Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

BODIPY-based conjugated microporous polymers as heterogeneous photosensitisers in a photochemical flow reactor

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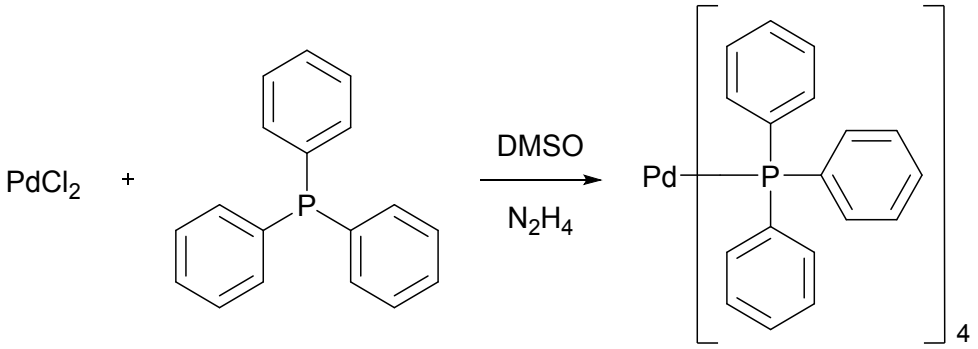
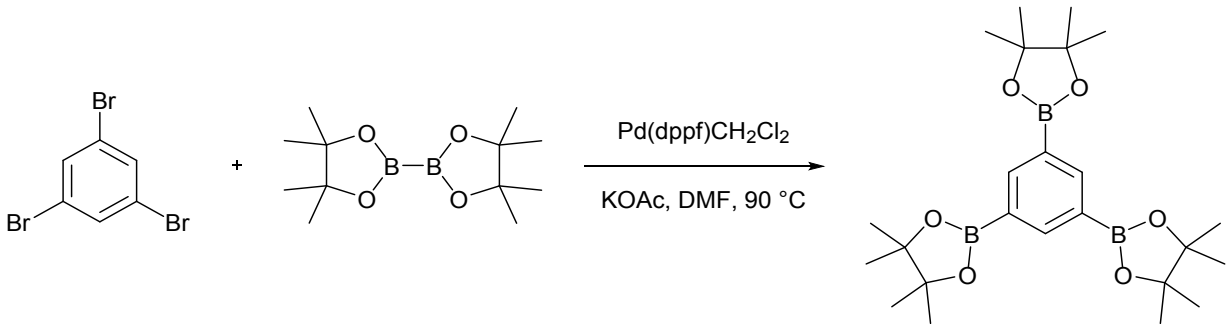
Experimental section

Synthesis of Tetrakis(triphenylphosphine) palladium(0) catalyst.



Tetrakis(triphenylphosphine) palladium(0) ($Pd[(C_6H_5)_3P]_4$) was prepared *via* modified literature methods[1] by dissolving palladium chloride (350 mg, 2 mmol) and triphenylphosphine (2.62 g, 10 mmol) in 25 mL of anhydrous dimethyl sulphoxide. The mixture was stirred and heated to 140-160 °C under nitrogen until an orange solution was formed and stirring continued for 15 minutes thereafter. Hydrazine hydrate (0.39 mL, 8 mmol) was charged quickly into the orange solution and taken from heat and left to cool to room temperature. During this time, yellow crystals formed and were then filtered through a sintered glass adaptor under nitrogen. The crystals were washed with dry methanol and dry diethyl ether and left to dry under nitrogen. The product was used without further purification.

Synthesis of 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene.

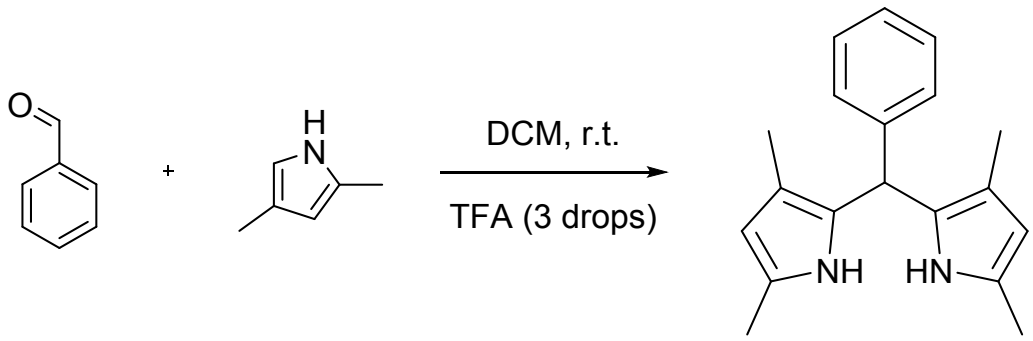


1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene was synthesised *via* literature methods[2] by dissolving 1,3,5-Tribromobenzene (3.0 g, 9.5 mmol), bis(pinacolato)diboron (7.7 g, 30.4 mmol), 1,1'-bis(diphenylphosphino) ferrocenepalladium (II) dichloride dichloromethane (0.24 g, 0.29 mmol), and KOAc (5.6 g, 57 mmol) in Dimethylformamide (DMF) (30 mL) in a 2-necked flask. The mixture was heated to 90 ºC under N_2 and left to react for 16 h. Deionised water (200 mL) was added to the cooled mixture resulting in a dark brown precipitate. Upon filtration, the product was obtained as a brown solid. Product was recrystallised with minimal MeOH to give a light brown solid. Product was dried *in vaco*. ^{1}H NMR was used to compare the product with literature and deemed to be pure.[2] (Dried yield: 2.9 g; 67%)

Synthesis of tetramethylphenyl-BODIPY and dibromotetramethylphenyl-BODIPY.

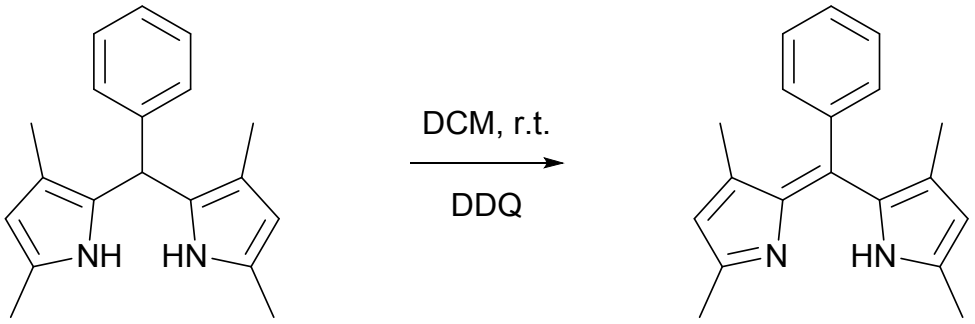
1,3,5,7-tetramethyl-8-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (**1,3,5,7-tetramethyl-8-phenyl-BODIPY**) and 2,6-dibromo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (**2,6-dibromo-1,3,5,7-tetramethyl-8-phenyl-BODIPY**) were synthesised using literature methods.[3, 4]

Step 1



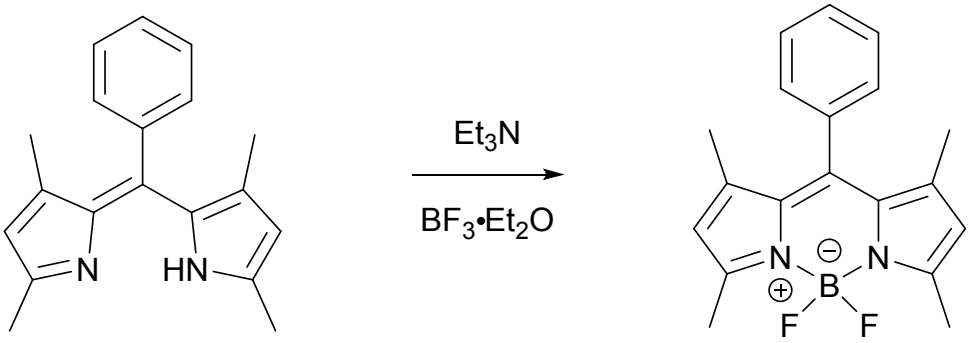
2,4-Dimethylpyrrole (1.05 g, 11 mmol) and benzaldehyde (0.58g, 5.5 mmol) were dissolved in 50 mL dry dichloromethane (DCM) under a nitrogen atmosphere. Three drops of trifluoroacetic acid (TFA) was added to the solution and the reaction mixture was stirred at room temperature overnight. The crude product was used in the following step without purification.

Step 2



After this time, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (5 mmol, 1.14 g) was dissolved in approximately 75 mL of DCM and added slowly by pipette to the reaction mixture. This mixture was then left to stir at room temperature under a nitrogen atmosphere for 15 minutes. The crude product was used in the following step without purification.

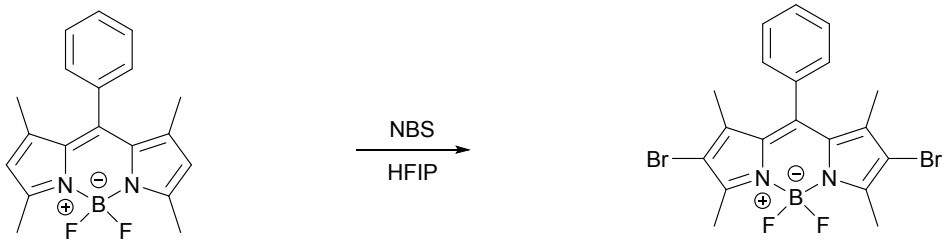
Step 3



Triethylamine (10 mL, excess) and boron trifluoride diethyl etherate (BF_3OEt_2) (10 mL, excess) were then added to the reaction and left to stir at room temperature under a nitrogen atmosphere for 3 hours. The solution was then diluted in 100 mL of

dichloromethane and washed with deionised water three times. The organic phase was dried over $MgSO_4$ and filtered. The crude product was purified through silica gel column chromatography with a DCM : hexane (1:1) eluent to yield a red-green solid (420 mg, 24%). ^{1}H NMR was used to compare the product with literature and deemed to be pure.[3]

Step 4

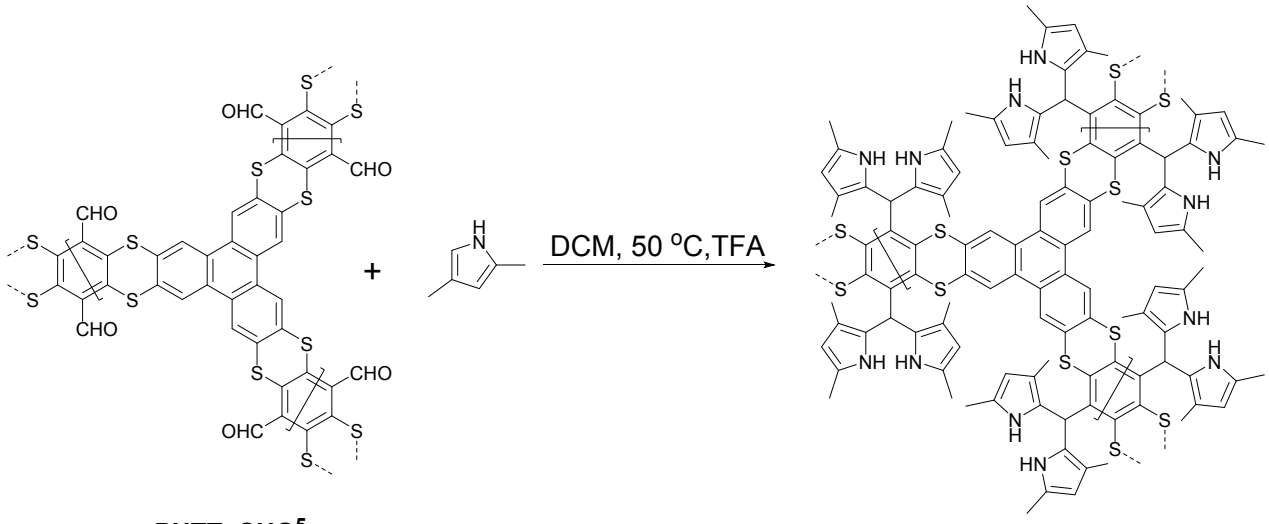


1,3,5,7-tetramethyl-8-phenyl-BODIPY **2,6-dibromo-1,3,5,7-tetramethyl-8-phenyl-BODIPY**

A mixture of **1,3,5,7-tetramethyl-8-phenyl-BODIPY** (0.2 mmol, 64.8 mg) and *n*-bromosuccinimide (NBS) (0.48 mmol, 85.5 mg) in 2 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was stirred at room temperature for 10 minutes. A colour change from yellow/orange to dark red occurred and TLC was used to confirm reaction completion. The residue was extracted with 25 mL of DCM and washed with deionised water three times. The organic phase was dried over Na_2SO_4 and evaporated to give a crude product. The crude product was further purified using silica gel column chromatography with a DCM: hexane (1:1) eluent to afford a dark red solid product (76 mg, 85%). ^{1}H NMR was used to compare the product with literature and deemed to be pure.[4]

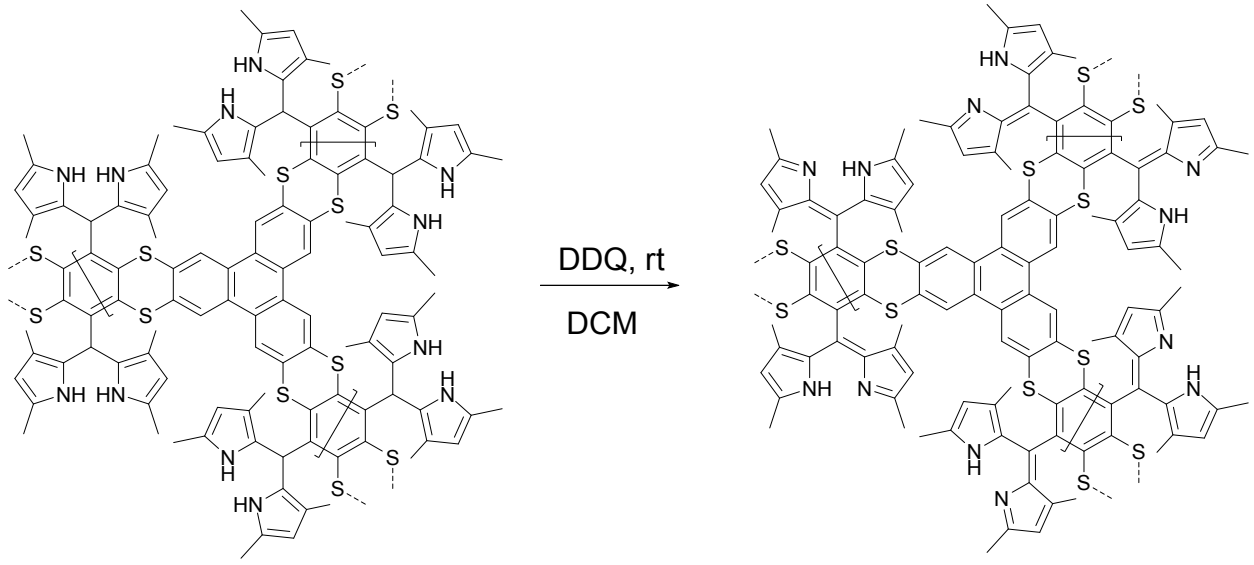
Synthesis of PHTT_BDP and proposed intermediate structures.

Step 1



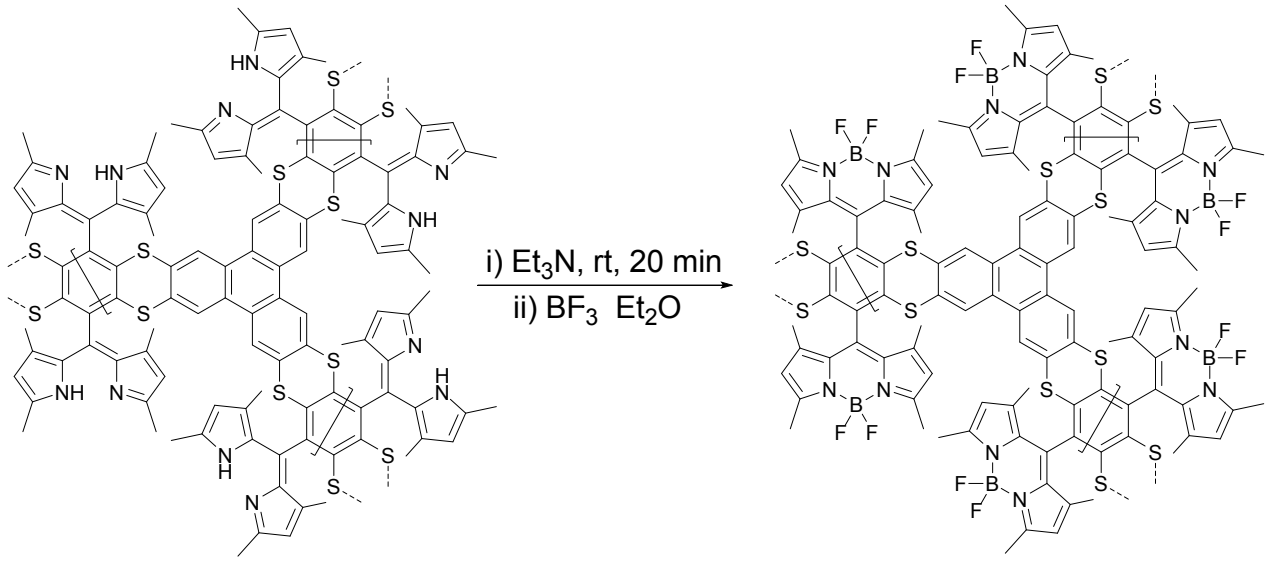
PHTT_CHO[5] **PHTT_DMP**

Step 2



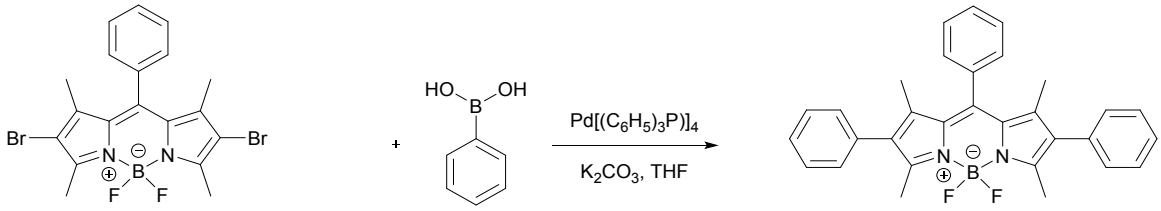
PHTT_DMP **PHTT_DMP_O**

Step 3



PHTT_DMP_O **PHTT_BDP**

Synthesis of 2,6-diphenyl-1,3,5,7-tetrametyl-8-phenyl-BODIPY.



2,6-dibromo-1,3,5,7-tetramethyl-8-phenyl-BODIPY **2,6-diphenyl-1,3,5,7-tetramethyl-8-phenyl-BODIPY**

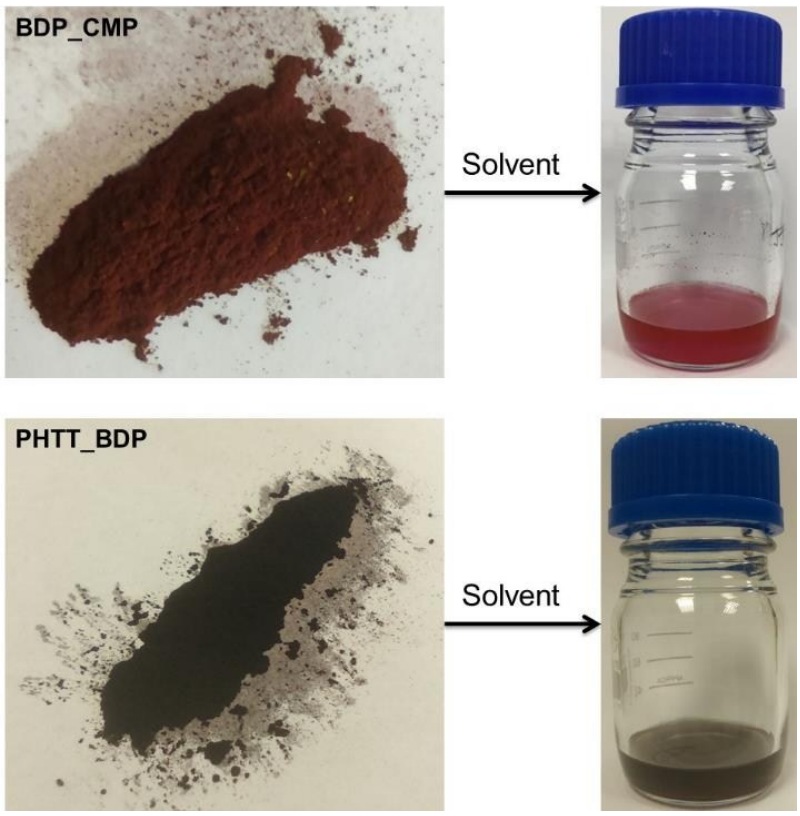


Fig. S1 BDP_CMP (top left) and **PHTT_BDP** (bottom left) as solids and as a dispersion in solvent (right).

Fig. S2 Easy-Photochem flow system from Vapourtec equipped with visible light LED module emitting light at 530nm.

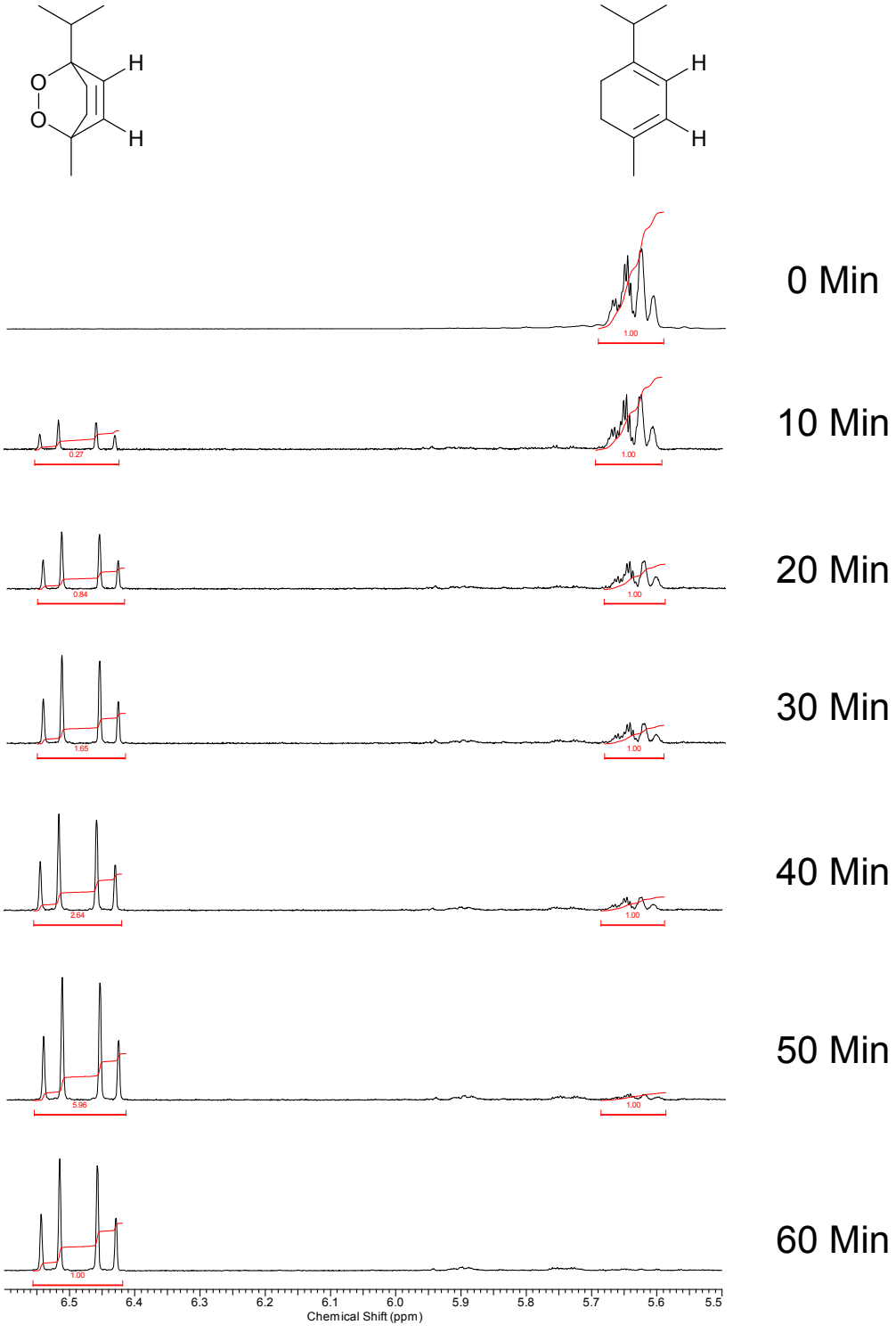


Fig. S3 Progress of the Alder-ene reaction in chloroform followed by ^{1}H NMR spectroscopy.

Table S1 Conversion of α-terpinene to ascaridole *via* ^{1}H NMR over time with a flow rate of 1mL.min^{-1} in the easy-Photochem flow reactor from Vapourtec.

	BDP_CMP 1h	***BDP_CMP 6h***	***PHTT_CMP 1h***	***PHTT_CMP 6h***
Time (min)	***Conv. (%)***	***Conv. (%)***	***Conv. (%)***	***Conv. (%)***
0	0	0	0	0
10	22	22	15	28
20	46	44	33	59
30	62	65	52	69
40	72	77	66	80
50	86	88	83	83
60	99	99	99	90

Spectroscopic Analysis

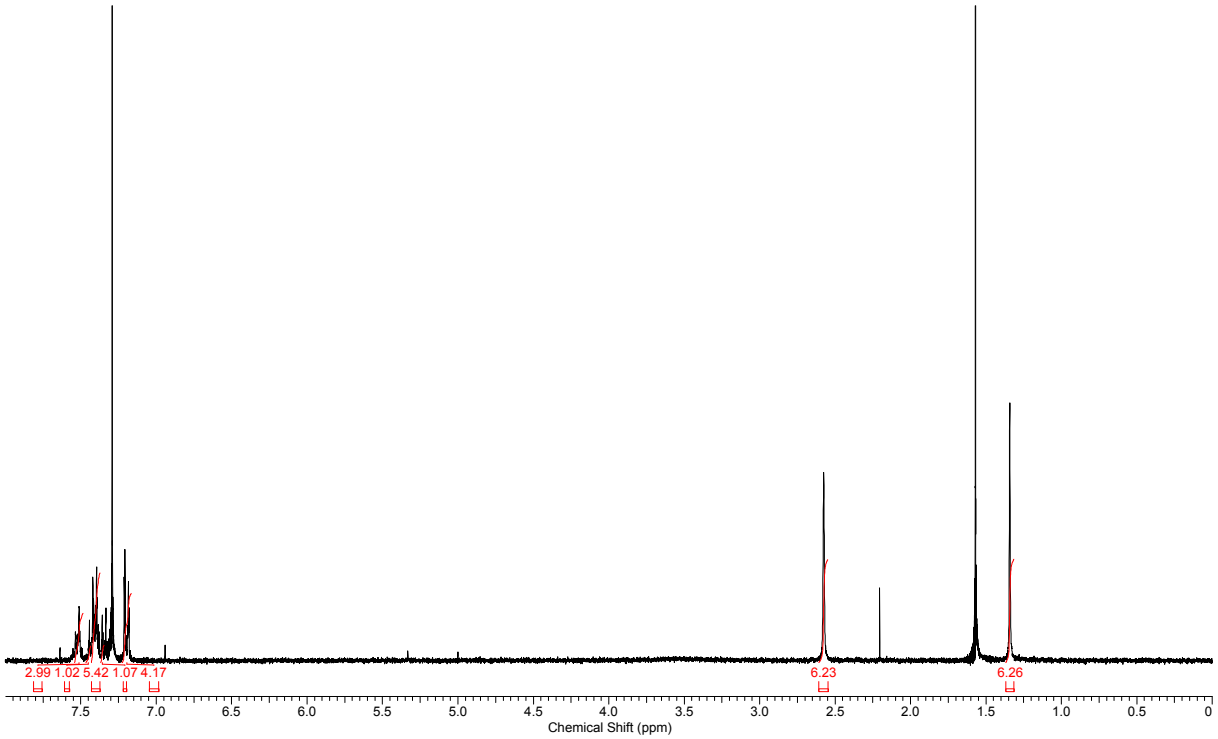


Fig. S4 ^{1}H NMR of 2,6-diphenyl-1,3,5,7-tetramethyl-8-phenyl-BODIPY(**BDP_Ph**).

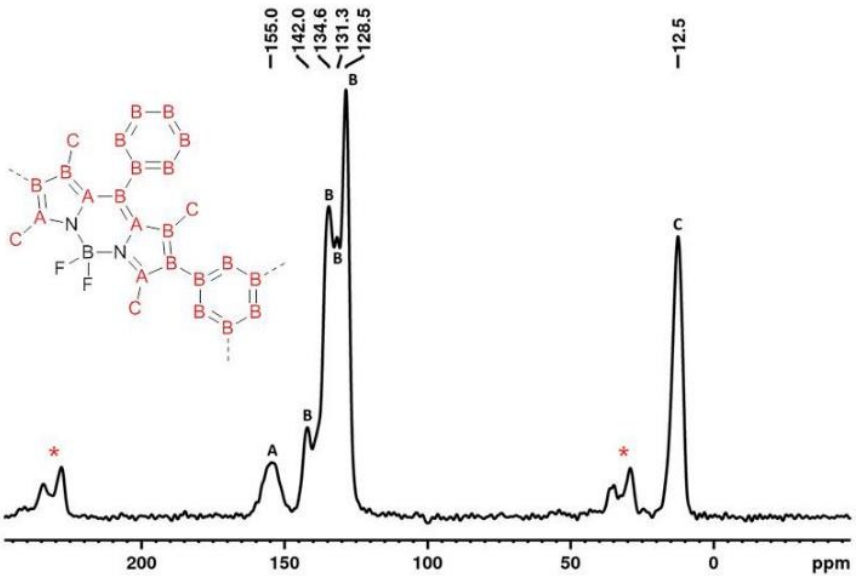


Fig. S5 Solid state ^{13}C NMR of **BDP_CMP** (δ155.0 (N-*C*), 142.0, 134.6, 131.3, 128.5 (other aromatic-*C*), 12.53 (methyl-*C*)). Peaks denoted by (*) indicate the presence of side bands.

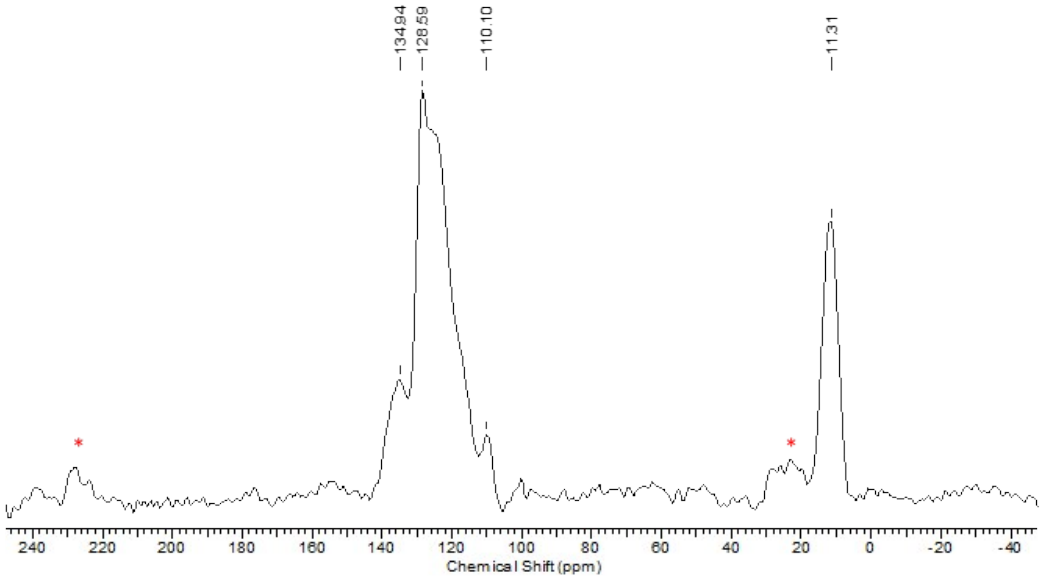


Fig. S6 Solid state ^{13}C NMR of **PHTT_DMP** (δ134.94, 128.59, 110.10, 11.31). Peaks denoted by (*) indicate the presence of side bands.

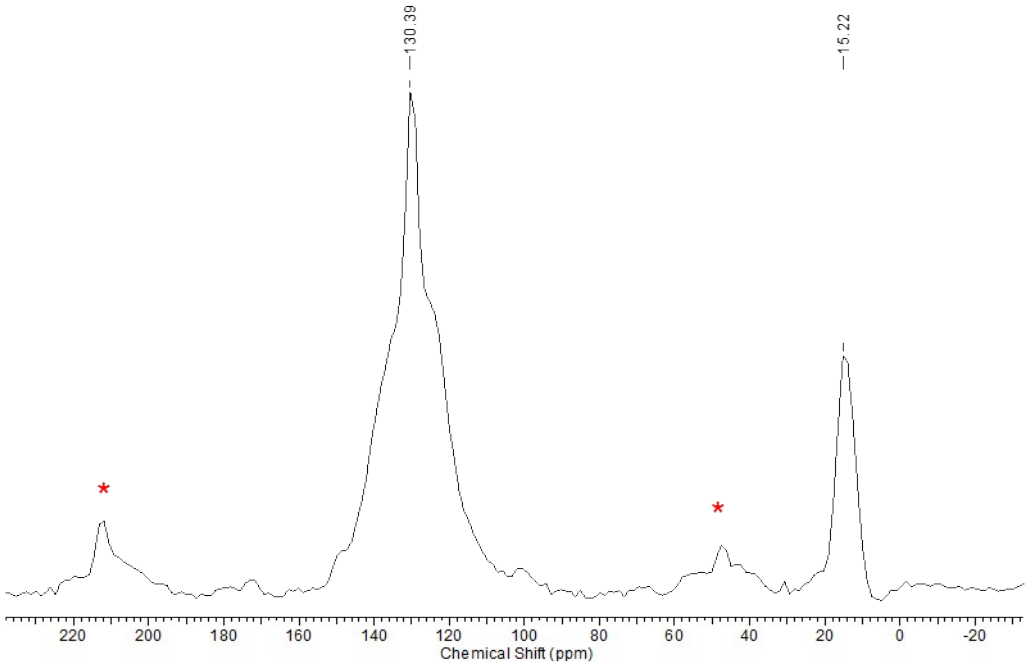


Fig. S7 Solid state ^{13}C NMR of **PHTT_DMP_O** (δ130.39, 15.22). Peaks denoted by (*) indicate the presence of side bands.

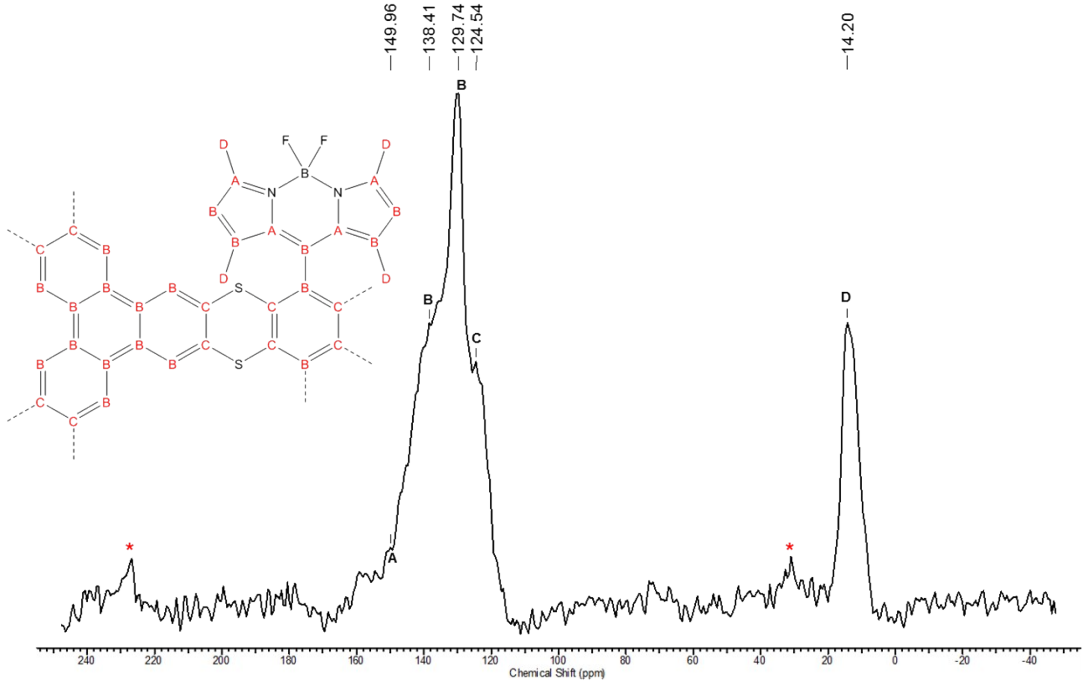


Fig. S8 Solid state ^{13}C NMR of **PHTT_BDP** (δ149.96, 138.41, 129.74 (aromatic-*C*), 124.54 (S-C), 14.20 (methyl-*C*)). Peaks denoted by (*) indicate the presence of side bands.

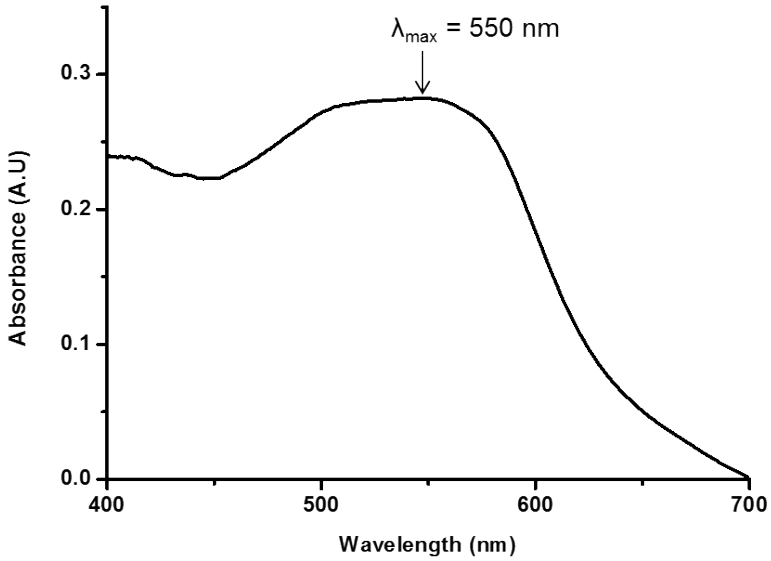


Fig. S9 Solid state UV-Vis spectrum of the **BDP_CMP** polymer with a λ_{max} = 550 nm and absorption edge ≈ 700 nm.

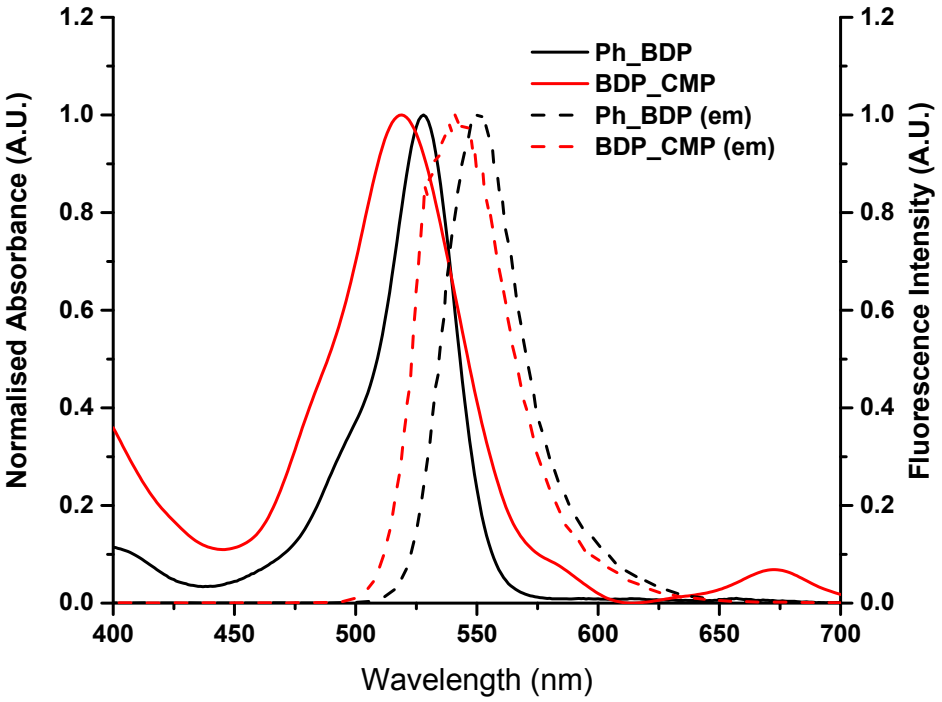


Fig. S10 UV-Vis (solid lines) and fluorescence (dashed lines) spectra of **Ph_BDP** and **BDP_CMP** with an excitation wavelength at 527 and 520 nm, respectively.

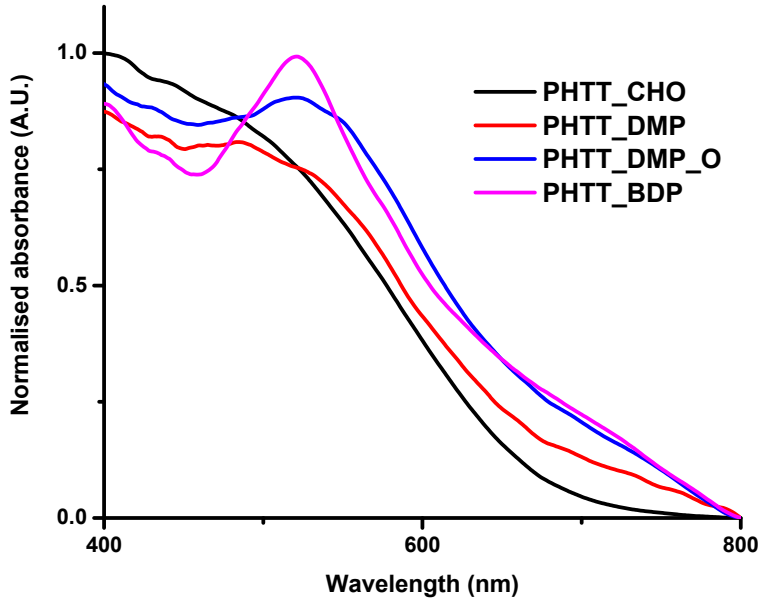


Fig. S11 Solid state UV-Vis spectrum of the **PHTT_CHO**, **PHTT_DMP**, **PHTT_DMP_O** and **PHTT_BDP** polymers. **PHTT_BDP** λ_{max} = 520 nm.

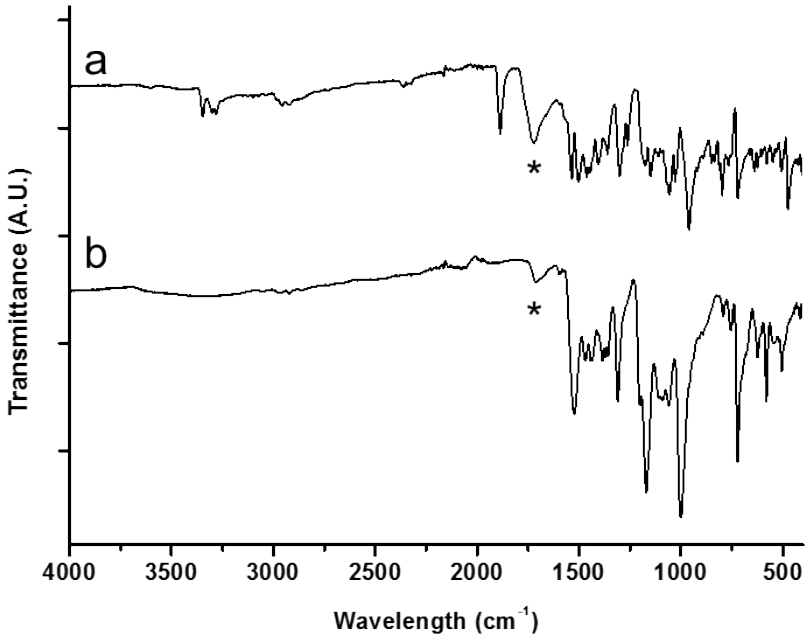


Fig. S12 FT-IR spectra of (a) 1,3,5,7-tetramethyl-8-phenyl-BODIPY and (b) **BDP_CMP**. The asterisked peak at ~1700 cm^{-1} is ascribed to the C=N bond.

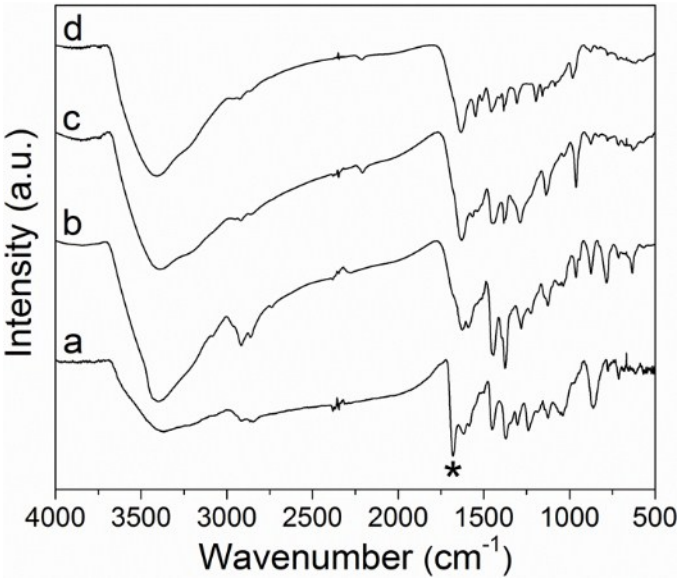


Fig. S13 FT-IR spectra of (a) a sample of **PHTT_CHO**, (b) a sample of **PHTT_DMP**, (c) a sample of **PHTT_DMP_O** and (d) a sample of **PHTT_BDP**. The asterisked peak is ascribed to the aldehyde group.

Physical and Thermal Analysis

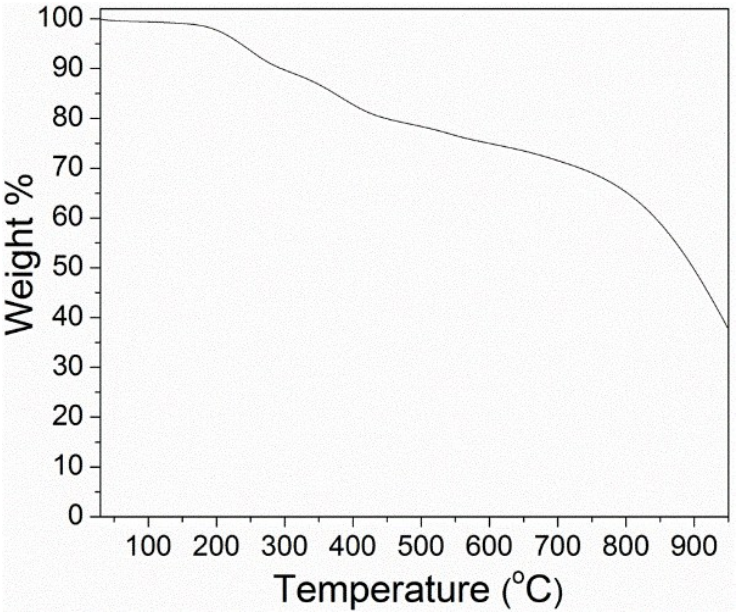


Fig. S14 Thermogravimetric analysis (TGA) of a sample of **BDP_CMP**.

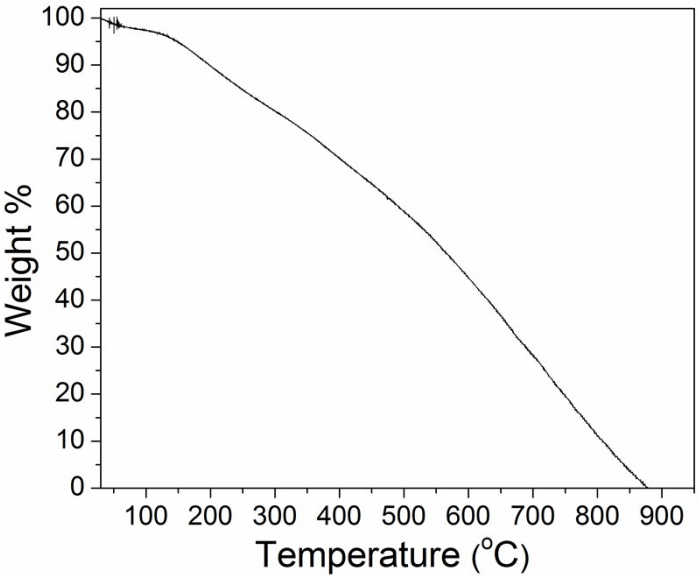


Fig. S15 Thermogravimetric analysis (TGA) of a sample of **PHTT_DMP**.

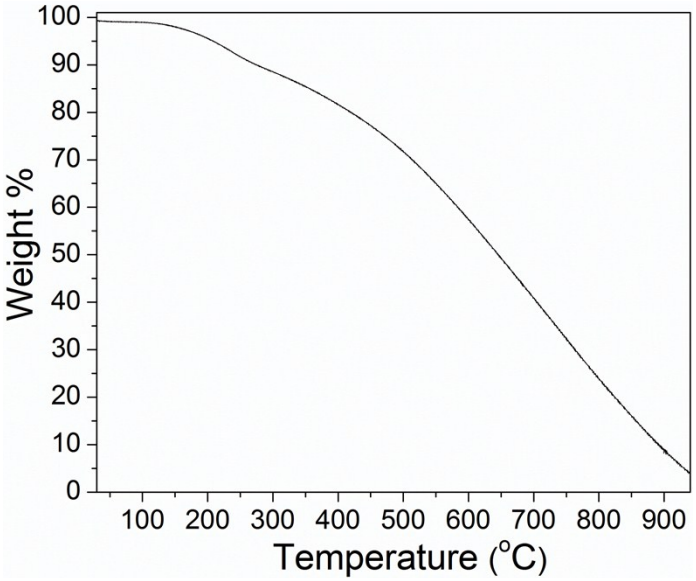


Fig. S16 Thermogravimetric analysis (TGA) of a sample of **PHTT_DMP_O**.

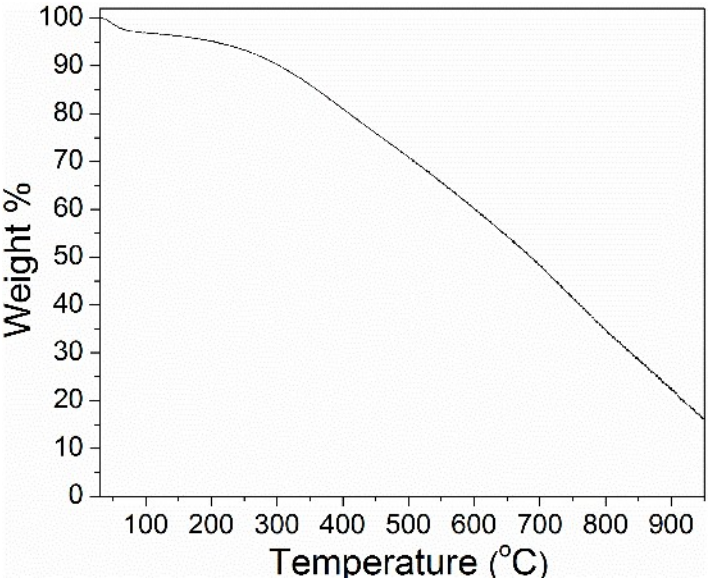


Fig. S17 Thermogravimetric analysis (TGA) of a sample of **PHTT_BDP**.

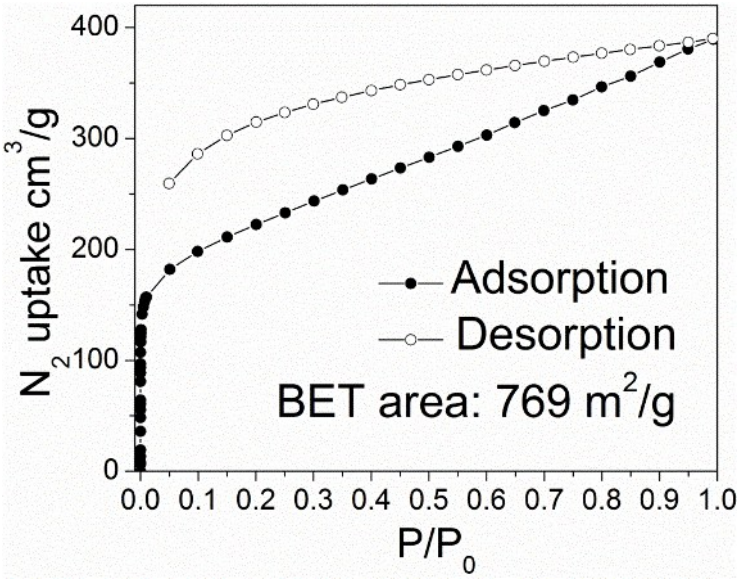


Fig. S18 N_2 sorption isotherm at 77 K for an activated **BDP_CMP** sample.

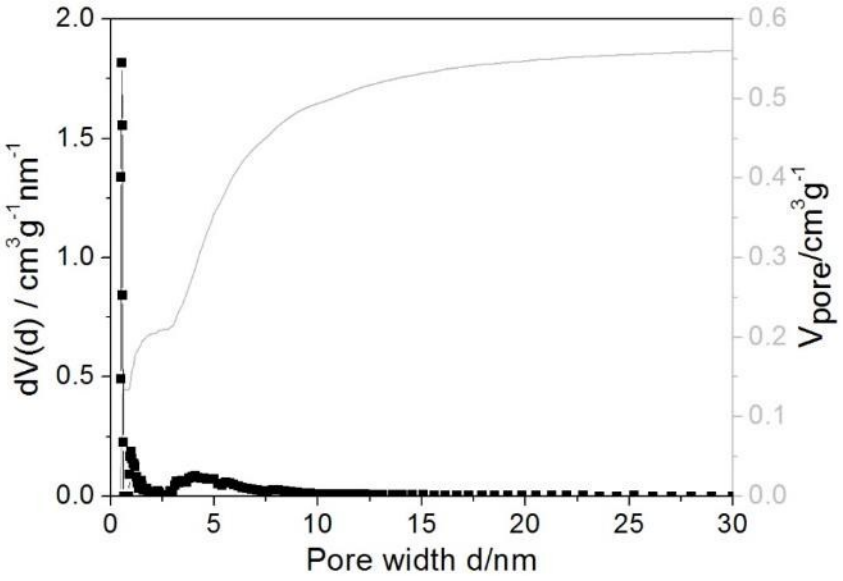


Fig. S19 Pore size distribution and pore volume of an activated **BDP_CMP** sample (N_2 gas at 77 K; QSDFT model). (average pore width 0.545 nm, pore volume 0.563 cm^3/g).

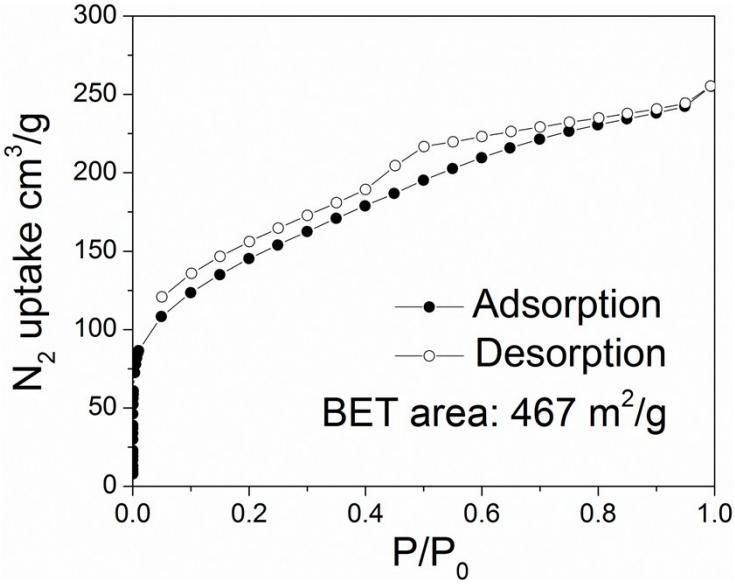


Fig. S20 N_2 sorption isotherm at 77 K for the activated solid sample of **PHTT_DMP**.

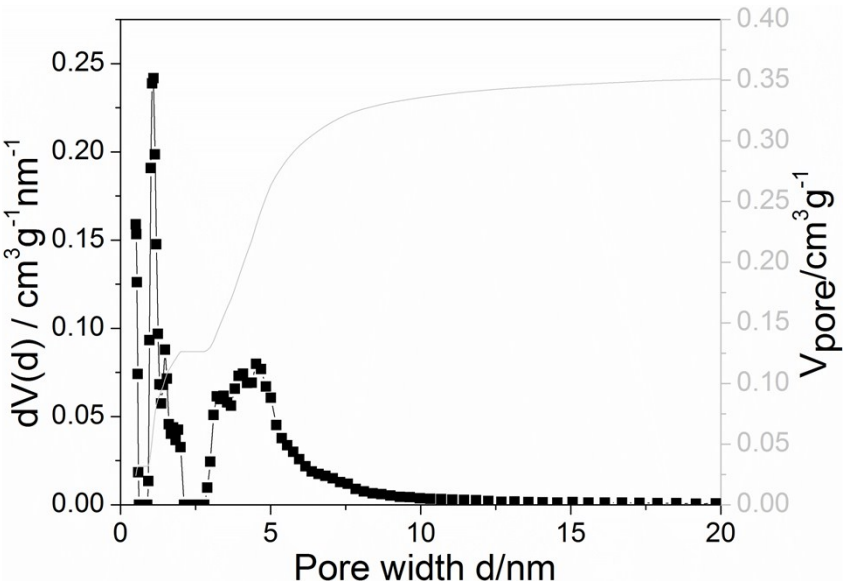


Fig. S21 Pore size distribution and pore volume of an activated **PHTT_DMP** sample (N_2 gas at 77 K; QSDFT model). (average pore width 1.096 nm, pore volume 0.364 cm^3/g).

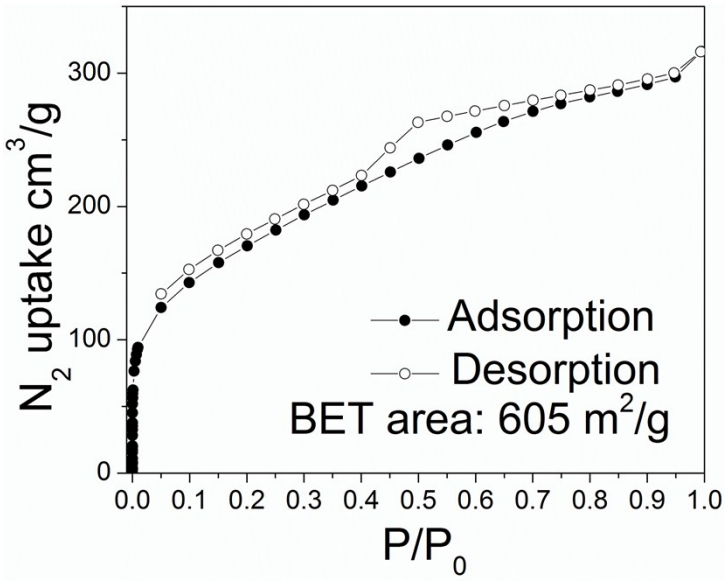


Fig. S22 N_2 sorption isotherm at 77 K for the activated solid sample of **PHTT_DMP_O**.

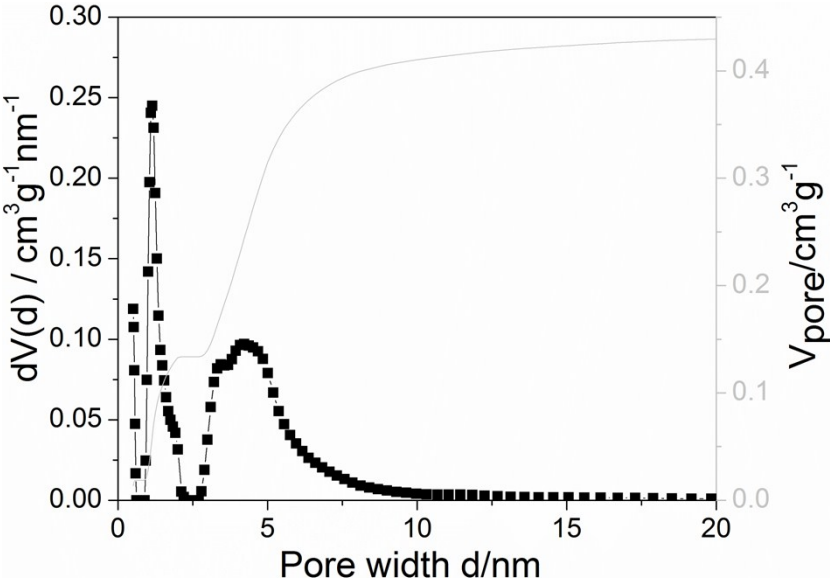


Fig. S23 Pore size distribution and pore volume of an activated **PHTT_DMP_O** sample (N_2 gas at 77 K; QSDFT model). (average pore width 1.144 nm, pore volume 0.448 cm^3/g).

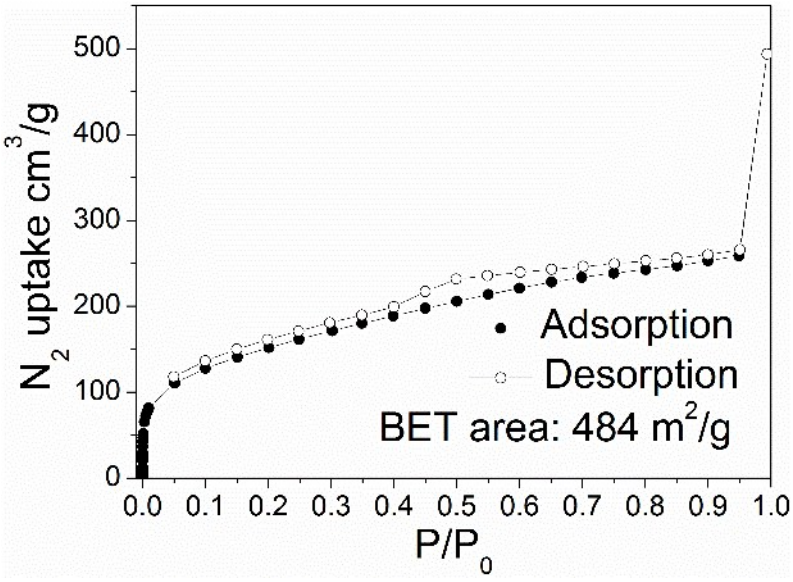


Fig. S24 N_2 sorption isotherm at 77 K for the activated solid sample of **PHTT_BDP**.

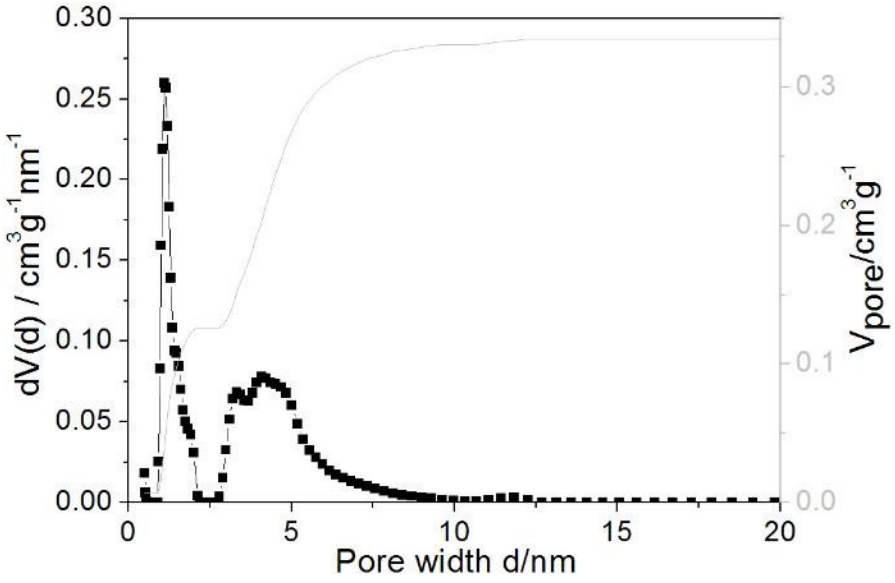


Fig. S25 Pore size distribution and pore volume of an activated **PHTT_BDP** sample (N_2 gas at 77 K; QSDFT model). (average pore width 1.096 nm, pore volume 0.523 cm^3/g).

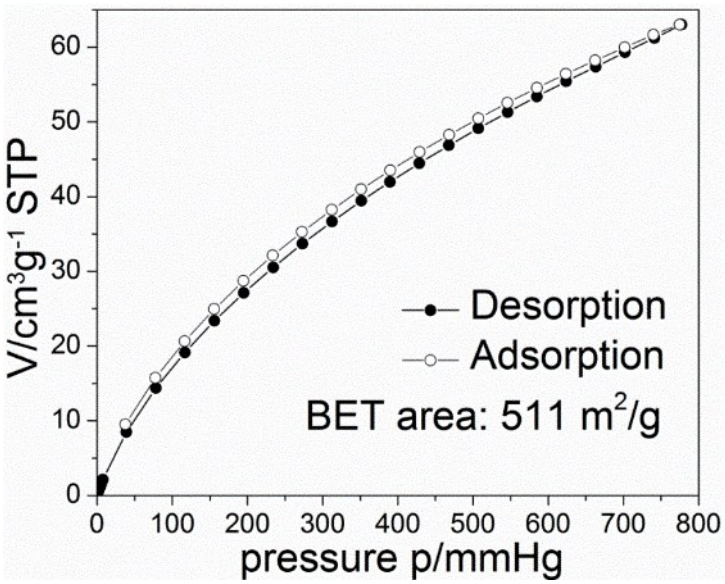


Fig. S26 CO_2 sorption isotherm at 273 K for an activated **BDP_CMP** sample.

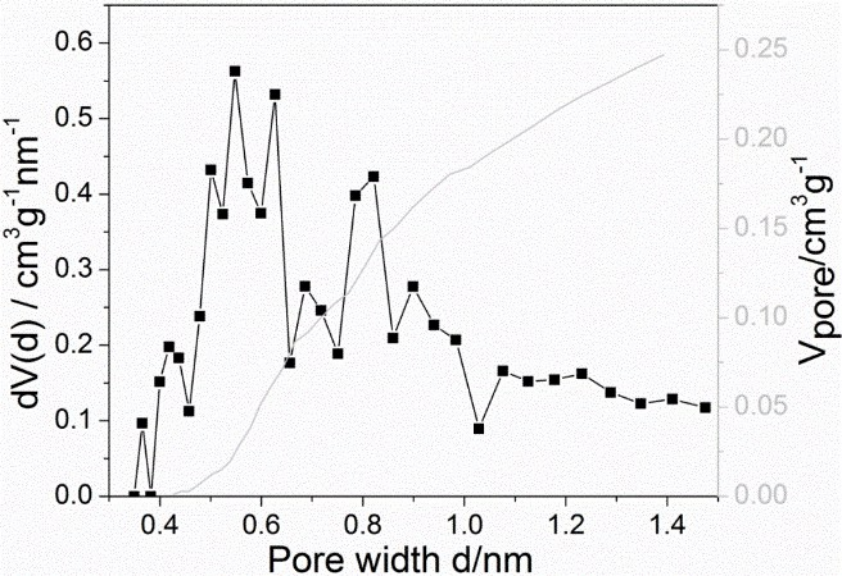


Fig. S27 Pore size distribution and pore volume of an activated **BDP_CMP** sample (CO_2 gas at 273 K; Monte-Carlo model). (average pore width: 0.548 nm, micropore volume: 0.247 cm^3/g).

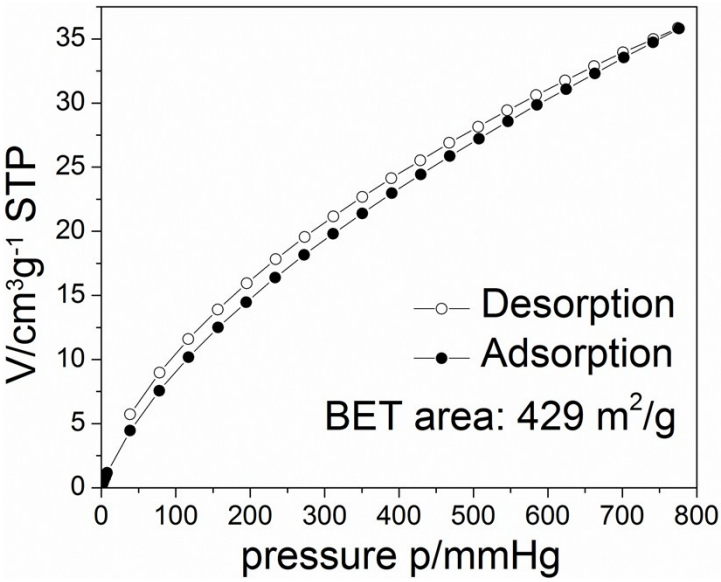


Fig. S28 CO_2 sorption isotherm at 273 K for an activated **PHTT_DMP** sample.

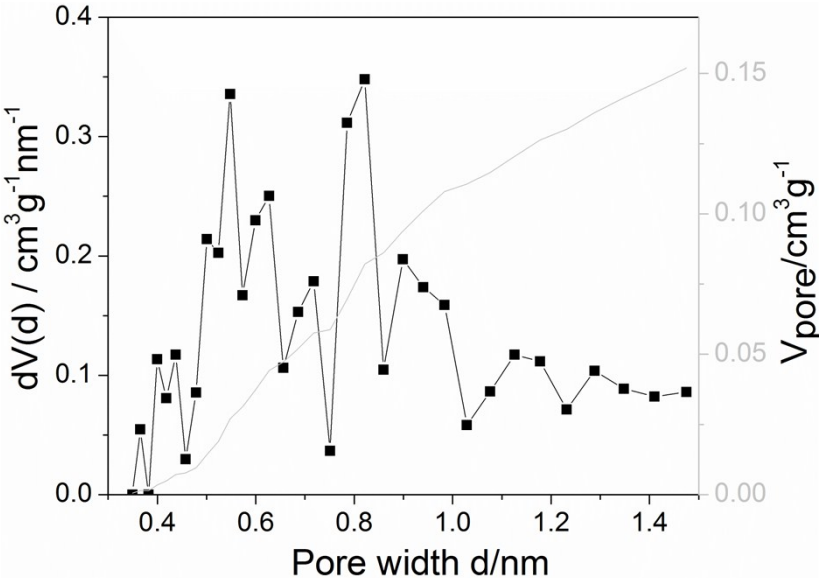


Fig. S29 Pore size distribution and pore volume of an activated **PHTT_DMP** sample (CO_2 gas at 273 K; Monte-Carlo model). (average pore width: 0.822 nm, micropore volume: 0.152 cm^3/g).

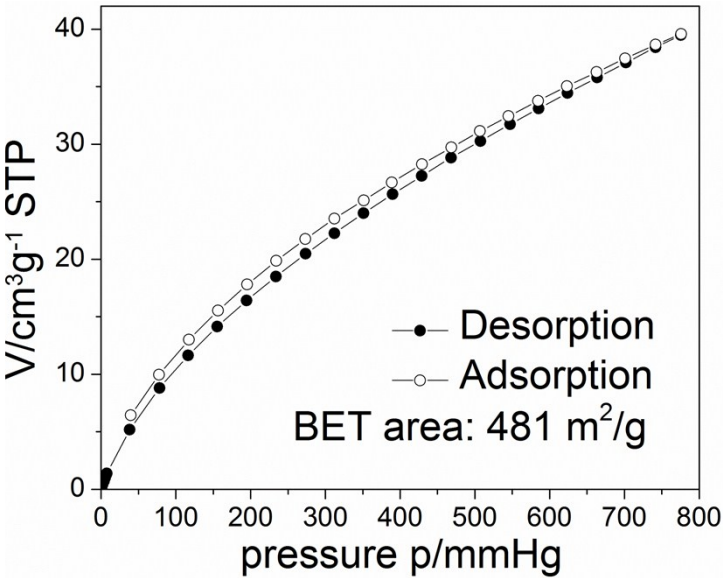


Fig. S30 CO_2 sorption isotherm at 273 K for an activated **PHTT_DMP_O** sample.

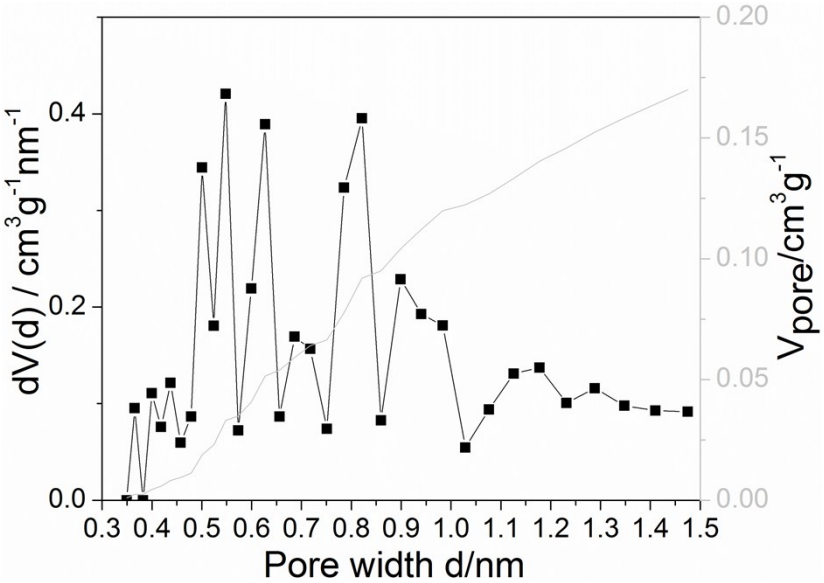


Fig. S31 Pore size distribution and pore volume of an activated **PHTT_DMP_O** sample (CO_2 gas at 273 K; Monte-Carlo model). (average pore width: 0.548 nm, micropore volume: 0.170 cm^3/g).

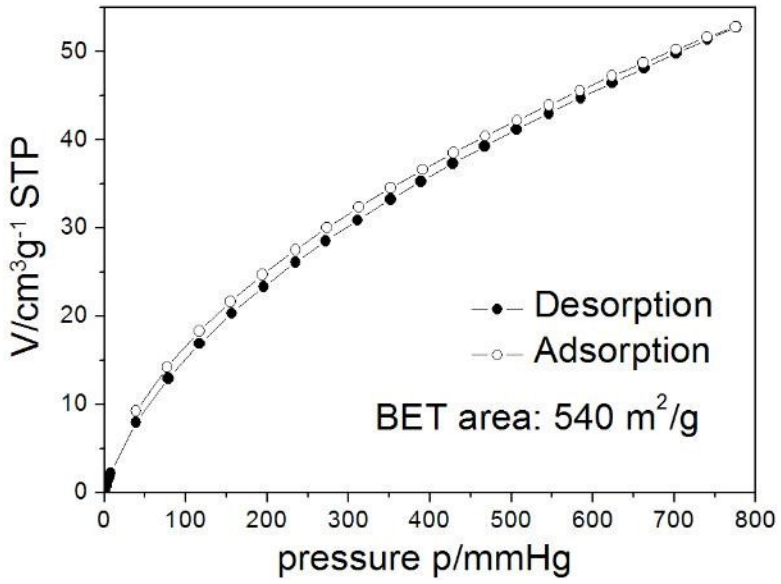


Fig. S32 CO_2 sorption isotherm at 273 K for the activated solid sample of **PHTT_BDP**.

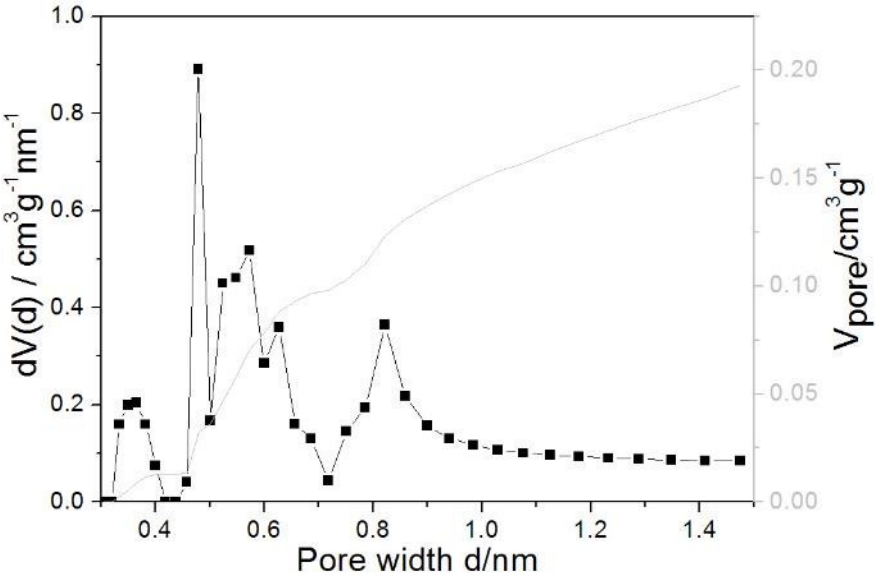


Fig. S33 Pore size distribution and pore volume of an activated **PHTT_BDP** sample (CO_2 gas at 273 K; Monte-Carlo model). (average pore width: 0.479 nm, micropore volume: 0.193 cm^3/g).

Table S2 Summary of surface area and porosity measurement values for the synthesised polymers.

Polymer	*SA_{BET} (m^2 g^{-1})[a]*	*Pore Width (nm)[b]*	*V_{micro} (cm^3 g^{-1})[b]*
BDP_CMP	769	0.545	0.563
PHTT_CHO[c]	686	1.030	0.374
PHTT_DMP	467	1.096	0.364
PHTT_DMP_O	605	1.144	0.448
PHTT_BDP	484	1.096	0.523

[a] Surface area calculated from the N_2 adsorption isotherm using the Brunauer-Emmett-Teller method. [b] The micropore size and micropore volume were derived using density functional theory. [c] Data obtained from Ref [5].

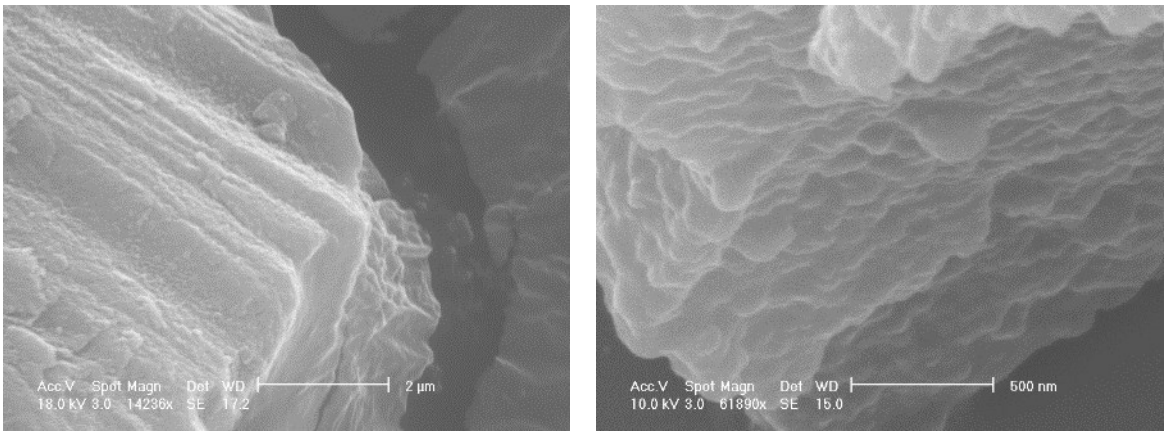


Fig. S34 SEM images of **BDP_CMP**.

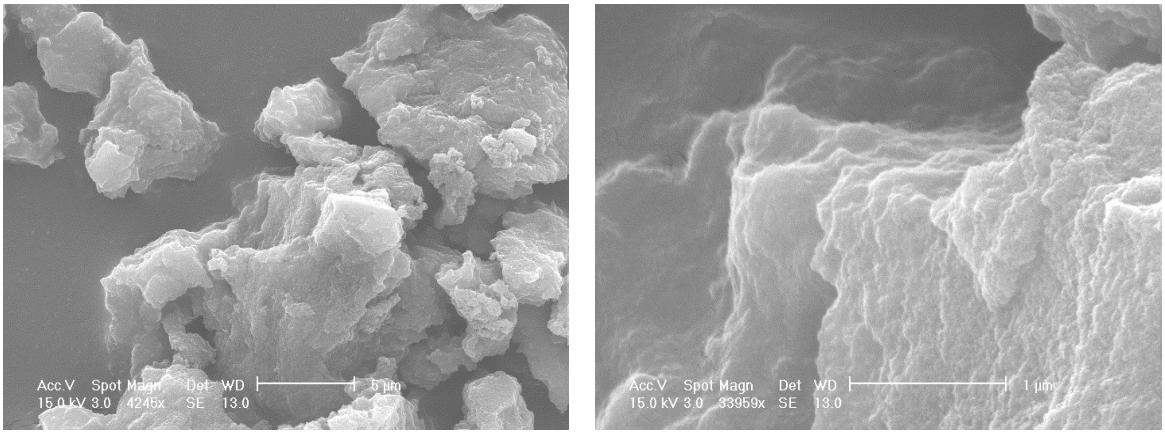


Fig. S35 SEM images of **PHTT_DMP**.

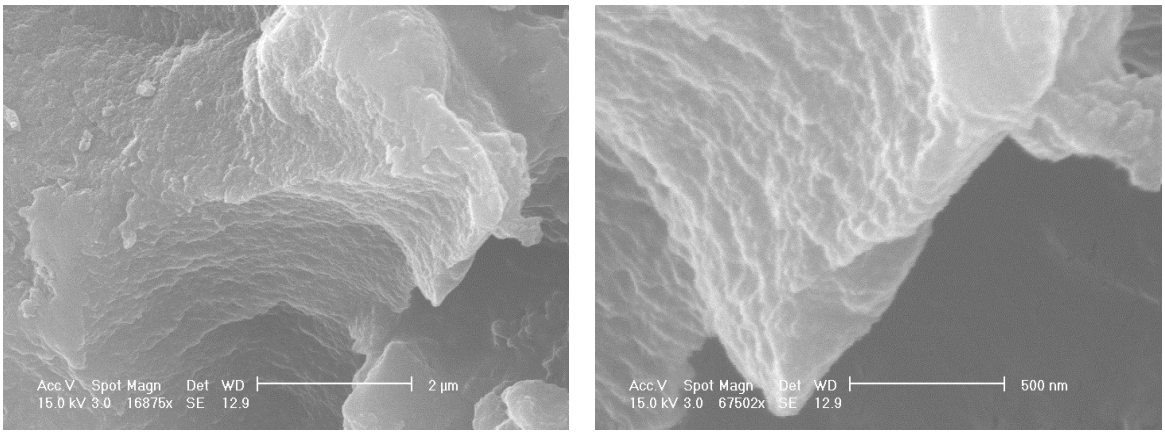


Fig. S36 SEM images of **PHTT_DMP_O**.

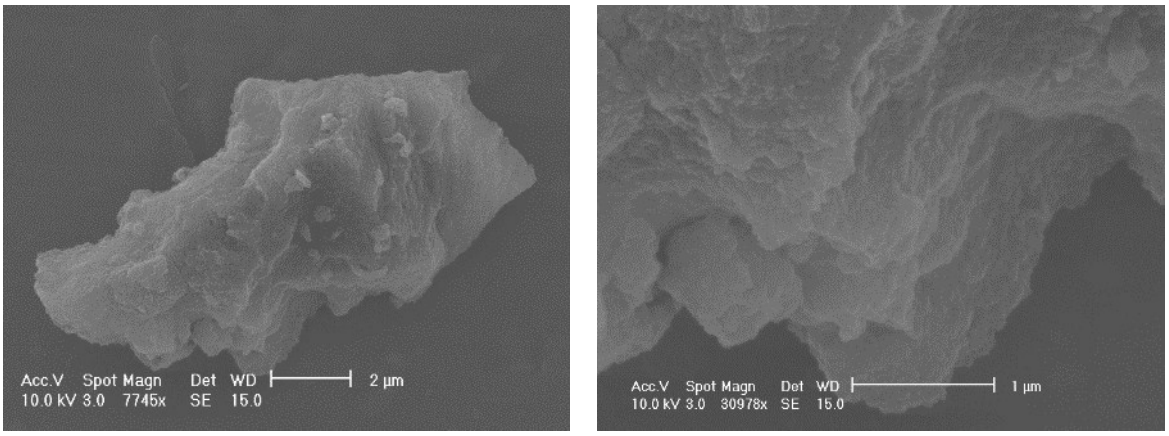


Fig. S37 SEM images of **PHTT_BDP**.

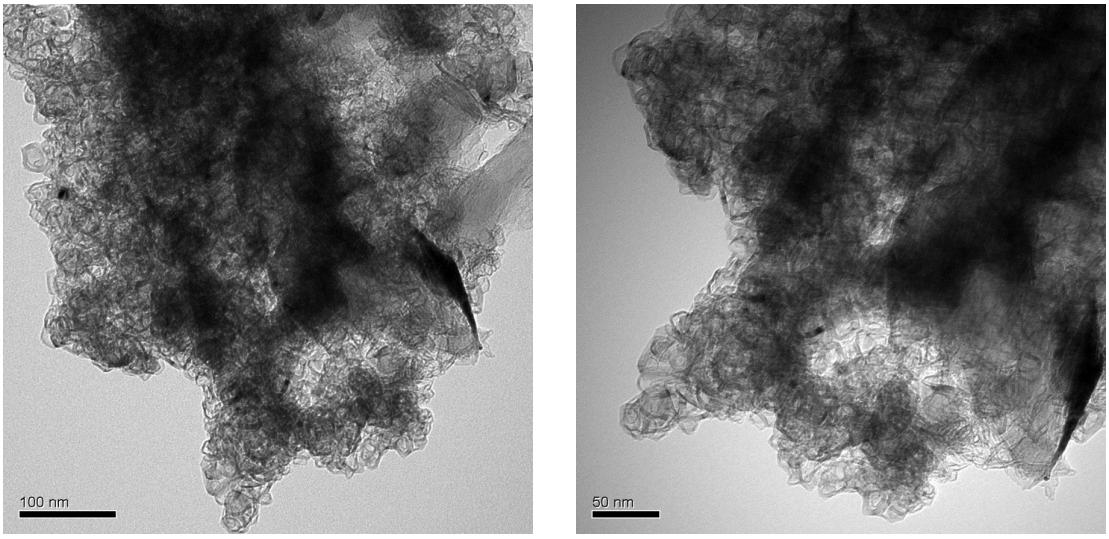


Fig. S38 TEM images of **BDP_CMP**.

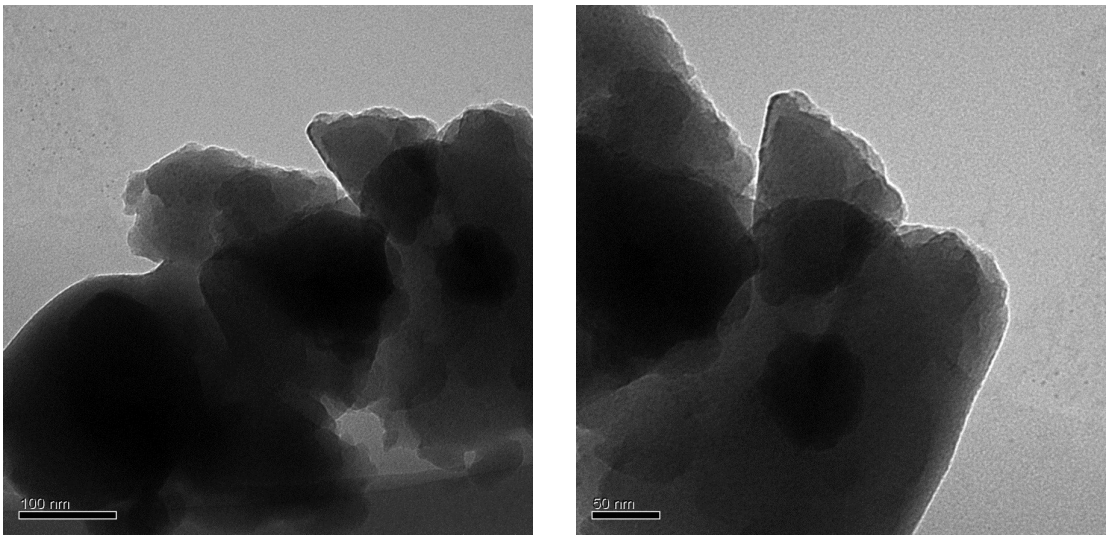


Fig. S39 TEM images of **PHTT_DMP**.

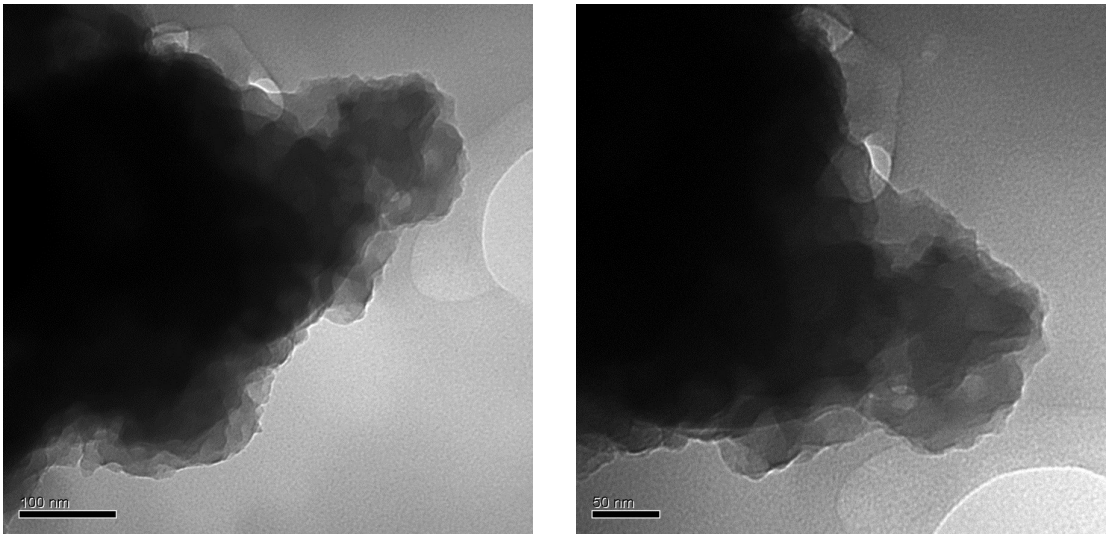


Fig. S40 TEM images of **PHTT_DMP_O**.

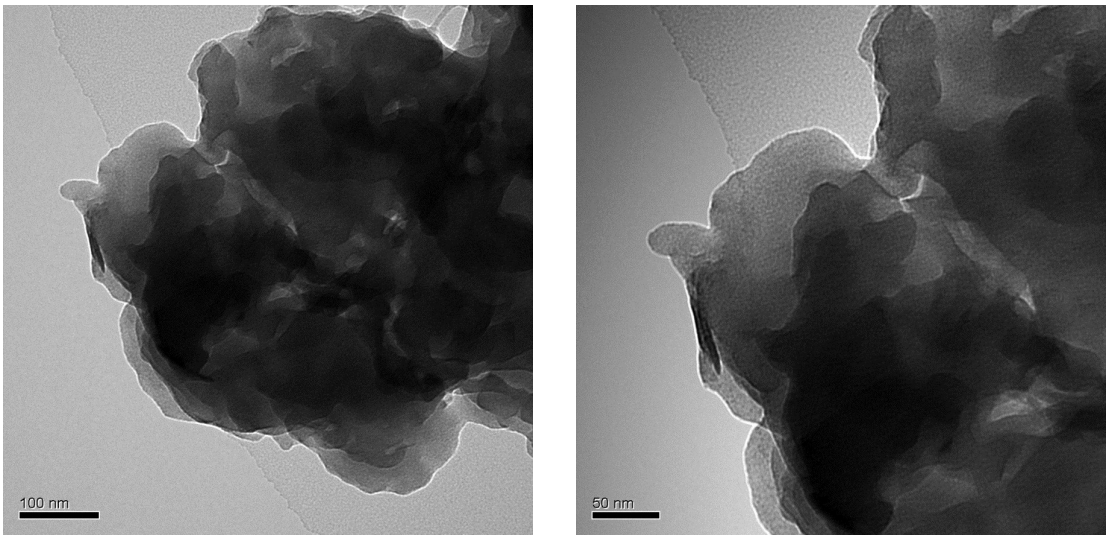


Fig. S41 TEM images of **PHTT_BDP**.

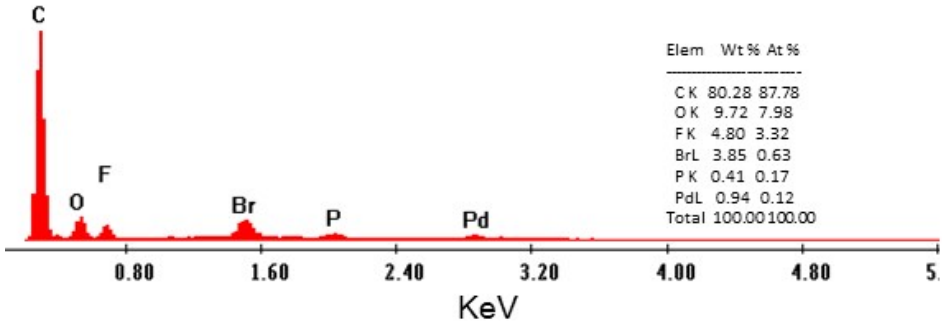


Fig. S42 EDX spectrum of **BDP_CMP**.

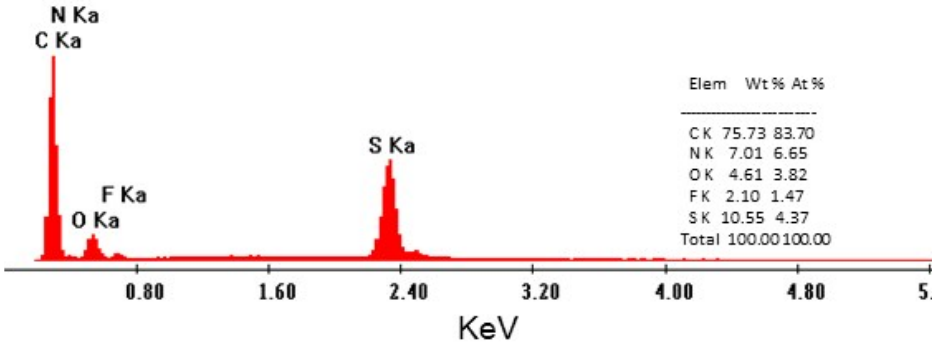


Fig. S43 EDX spectrum of **PHTT_DMP**.

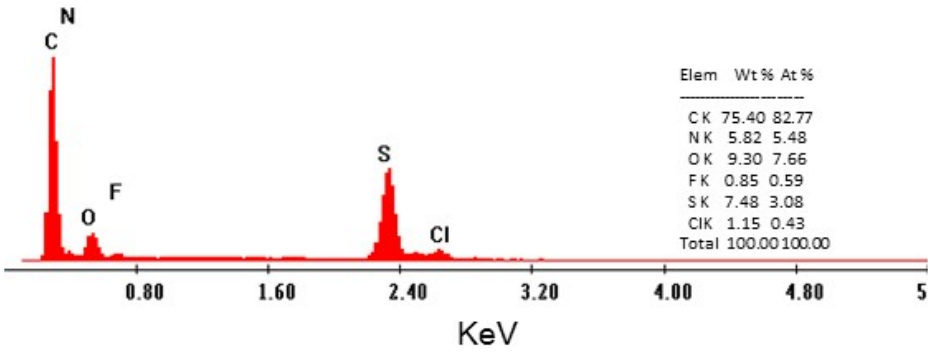


Fig. S44 EDX spectrum of **PHTT_DMP_O**.

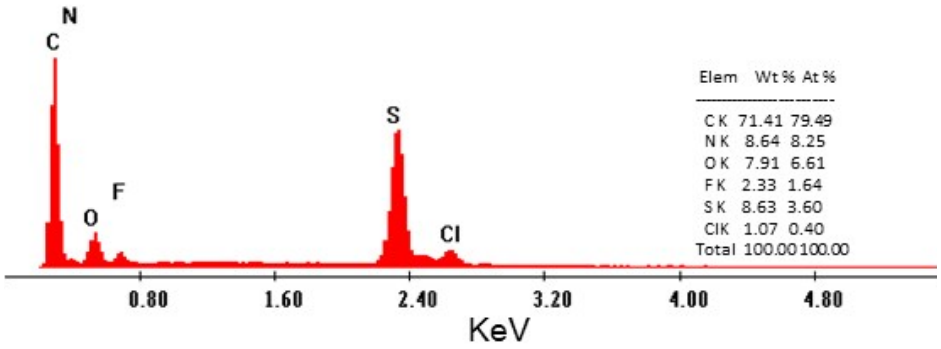


Fig. S45 EDX spectrum of **PHTT_BDP**.

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2) P. V. Dau, K. K. Tanabe, S. M. Cohen, *Chem. Commun.*, 2012, **48**, 9370-9372.
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