

Supporting Information

“Greener” and modular synthesis of triazine-based conjugated porous polymers via direct arylation polymerization: structure-function relationship and photocatalytic application

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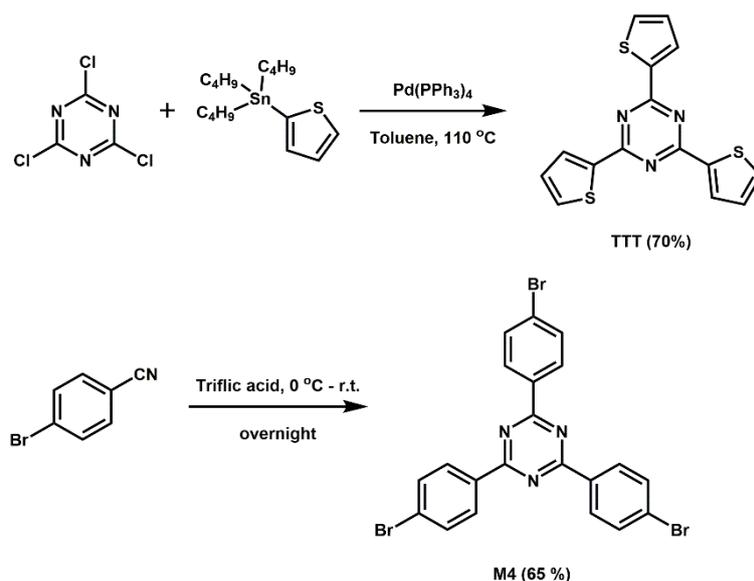
Materials and methods

1,3,5-Tribromobenzene (**M1**), tris-(4-bromophenyl)amine (**M2**) and 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (**M3**) were purchased from Sigma Aldrich. 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine (**TTT**)¹ and 2,4,6-tri(4-bromophenyl)-1,3,5-triazine (**M4**)² were synthesized according to literature procedure. All solvents were obtained from commercial sources and used as received unless otherwise specified. ¹H-NMR was performed on a Bruker AV 300 spectrometer in deuterated chloroform (CDCl₃) at room temperature with TMS as internal reference; chemical shifts (δ) are reported in parts per million. Solid state ¹³C magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were collected by a JEOL ECA 400 spectrometer. FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Thermo- gravimetric analyses were performed on a Pyris Diamond TGA (Perkin Elmer) instrument, at a heating rate of 10 °C min⁻¹ under N₂ atmosphere from 40 °C to 700 °C. SEM imaging was carried out using a JEOL JSM 6701F SEM (Scanning Electron Microscope) operating in scanning mode. Samples were prepared by depositing dry samples on aluminum stubs using an adhesive high purity carbon tape. TEM images were obtained using a Carl Zeiss Libra 120 Plus transmission electron microscope (TEM). Nitrogen sorption isotherms were obtained at 77 K using Quantachrome Instruments Autosorb-6 with extra-high purity gases. All samples were degassed at 110 °C for 16 h in vacuum before analysis. Surface areas were calculated in the relative pressure (p/p⁰) range from 0.05 to 0.35 of the adsorption branch. Pore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) method using the adsorption curve of the isotherm. The total pore volume was estimated by the amount of nitrogen adsorbed at the relative pressure of 0.99. The UV-visible absorption spectra were obtained on a UV-visible spectrophotometer (UV-2450, Shimadzu). Cyclic voltammograms (CVs) were recorded on an CHI Electrochemical Analyzer Model 660D at room temperature using 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte at a scan rate of 100 mV/s. Glassy carbon was used as working electrode, platinum wire as counter electrode and silver as the reference electrode. CVs of CPP-(1-3) were measured in 0.1 M electrolyte solution in CH₃CN by drop-casting a suspension of CPPs and Nafion on the glassy carbon electrode. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc⁺). Powder X-ray diffraction patterns were obtained at 40 kV and 40 mA on a Bruker Advanced D8 XRD using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) over 2θ range of 5.0° - 60° at room temperature. Elemental analysis was carried out on a Vario EL III CHNS Elemental Analyzer. Palladium content was measured by inductively coupled plasma-optical

emission spectrometer ICP-OES using Prodigy High Dispersion ICP. Samples were prepared by digesting the 10 mg of polymers in a solution of HNO₃ (70 %)/HCl (37 %) (2.5/0.5 v/v) at 120 °C for 2 days.³

General procedure for photocatalyzed oxidative coupling of benzylamine: A 15 cm pyrex tube (1 cm dia.) was charged with 107 mg (1 mmol) of benzylamine, 6 mg of the polymer (**P1-4**) as the photocatalyst and 3 mL of CH₃CN. The tube was sealed with a rubber septum and oxygen was bubbled into the solution at 1 atm. The tube was placed in a water bath at room temperature and irradiated with 20W white LED lights for 5 hours. To test the stability of the photocatalyst, the polymers were recycled by first diluting the reaction mixture with THF and sonicating the solution for 5 minutes. The solution was then centrifuged at 8000 rpm for 8 minutes after which the solvent was decanted. This process was repeated three times to ensure removal of all reactants and products. The catalyst was then dried at 60° C and reused for the next cycle.

Synthesis of monomers



Scheme S1 Synthesis of triazine-core monomers, 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine (**TTT**) and 2,4,6-tri(4-bromophenyl)-1,3,5-triazine (**M4**).

2,4,6-tri(thiophen-2-yl)-1,3,5-triazine (TTT). (2.5 g, 70 %). ¹H NMR (CDCl₃, 300 MHz) δ ppm, 7.97 (m, 3 H), 7.63 (m, 3 H), 7.21 (m, 3 H).

2,4,6-tri(4-bromophenyl)-1,3,5-triazine (M4). (650 mg, 65 %). ¹H NMR (CDCl₃, 300 MHz) δ ppm, 8.56 (d, 6H), 7.68 (d, 6H)

Table S1 Elemental analysis of triazine polymers synthesised with C-H : C-Br ratio of 1:1.

Element (wt %)	P1-1		P2-1		P3-1		P4-1	
	C ₂₁ H ₉ N ₃ S ₃		C ₃₃ H ₁₈ N ₄ S ₃		C ₁₃₅ H ₆₀ N ₁₂ S ₁₂		C ₃₆ H ₁₈ N ₆ S ₃	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
C	63.2	59.5	70.0	66.7	72.6	66.5	68.6	65.4
H	2.3	1.2	3.2	1.4	2.7	1.5	2.9	1.5
N	10.5	8.6	9.9	8.3	7.5	6.0	13.3	11.1
S	24.1	19.6	17.0	14.3	17.2	13.6	15.2	12.7

Table S2 Elemental analysis of triazine polymers synthesised with C-H : C-Br ratio of 1.5:1.

Element (wt %)	P1-1.5		P2-1.5		P3-1.5		P4-1.5	
	C _{28.5} H ₁₂ N _{4.5} S _{4.5}		C _{40.5} H ₂₁ N _{5.5} S _{4.5}		C ₁₆₅ H ₇₂ N ₁₈ S ₁₈		C _{43.5} H ₂₁ N _{7.5} S _{4.5}	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
C	61	59.5	66.8	66.7	68.8	65	66	63.2
H	2.1	1.3	2.9	1.6	2.5	1.3	2.7	1.3
N	11.2	9.6	10.6	9.0	8.8	7.0	13.3	11.5
S	25.7	21.9	19.8	16.4	20.0	15.8	18.2	16.0

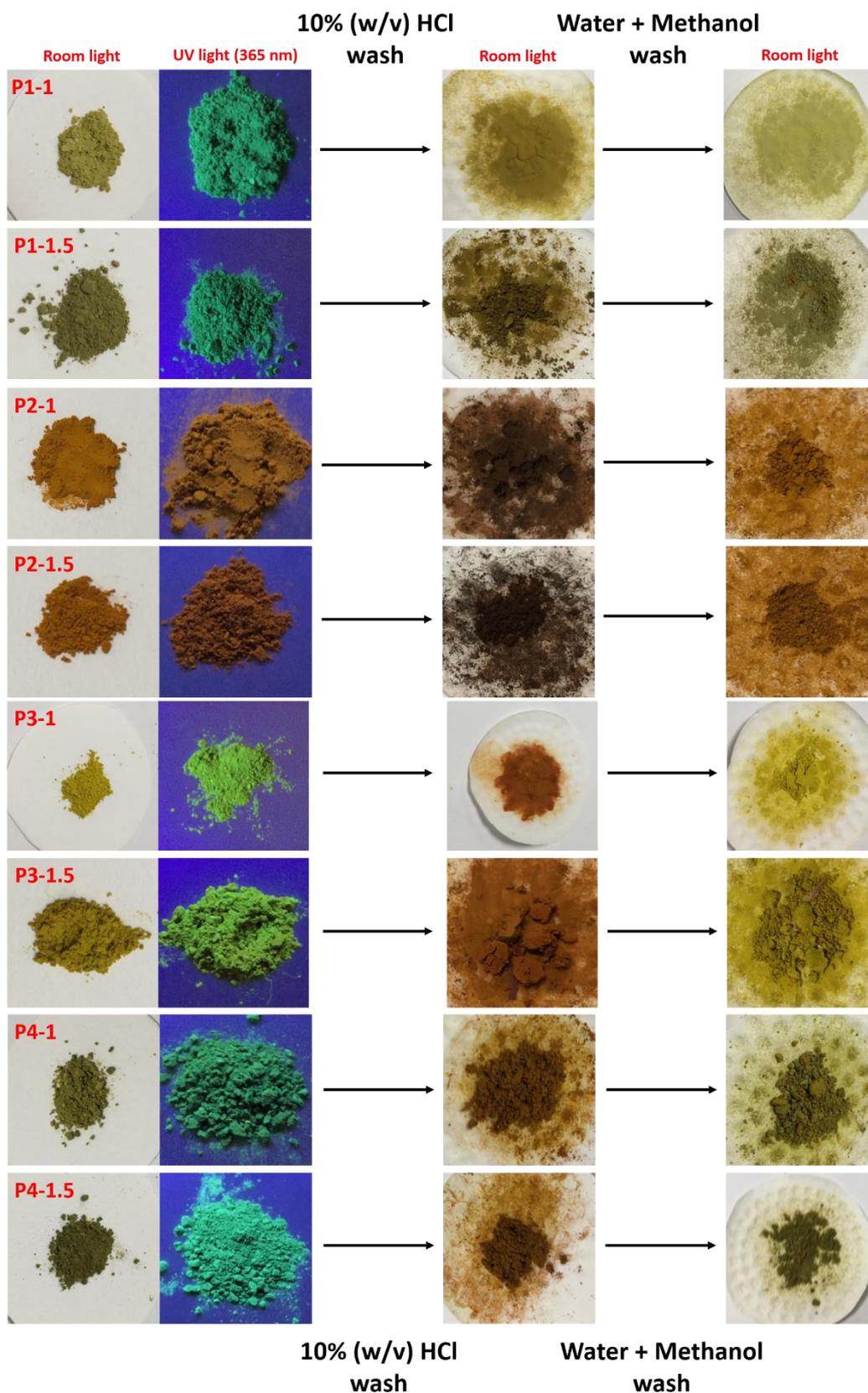


Figure S1 Digital images of pristine polymers under room light and UV (365 nm) light (left column); after washing with 10% (w/v) HCl (center column) and after washing with water and methanol (right column).

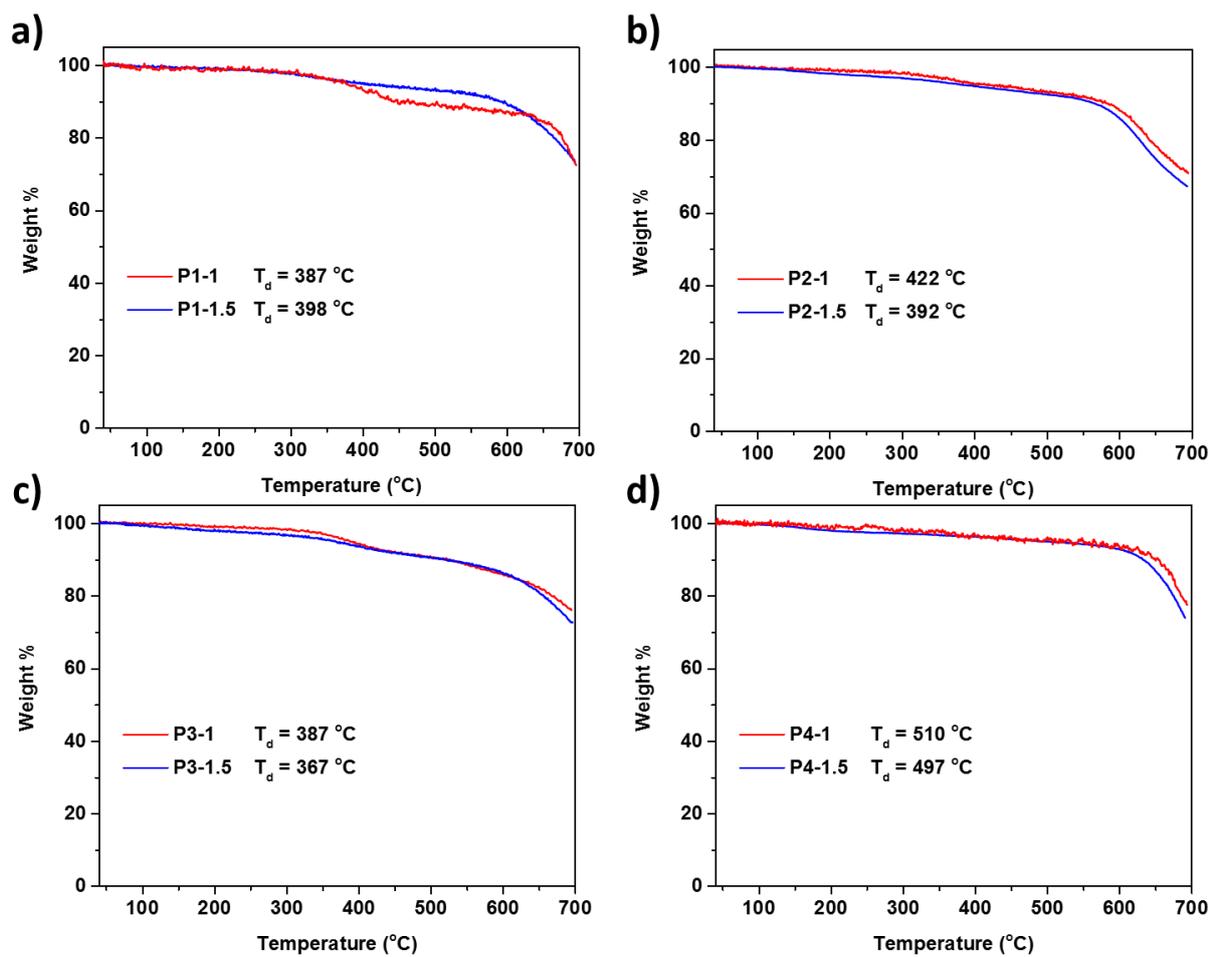


Figure S2 TGA plots of triazine polymers synthesized by direct arylation.

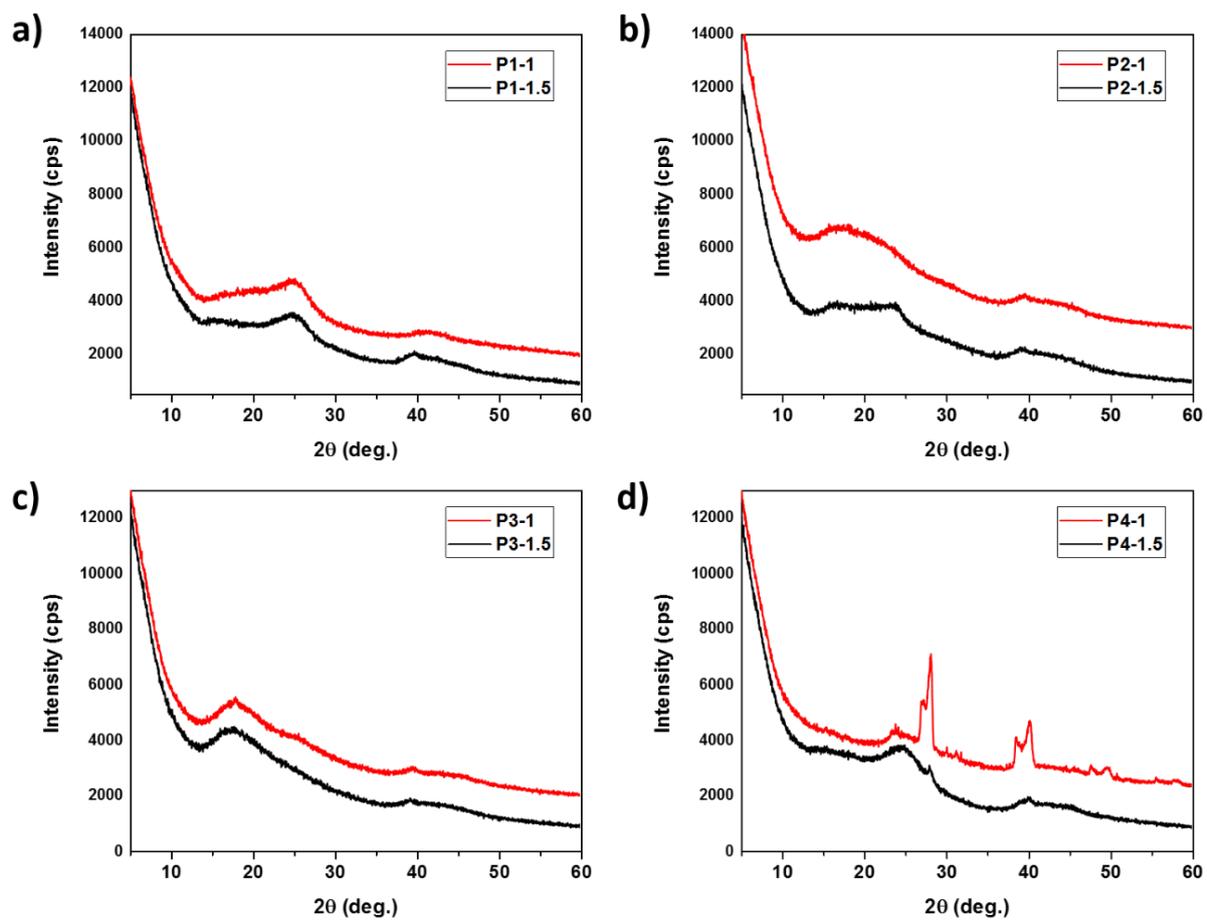


Figure S3 Powder X-ray diffraction patterns of triazine-based CPPs.

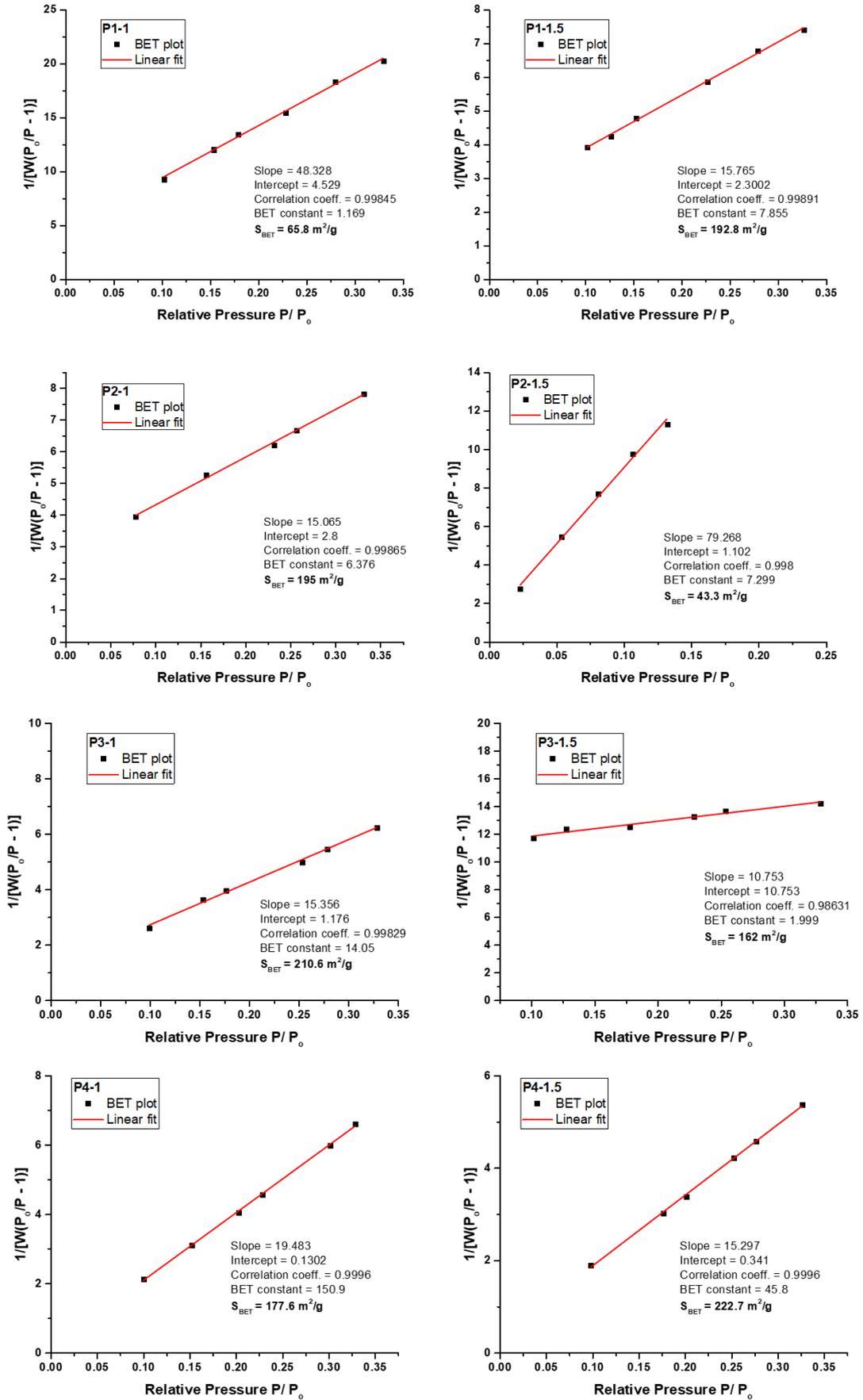


Figure S4 BET specific surface area plots of triazine-based CPPs.

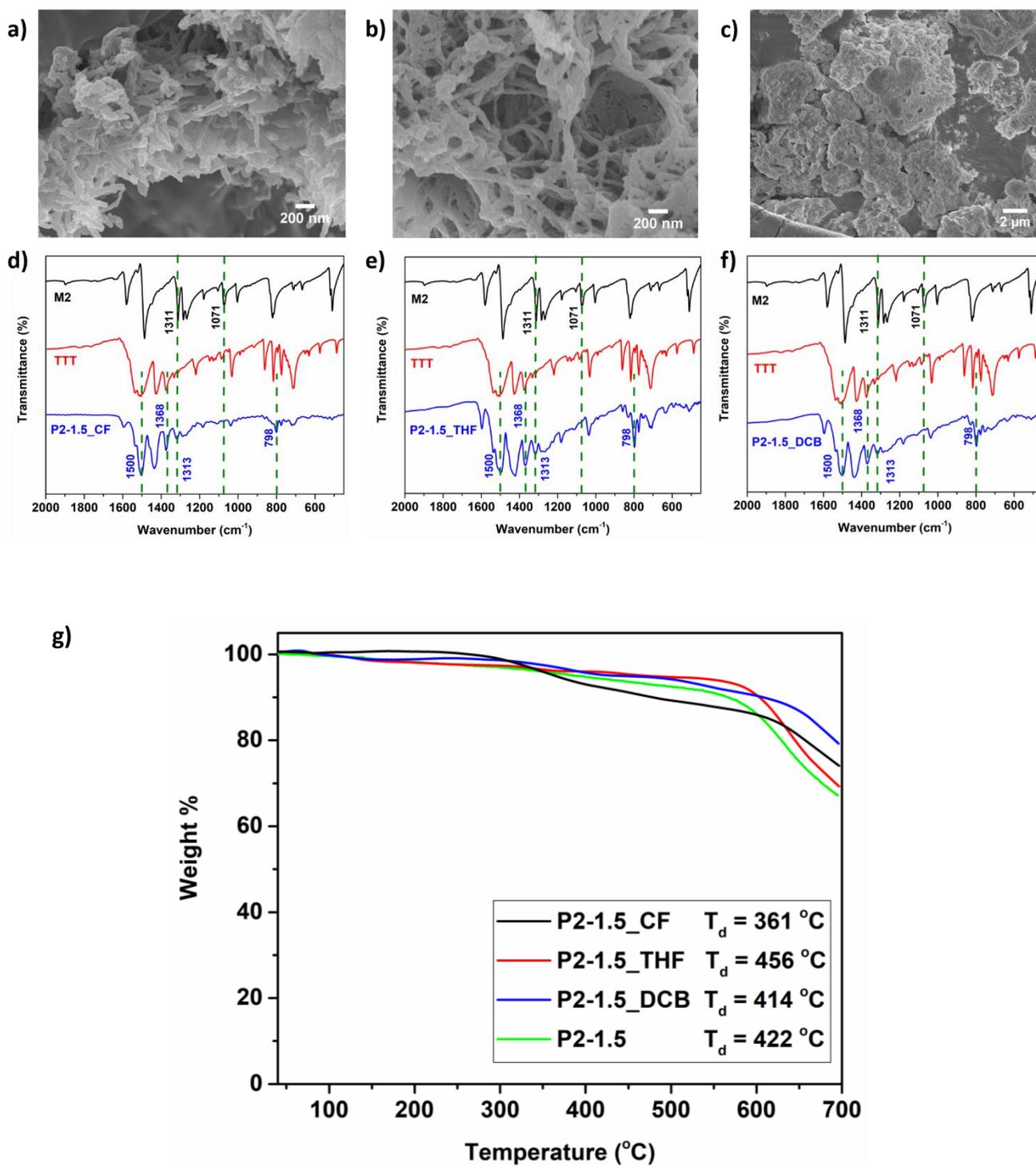


Figure S5 SEM images (a-c) and FT-IR spectra (d-e) of **P2-1.5** synthesized in chloroform (a,d), tetrahydrofuran (b,e) and dichlorobenzene (c,f). g) TGA plots of **P2-1.5** synthesized in different solvents.

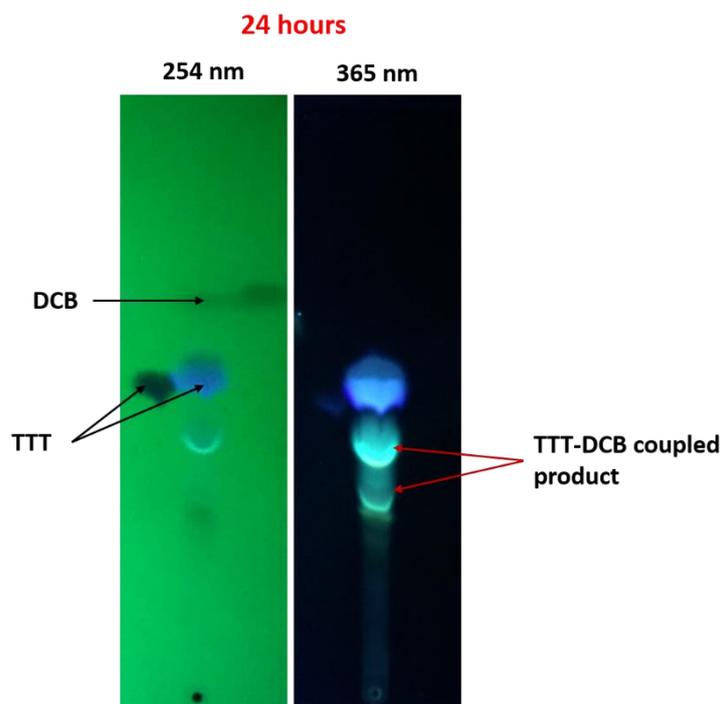


Figure S6 TLC results of TTT-DCB coupling reaction after 24 hours under 254 nm (left) and 365 nm (right) UV light.

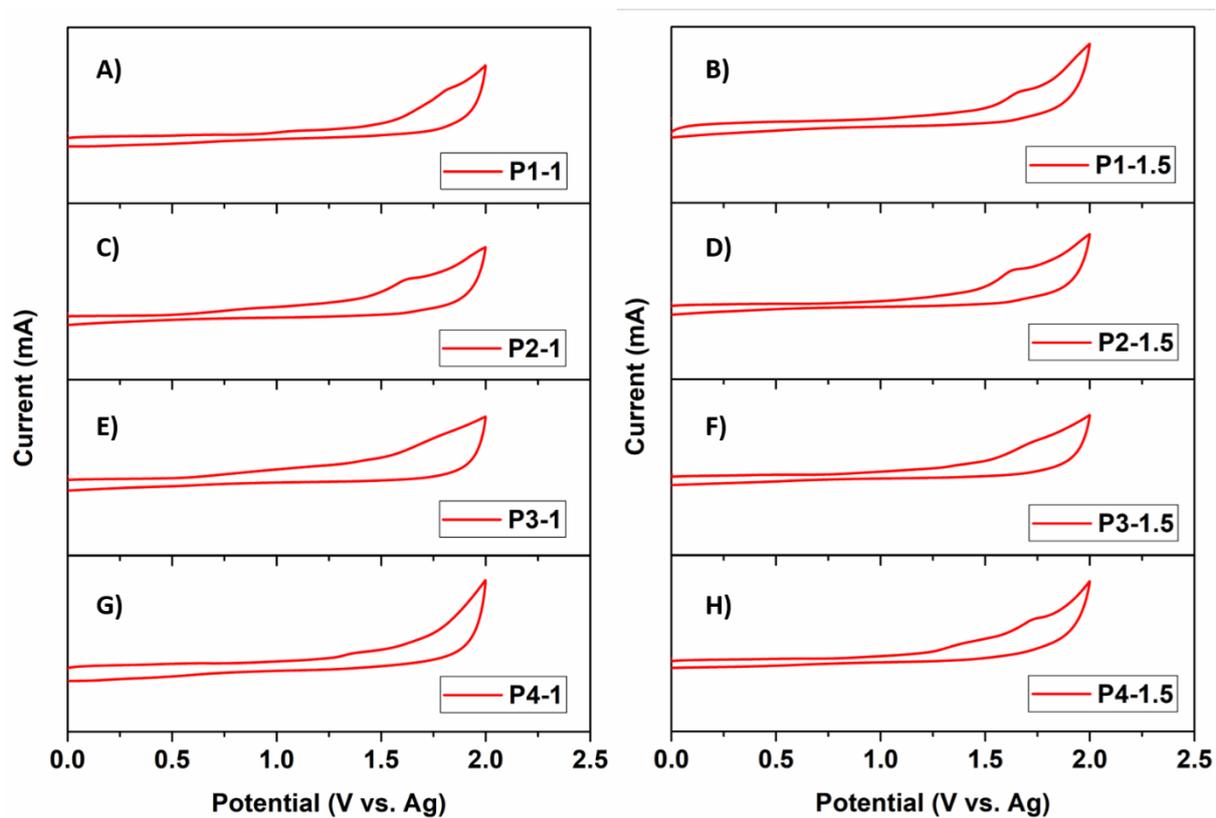


Figure S7 Cyclic voltammograms of (a) P1-1, (e) P1-1.5, (b) P2-1, (f) P2-1.5, (c) P3-1, (g) P3-1.5, (d) P4-1 and (h) P4-1.5.

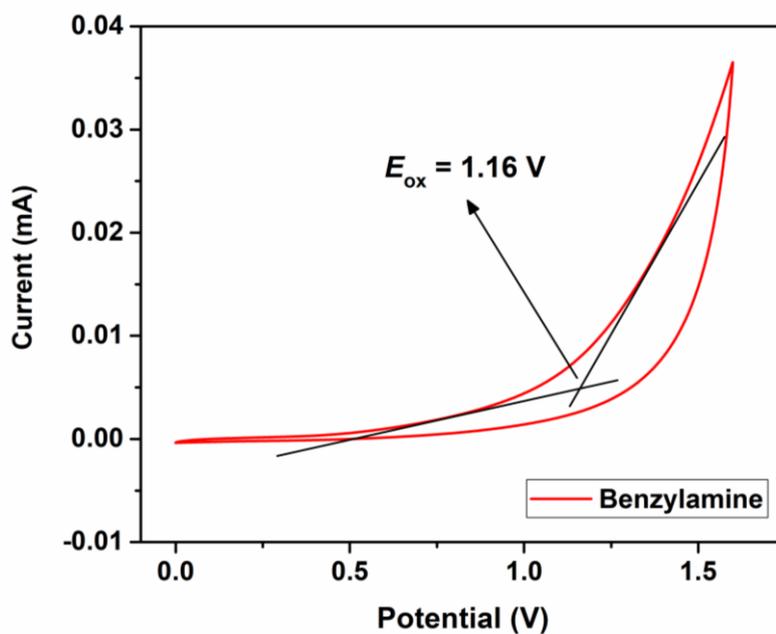


Figure S8 Cyclic voltammogram of benzylamine.

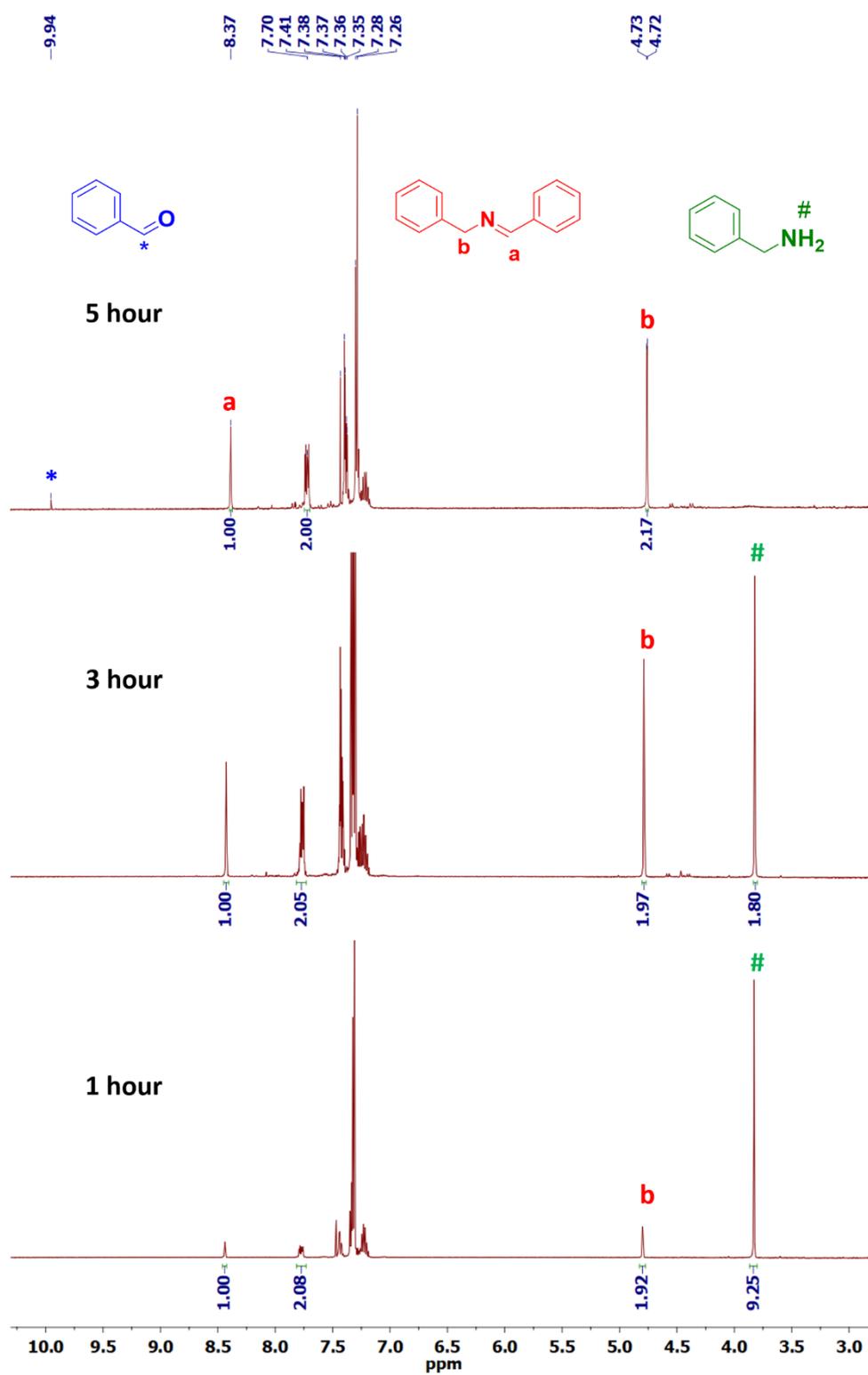
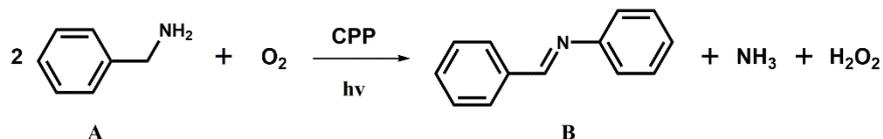
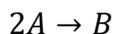


Figure S9 $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectra of the crude product mixture at different reaction times for the photocatalysis of benzylamine using **P4-1** as the photo-catalyst.

Calculation of conversion of benzylamine from ¹H-NMR spectra



The above reaction can be reduced to the following:



For a ¹H-NMR spectrum of a mixture of two compounds A and B, the molar ratio of A to B (n_A/n_B) can be written as

$$\frac{n_A}{n_B} = \frac{(\text{Integral of A})/N_A}{(\text{Integral of B})/N_B} = \theta$$

Where, n_A and n_B are the moles of A and B in the product mixture,

while N_A and N_B are the number of protons represented by the peaks chosen.

Conversion (C) of A is defined as the ratio of moles of A reacted (n_A^R) to the initial number of moles of A in the reaction (n_A^0).

$$\text{Therefore, } C = n_A^R/n_A^0$$

Since 2 moles of A react to give one mole of B,

$$n_A^R = 2n_B, \text{ and } n_A^0 = 2n_B + n_A$$

$$\text{Hence, } C = \frac{2n_B}{2n_B + n_A}$$

$$\frac{1}{C} = \frac{2n_B + n_A}{2n_B}$$

$$\frac{1}{C} = 1 + \frac{n_A}{2n_B}$$

$$\frac{1}{C} = 1 + \frac{\theta}{2}$$

$$C = \frac{2}{(2 + \theta)}$$

Conversion % =

$$C\% = \frac{2}{(2 + \theta)} * 100$$

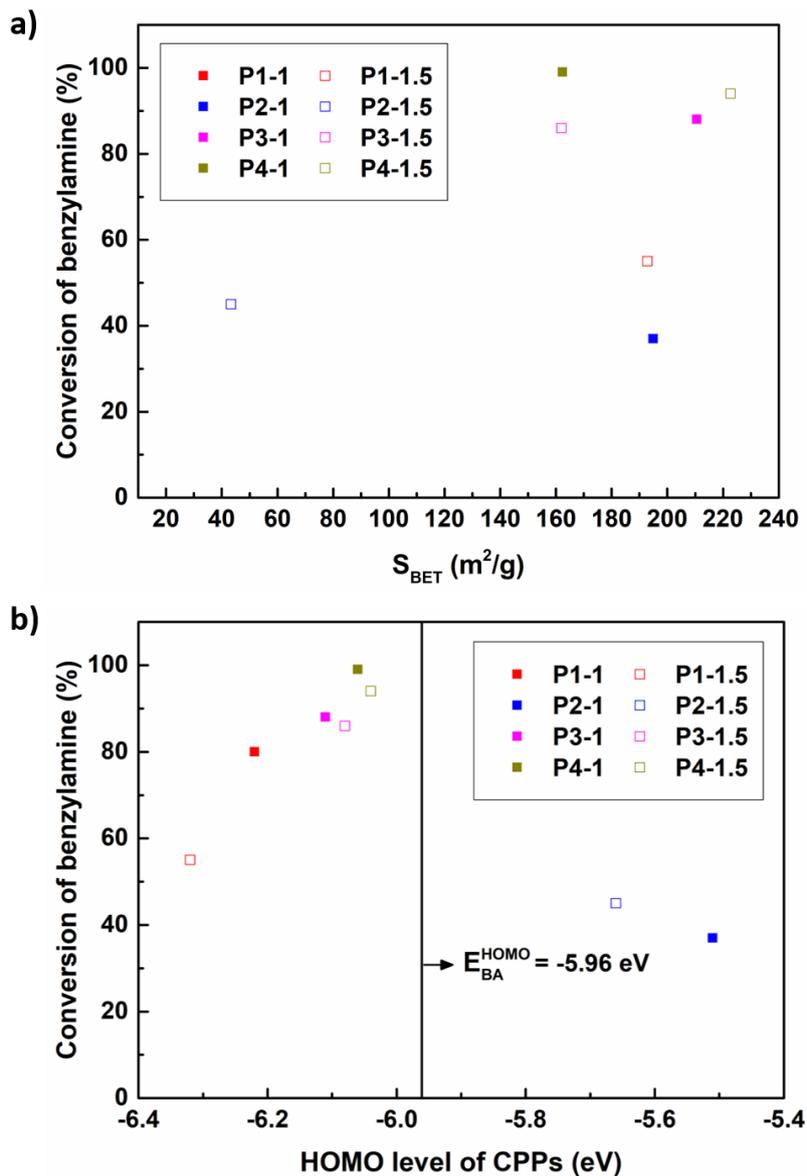


Figure S10 Correlation of the a) BET surface area and b) the HOMO level of triazine-based CPPs with the conversion of benzylamine.

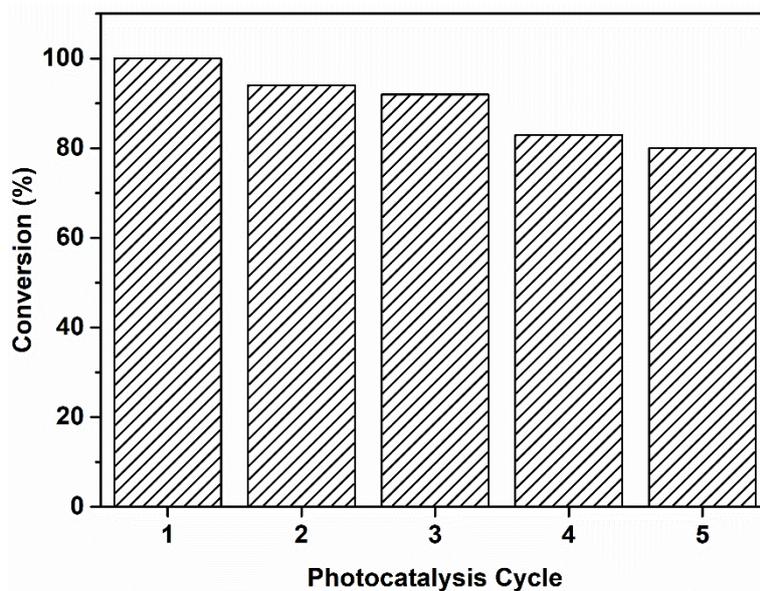


Figure S11 Conversion of benzylamine in the aerobic photocatalyzed oxidative coupling by **P4-1** which was recycled and reused in 5 cycles of the photocatalytic reaction.

References

1. P. Leriche, F. Piron, E. Ripaud, P. Frère, M. Allain and J. Roncali, *Tetrahedron Lett.*, 2009, **50**, 5673-5676.
2. H. Tanaka, K. Shizu, H. Nakanotani and C. Adachi, *Chem. Mater.*, 2013, **25**, 3766-3771.
3. S. Ashoka, B. M. Peake, G. Bremner, K. J. Hageman and M. R. Reid, *Anal. Chim. Acta*, 2009, **653**, 191-199.