Supporting Information (SI)

Structural and Morphological Engineering of Benzothiadiazole-Based Covalent Organic Frameworks for Visible-Light-Driven Oxidative Coupling of Amines

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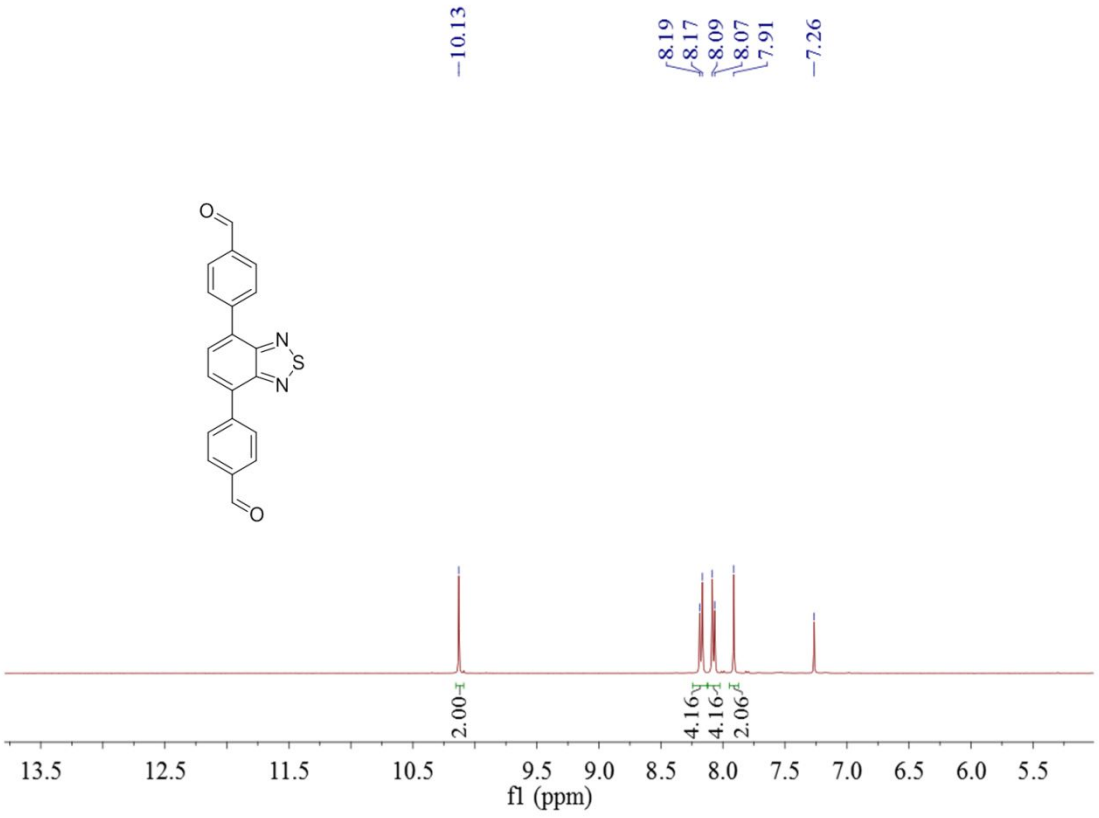
S1. Experimental Section

Materials and synthesis

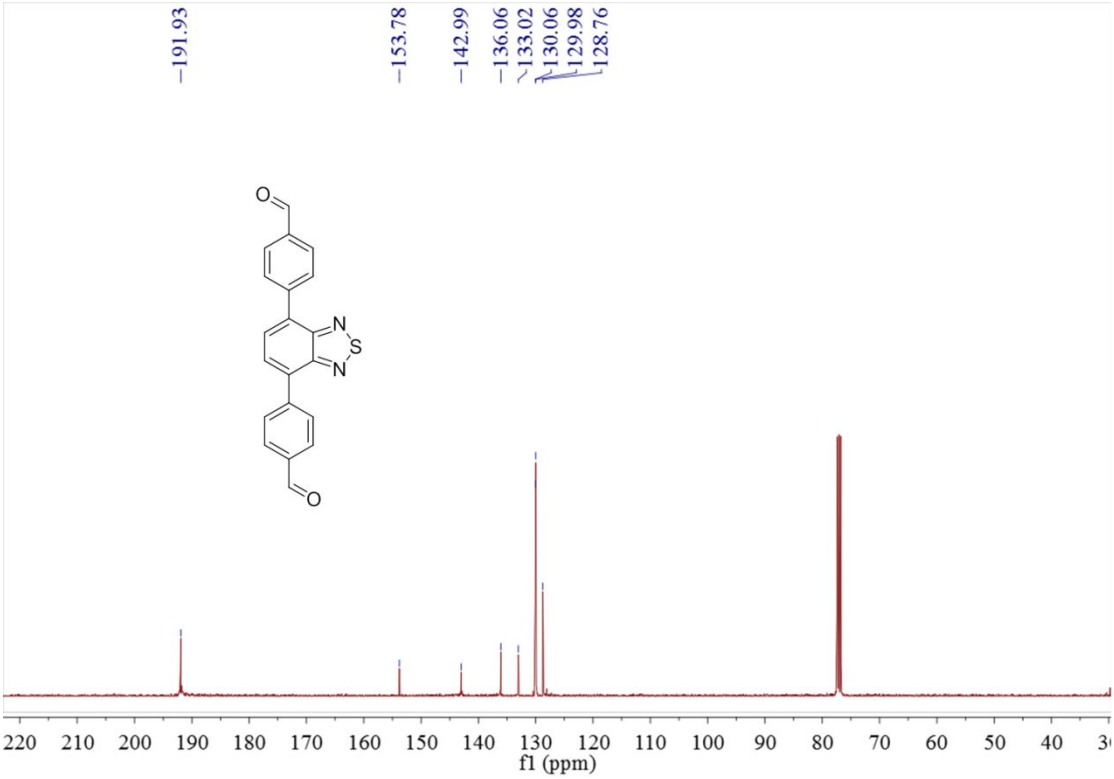
4,7-Dibromo-2,1,3-benzothiadiazole, tetrakis(triphenylphosphine)palladium(0), 4-formylphenylboronic acid, 4-aminobenzonitrile, *p*-benzoquionone, 1,3,5-tris(4-aminophenyl) benzene (TAPB), *N,N*-diethyl-1,4-phenylenediamine (DPD) and benzylamine derivatives were obtained from Energy Chemical Co. Ltd. and *J&K* Scientific Co. Ltd. *p*-Phthalaldehyde, trifluoromethanesulfonic acid and *p*-tolunitrile were purchased from Aladdin Chemicals. Potassium iodide (KI), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), hydroquinone, silver nitrate ($AgNO_3$), tertiary butanol (*t*-BuOH), potassium bromide (KBr) and all the solvents were purchased from local supplier (Baoding Huaxin Reagent and Apparatus Co. Ltd.). Chemicals involved in this work were used as received without further purification unless note.

Synthesis of 4,4'-(Benzothiadiazole-4,7-diyl)dibenzaldehyde

4,4'-(Benzothiadiazole-4,7-diyl)dibenzaldehyde was synthesized according to the previous literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 10.13 (s, 2H), 8.18 (d, J = 8.0 Hz, 4H), 8.08 (d, J = 8.0 Hz, 4H), 7.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 191.93, 153.78, 142.99, 136.06, 133.02, 130.06, 129.98, 128.76.



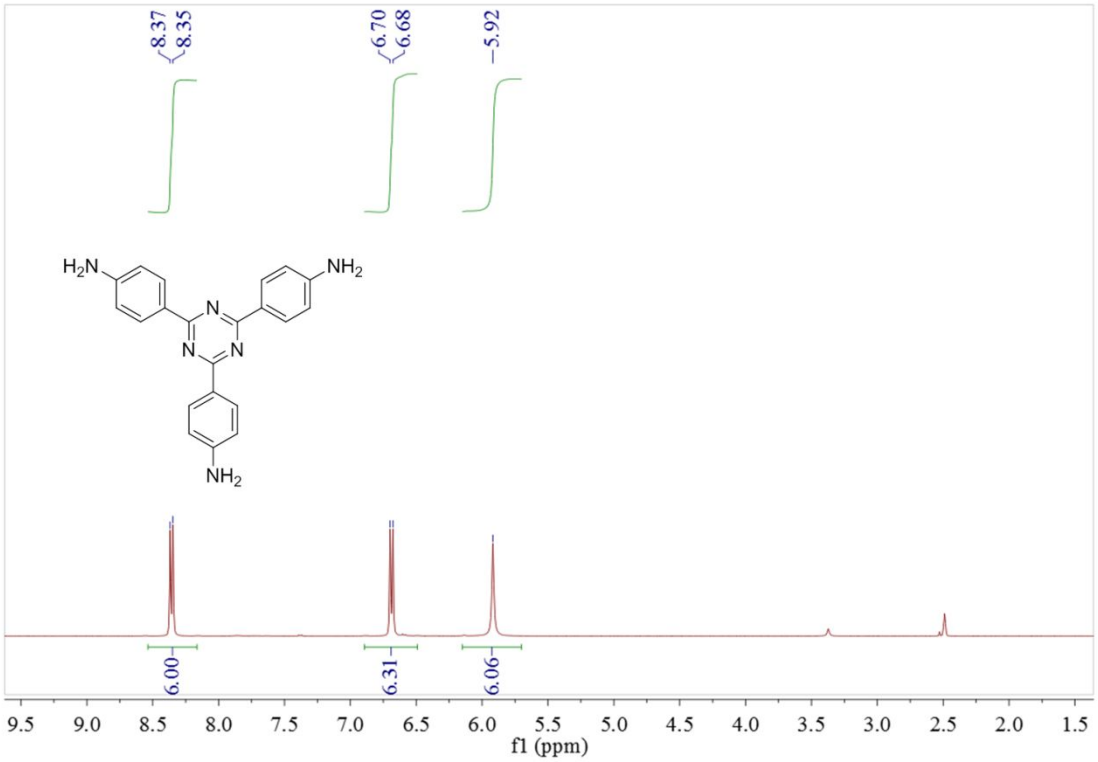
^{1}H NMR spectrum of 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde



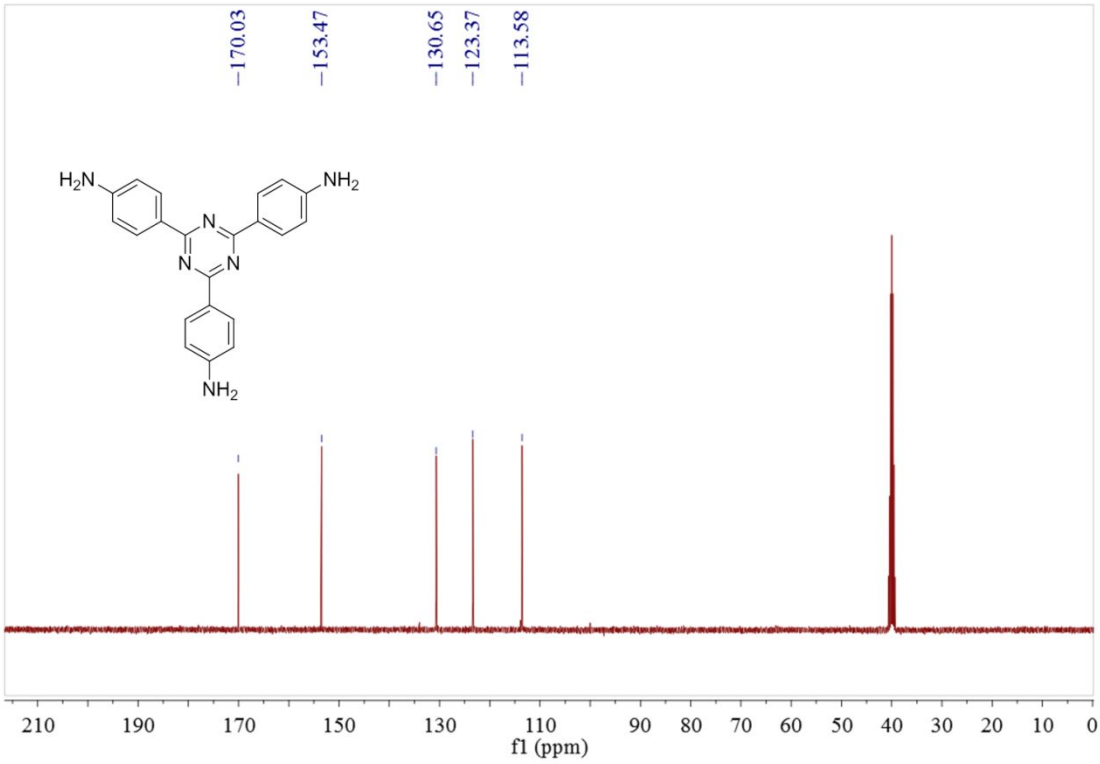
^{13}C NMR spectrum of 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde

Synthesis of 1,3,5-tris-(4-aminophenyl)triazine (TAPT)

1,3,5-Tris-(4-aminophenyl)triazine was synthesized according to the previous literature.[2] ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 8.36 (d, J = 8.0 Hz, 6H), 6.69 (d, J = 8.0 Hz, 6H), 5.92 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm):170.03, 153.47, 130.65, 123.37, 113.58.



^{1}H NMR spectrum of 1,3,5-tris-(4-aminophenyl)triazine



^{13}C NMR spectrum of 1,3,5-tris-(4-aminophenyl)triazine

Quenching experiments

A series of scavengers such as hydroquinone, $AgNO_3$, KI, *p*-benzoquinone (BQ), TEMPO and

t-BuOH were employed as trapping agents for free radical, electron, hole, superoxide radical ($\bullet O_2^-$), singlet oxygen ($^1O_2$), hydroxyl radical (•OH), respectively. For the trapping experiments, apart from that 10 mg of scavengers was added into the reaction mixture with the BTDA-TAPT, the procedure was completely same with that mentioned-above.

Detection of reactive oxygen species (ROS) by ESR measurements

The active trapping experiments were conducted by adding different types of excess trapping agents into reaction system, which was then monitored by *in situ* ESR measurements. DMPO, TEMP and $AgNO_3$ were used to trap the $\bullet O_2^-$, $^1O_2$ and electrons, respectively. In a typical measurement, 10 mg BTDA-TAPT and 0.1 M DMPO or TEMP or $AgNO_3$ were added into a quartz tube with charged acetonitrile (1 mL) under oxygen atmosphere. The signals of 0 min in dark and after 3 min illumination were collected. After that, the mixture was detected again after adding benzylamine (0.1 mmol) under light illumination (300 W Xe lamp with 420nm UVCUT) for 3 min.

ATR-FT-IR measurements

The photocatalytic oxidative coupling of benzylamine with increasing reaction time was surveyed by *ex situ* ATR–FTIR spectra to identify the key reaction intermediates. The typical procedure was as follows: BTDA-TAPT (10 mg) was ultrasonically dispersed into 3 mL acetonitrile solution of 1.0 mmol amines in a quartz glass vial, which was then carefully placed into the stainless-steel top-visible reactor and charged oxygen pressure into 0.1 Mpa. Prior to light irradiation, the mixtures were stirred for 60 min in the dark to achieve adsorption-desorption equilibrium. Afterwards, a 300 W xenon lamp (15 A, PLS-SXE 300) with a 420 nm-cut filter was used as a light source and illuminated from the reactor's top to the reaction solution (the distance in about 8 cm) under magnetic stirring for a suitable reaction time. Subsequently, the reaction mixture was taken out every one hour, which was recorded by dropping the mixture on the ATR accessories.

The DPD control experiment.

In a typical test, BTDA-TAPT (10 mg) was ultrasonically dispersed into 3 mL acetonitrile solution of 0.5 mmol amines in a quartz glass vial, and then 5 μL *N,N*-diethyl-1,4-phenylenediamine (DPD) was added into this solution. The reaction process was very similar with reaction procedure above-mentioned. After every one hour interval, the solution was tested by a UV-vis spectrophotometry.

S2. Sectional Results and Figures

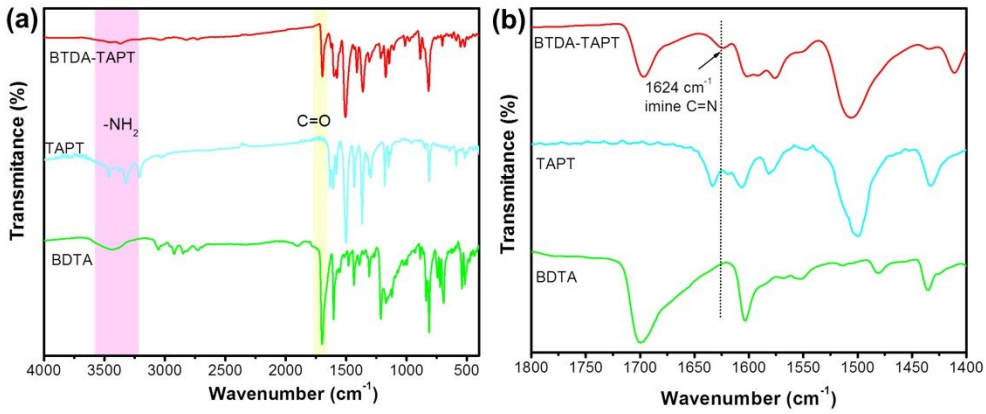


Figure S1. FT-IR spectra of (a) BTDA-TAPT and its monomers with its (b) partial enlarged detail.

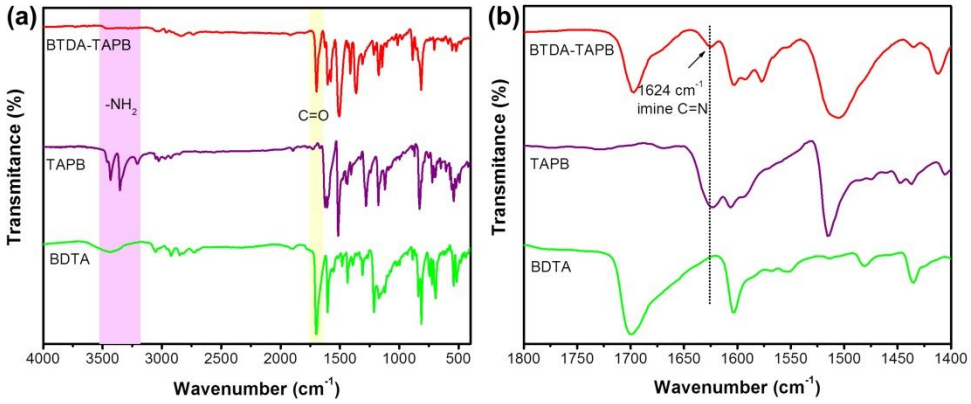


Figure S2. FT-IR spectra of (a) BTDA-TAPB and its monomers with its (b) partial enlarged detail.

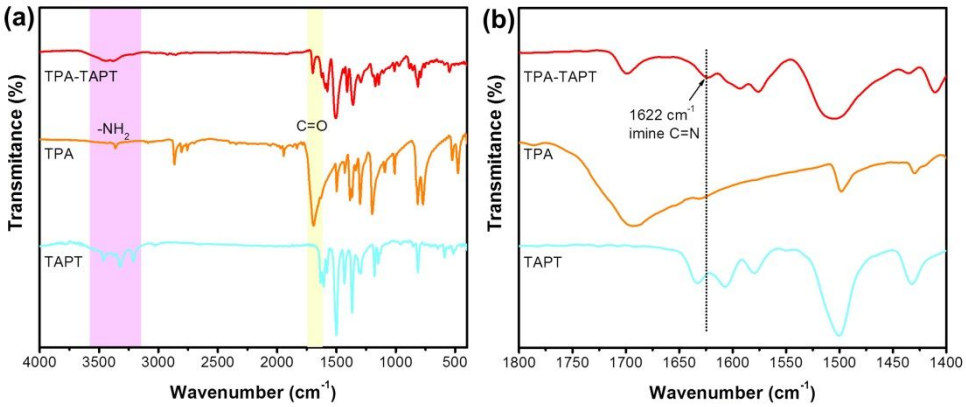


Figure S3. FT-IR spectra of (a) TPA-TAPT and its monomers with its (b) partial enlarged detail.

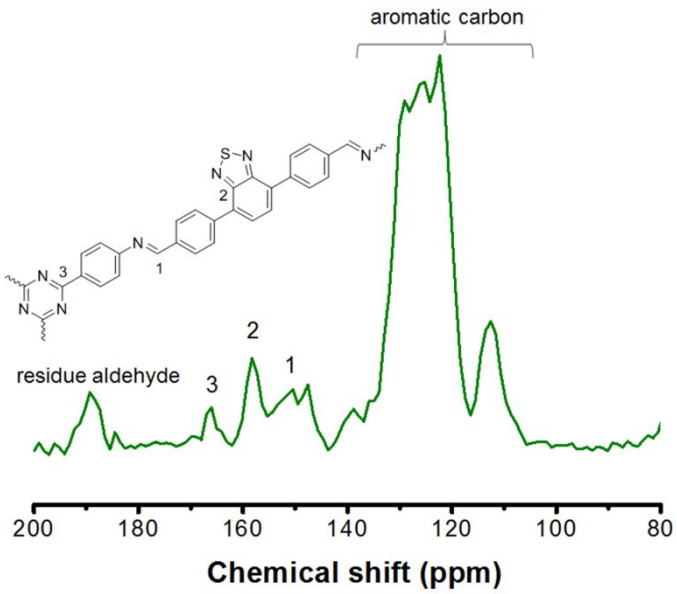


Figure S4. ^{13}C CP-MAS NMR of BTDA-TAPT.

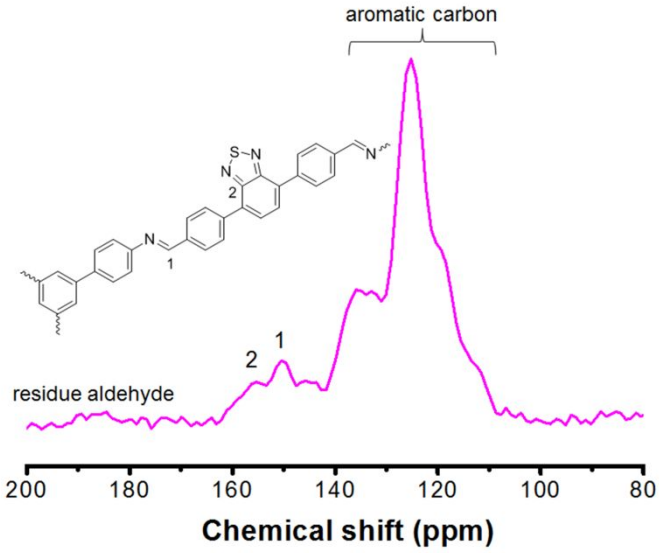


Figure S5. ^{13}C CP-MAS NMR of BTDA-TAPB.

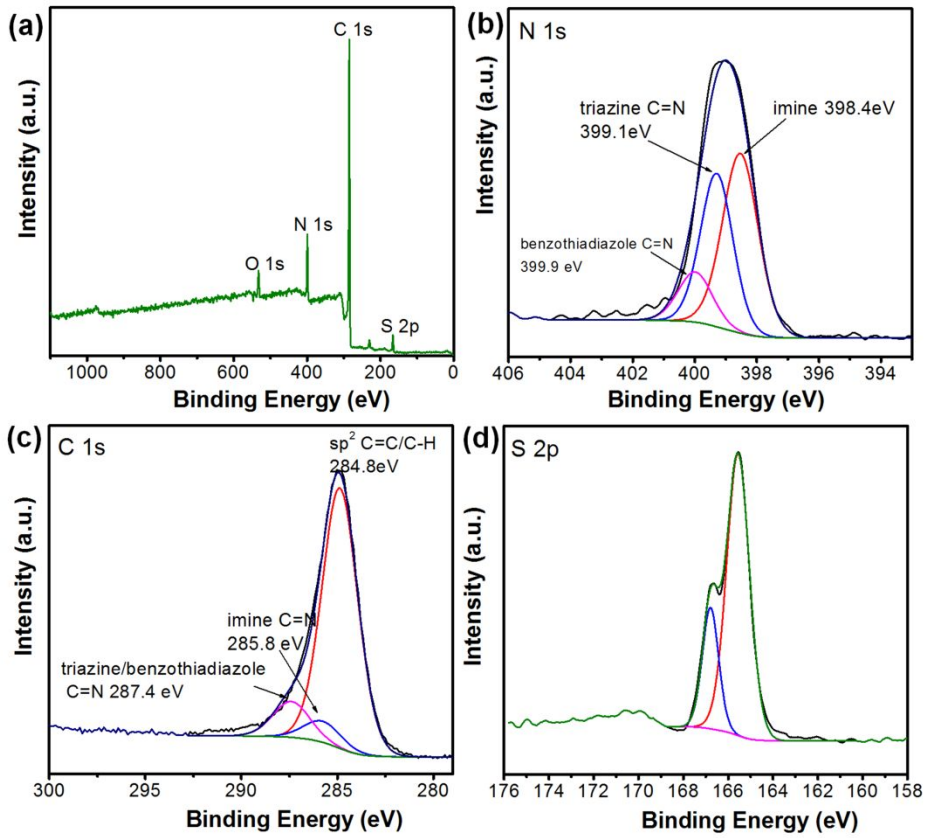


Figure S6. XPS spectra of BTDA-TAPT. (a) Survey, (b) N 1s, (c) C 1s, and (d) S 2p.

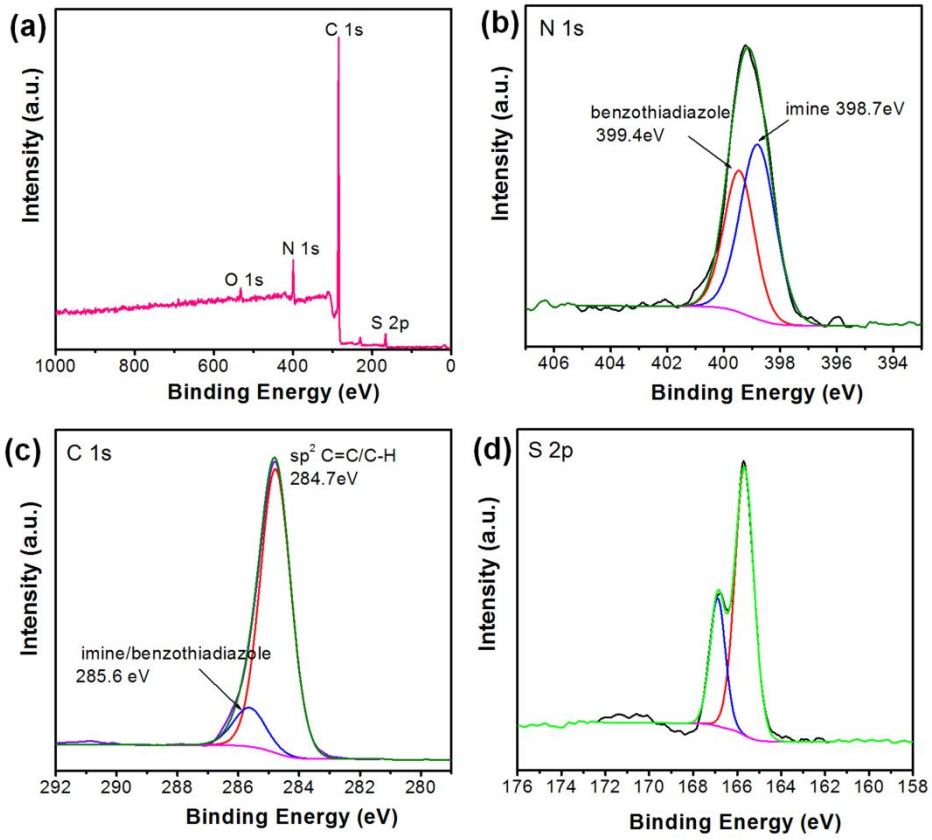


Figure S7. XPS spectra of BTDA-TAPB. (a) Survey, (b) N 1s, (c) C 1s, and (d) S 2p.

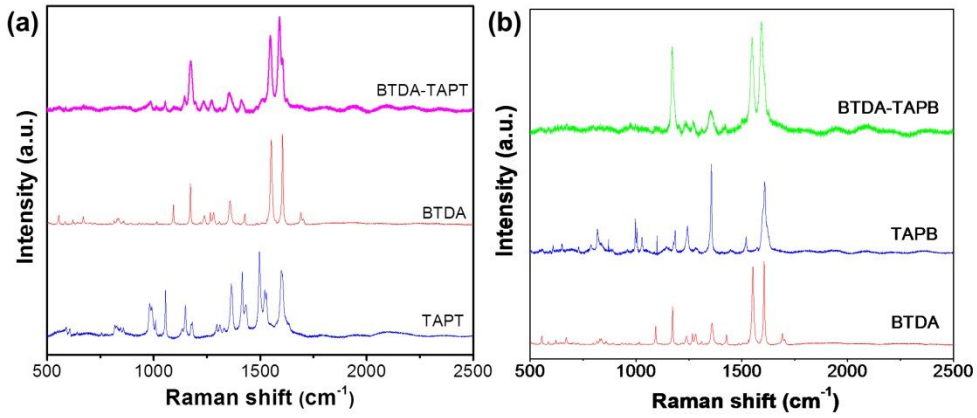


Figure S8. Raman spectra of (a) BTDA-TAPT and (b) BTDA-TAPB with their corresponding monomers.

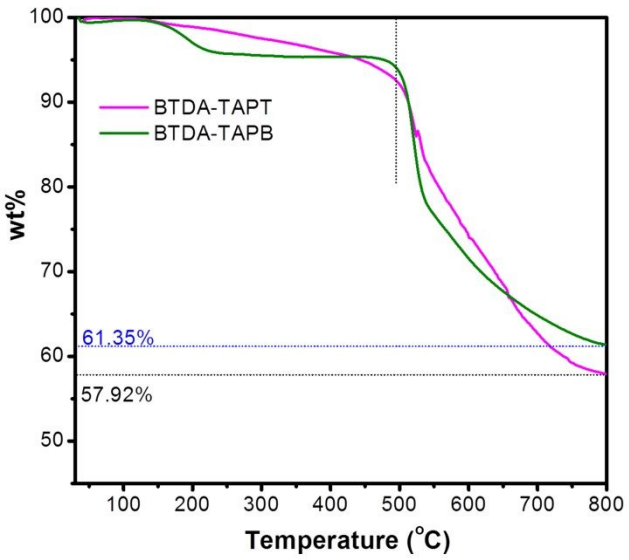


Figure S9. TGA curves of BTDA-TAPT and BTDA-TAPB.

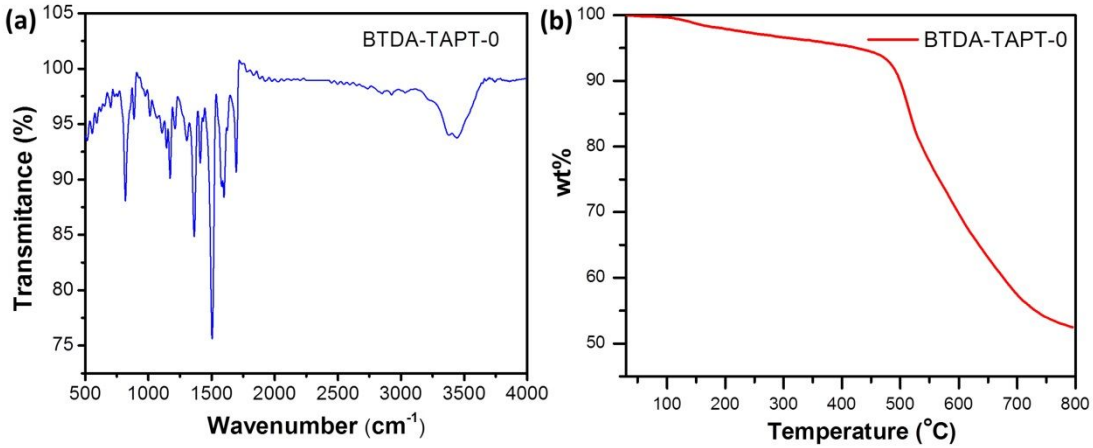


Figure S10. (a) FT-IR spectrum and (b) TGA curve of BTDA-TAPT-0.

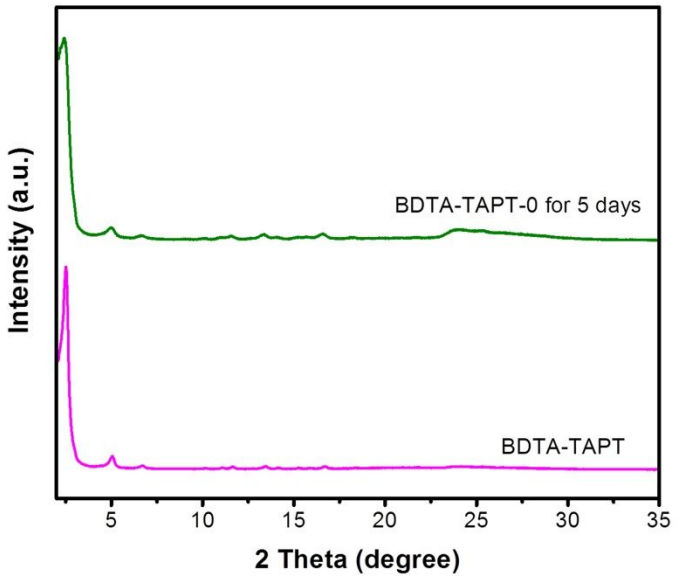


Figure S11. PXRD patterns of BDTA-TAPT in 550 rmp for 3 days and BDTA-TAPT-0 in 0 rmp for 5 days.

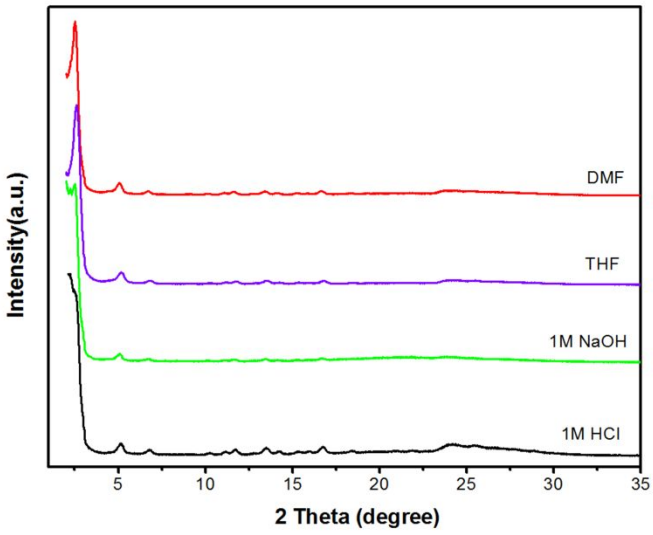


Figure S12. PXRD patterns of BTDA-TAPT in different solvents for 2 days.

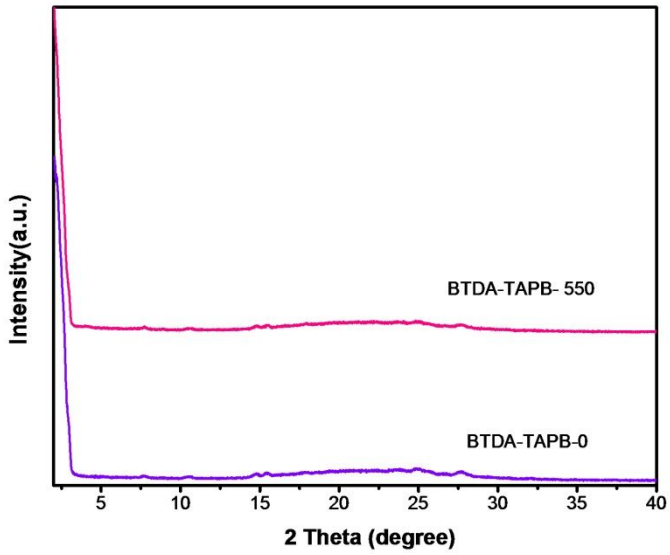


Figure S13. PXRD patterns of BTDA-TAPB in 0 and 550 rmp for 3 days.

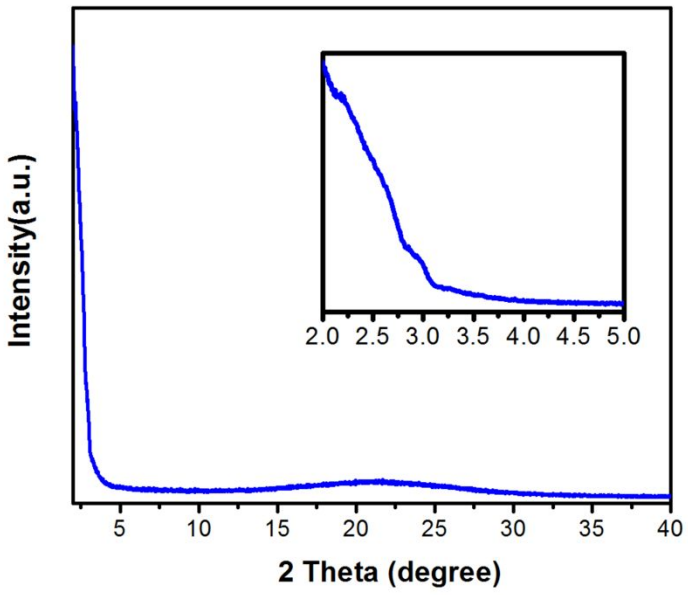


Figure S14. PXRD pattern of TPA-TAPT.

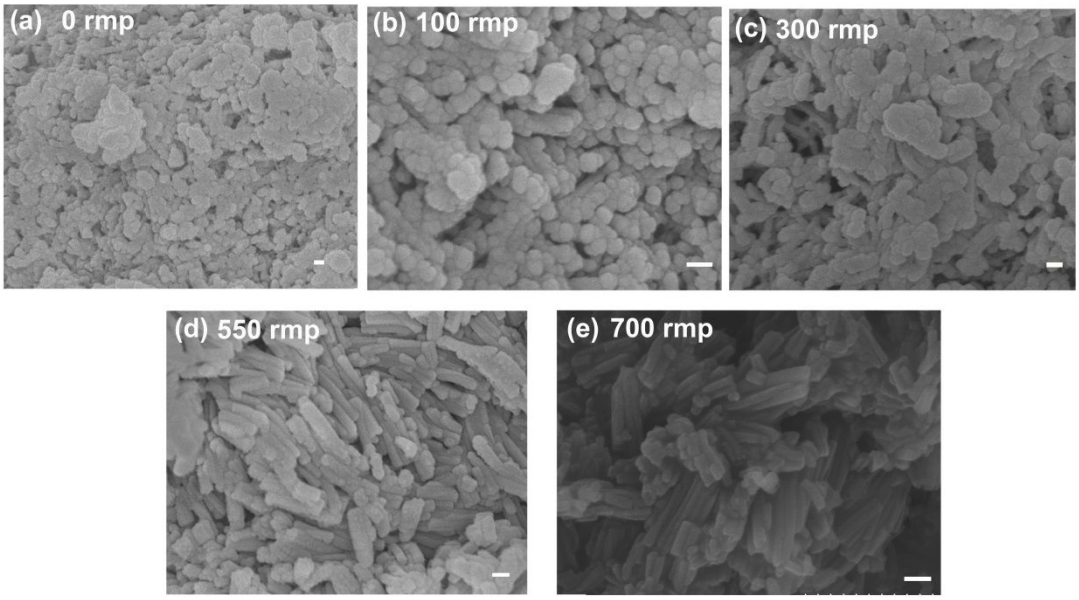


Figure S15. SEM images of BTDA-TAPT obtained with stirring rate at (a) 0, (b)100, (c) 300, (d) 550, (e) 700 rmp. The scale bar 100 nm.

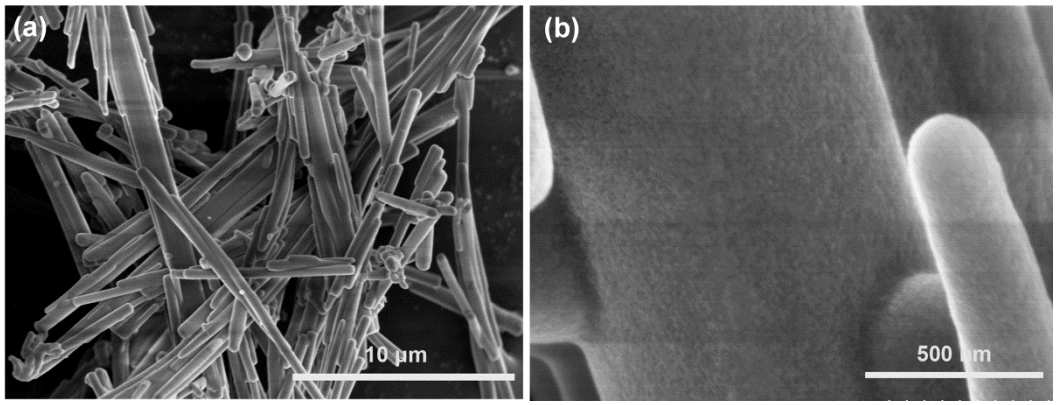


Figure S16. SEM images of BTDA-TAPB with (a) 10 μm and (b) 500 nm scaleplate

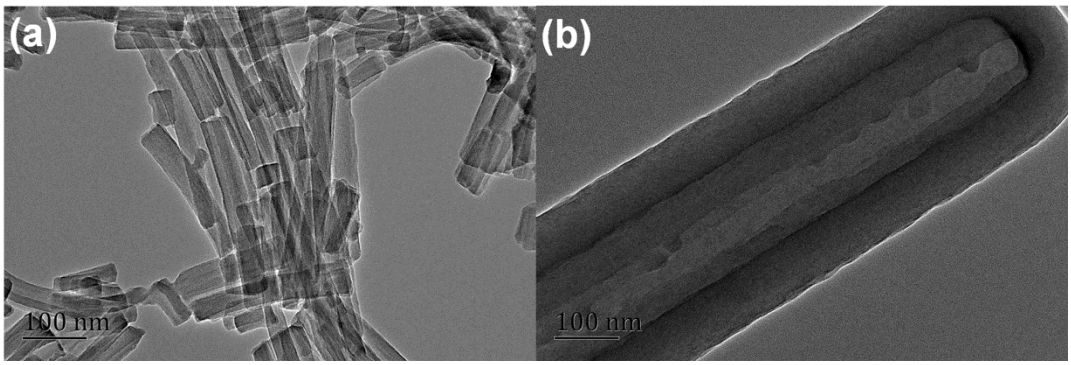


Figure S17. TEM images of (a) BTDA-TAPT and (b) BTDA-TAPB.

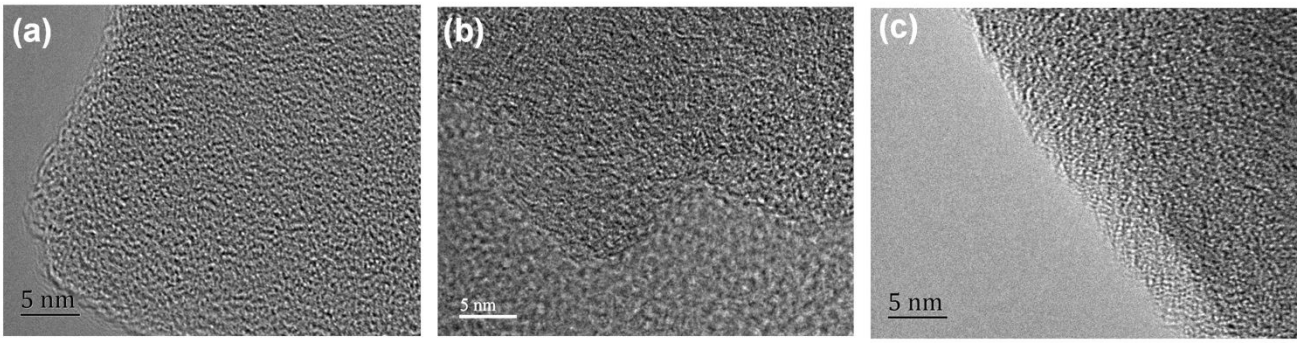


Figure S18. HRTEM images of (a) BTDA-TAPT, (b) BTDA-TAPT-0, and (c) BTDA-TAPB.

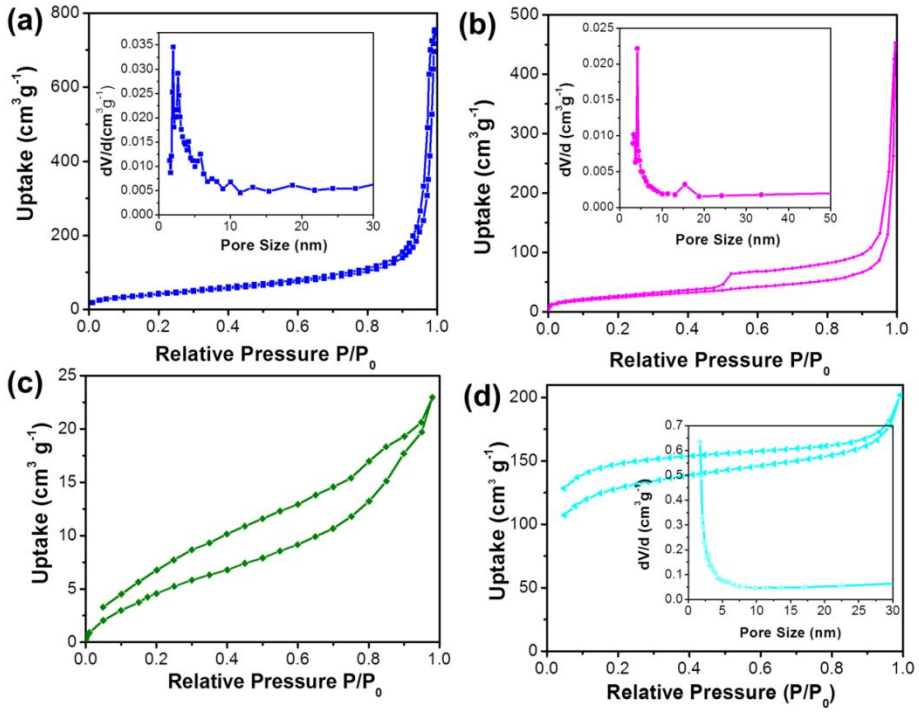


Figure S19. N_2 adsorption-desorption analyses of (a) BTDA-TAPT, (b) BTDA-TAPT-0, (c) BTDA-TAPB and (d) TPA-TAPT.

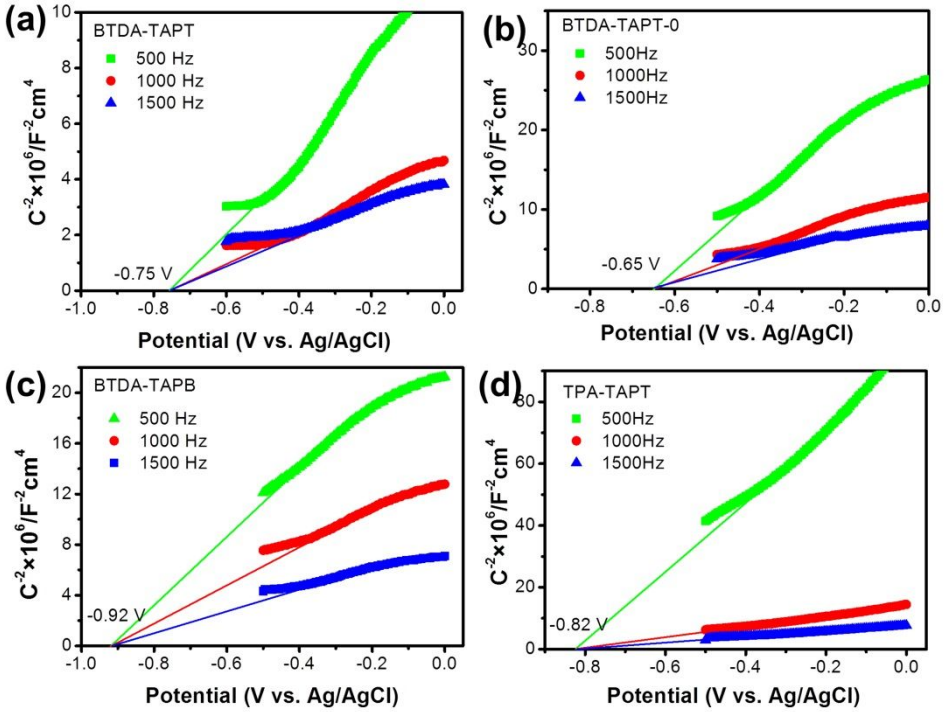


Figure S20. Mott-Schottky plots of (a) BTDA-TAPT, (b) BTDA-TAPT-0, (c) BTDA-TAPB and (d) TPA-TAPT.

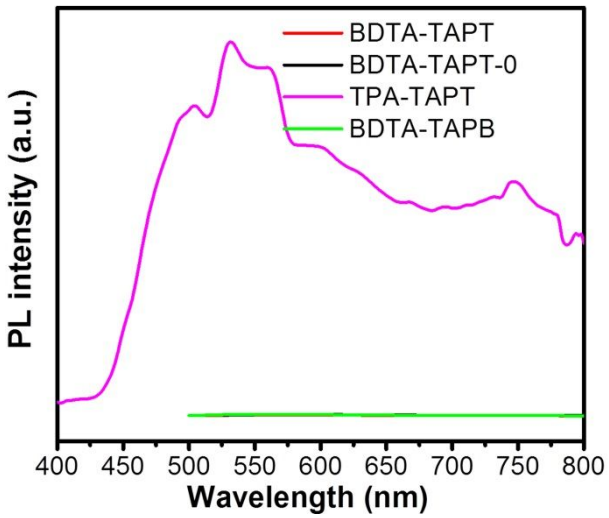


Figure S21. PL spectra of BTDA-TAPT, BTDA-TAPT-0, BTDA-TAPB (excitation wavelength at 450 nm) and TPA-TAPT (excitation wavelength at 223 nm).

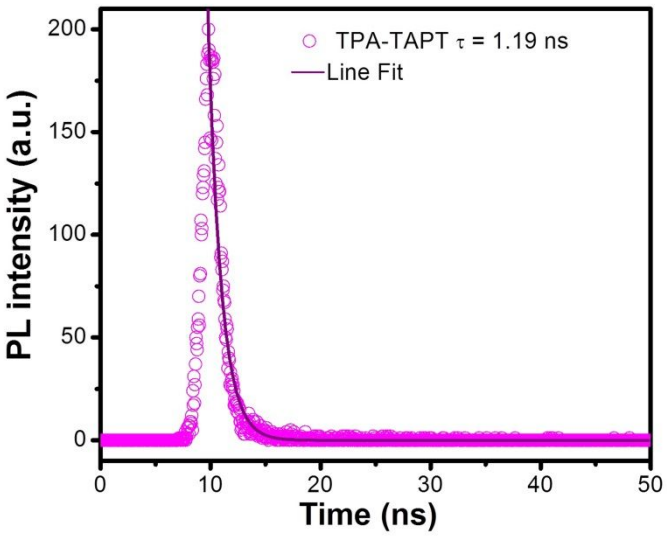


Figure S22. PL lifetime of TPA-TAPT with excitation wavelength at 223 nm.

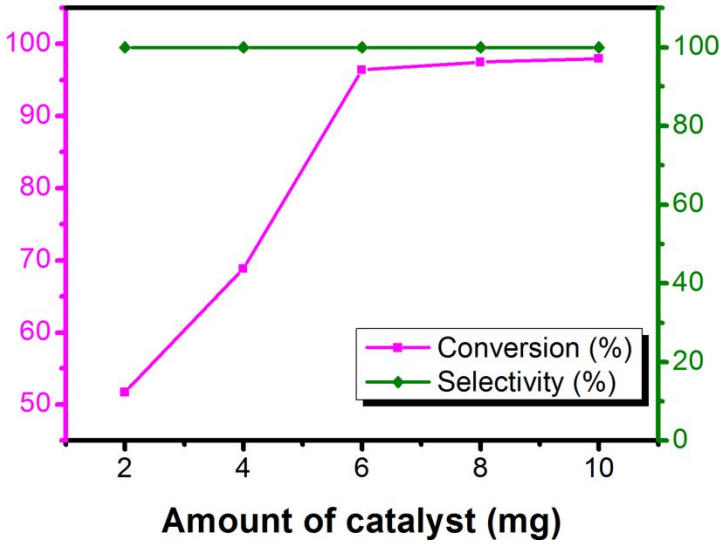


Figure S23. The influence of photocatalyst concentration for this reaction. Reaction conditions: benzylamine (0.1 mmol), BTDA-TAPT photocatalyst, acetonitrile (3 mL), O_2 (1 atm), 300 W Xe lamp (λ = 420-780 nm), room temperature, 3.0 h.

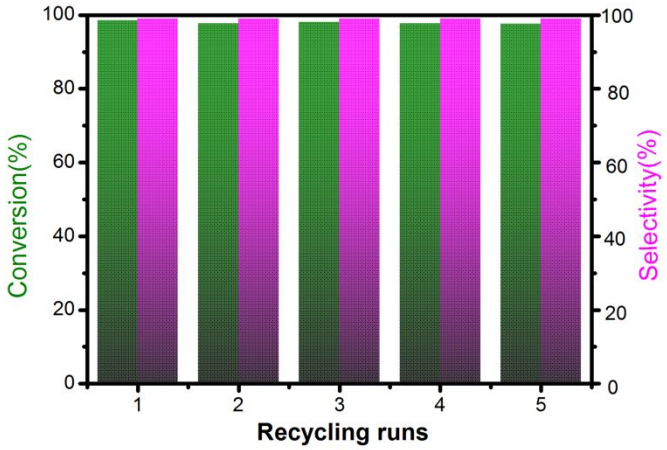


Figure S24. Stability of BTDA-TAPT photocatalyst for the oxidative coupling of benzylamine under visible light irradiation.

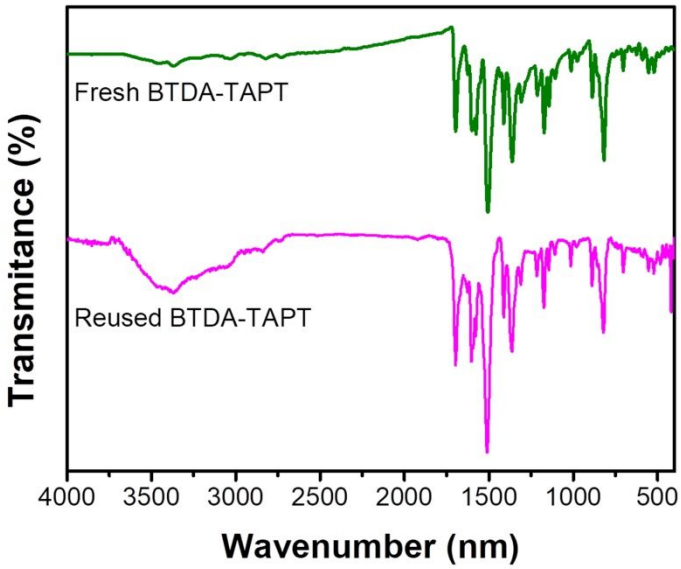


Figure S25. FT-IR spectra of fresh and reused BTDA-TAPT.

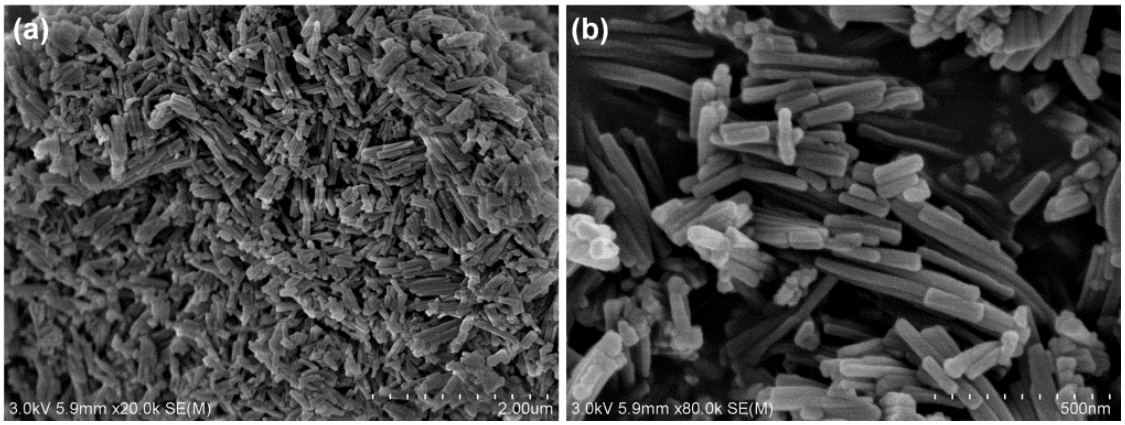


Figure S26. (a, b) SEM images of used BTDA-TAPT after five cycles.

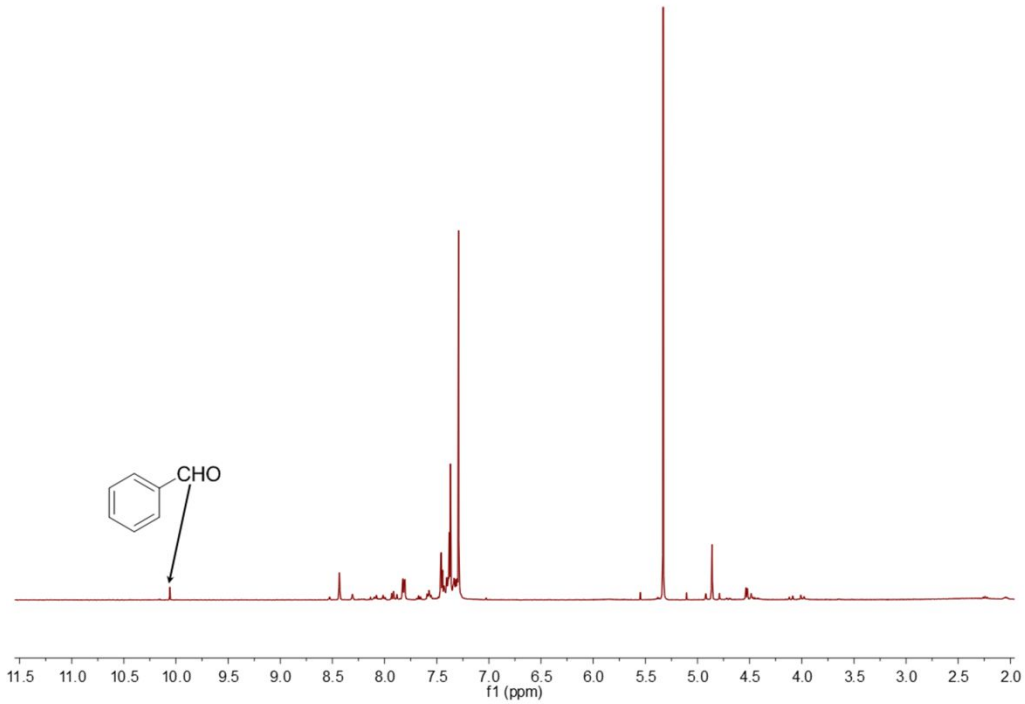


Figure S27. ^{1}H NMR spectrum of the reaction mixture of the photocatalytic benzylamine oxidation with BTDA-TAPT after 3 h. The typical peaks at 10.06 ppm was ascribed to hydrogen atom of the aldehyde group belonged to generated benzaldehyde from benzylamine.

References

(1) Li, Z.; Zhi, Y.; Shao, P.; Xia, H.; Li, G.; Feng, X.; Chen, X.; Shi, Z.; Liu, X. Covalent organic framework as an efficient, metal-free, heterogeneous photocatalyst for organic transformations under visible light, *Appl. Catal. B: Environ.* **2019**, *245*, 334-342.

(2) Gomes, R.; Bhanja P.; Bhaumik, A. A triazine-based covalent organic polymer for efficient CO_2 adsorption, *Chem. Commun.* **2015**, *51*, 10050-10053.