQ (green) and PTPA-AM (blue) under light illumination for 45 min.

### 4.3. Reusability



**Fig. S13.** a) Reusability of PTPA-AQ in oxidative hydroxylation of phenylboronic acid. b) SEM image of recovered PTPA-AQ. c) FTIR spectra of recovered PTPA-AQ in comparison with fresh PTPA-AQ.



## 5. References

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- [4] H. Xu, X. Li, H. Hao, X. Dong, W. Sheng, X. Lang, *Appl. Catal. B: Environ.* **2021**, 285, 119796.