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Band gap modulation in zirconium-based metal-organic frameworks by defect engineering

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ELECTRONIC SUPPLEMENTARY INFORMATION

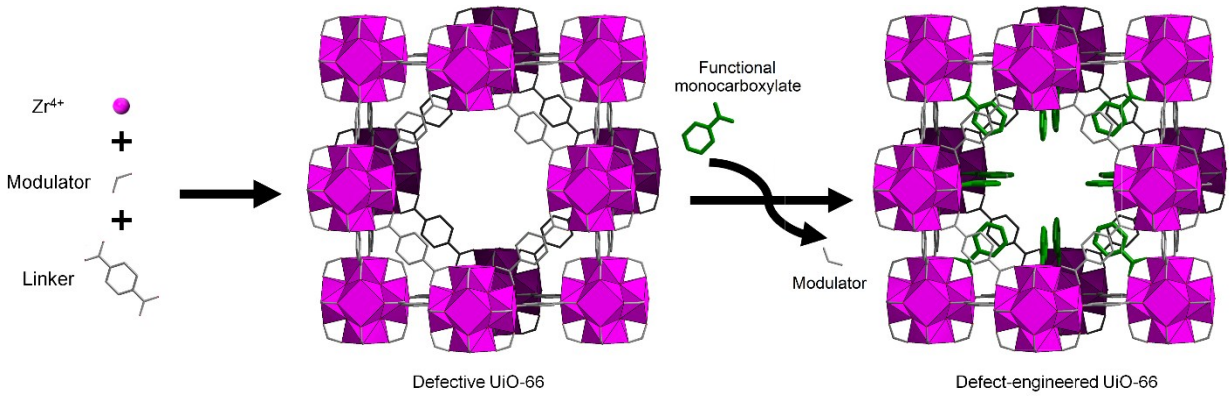

Figure S1. Post-synthetic defect-exchange route to defect-engineered UiO-66: first, a defective MOF is synthesised employing a crystallisation modulator (e.g. formic acid), then the desired functional monocarboxylate is grafted at defective sites, replacing the modulator.

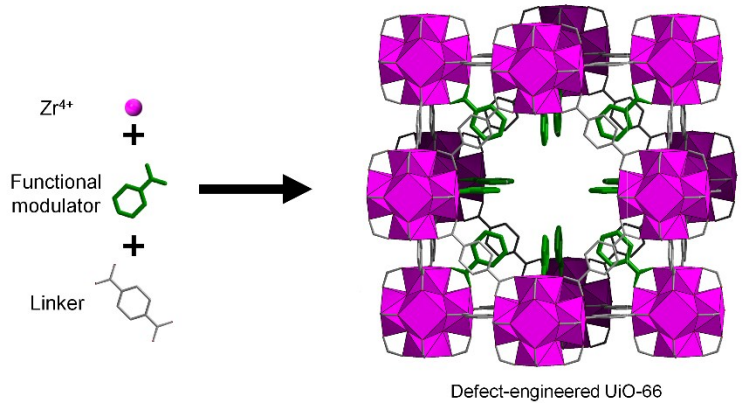

Figure S2. Modulated synthesis route to defect-engineered UiO-66: the desired functional monocarboxylate is employed as crystallisation modulator during synthesis and retained in the structure of the resulting defective MOF.

SYNTHESIS AND CHARACTERISATION

Chemicals

$ZrCl_4$ (98%) was purchased from Acros Organics. 1,4-benzenedicarboxylic acid (BDC, 98%) and benzoic acid (BA, 99%) were purchased from Alfa Aesar. Formic acid (FA, 98-100%) and 2-aminobenzoic acid (2ABA, 99%) were purchased from Merck Millipore. *N,N*-dimethylformamide (DMF) was purchased from Sigma. 3-aminobenzoic acid (3ABA, 99%), 4-aminobenzoic acid (4ABA, 99%), 3,5-diaminobenzoic acid (35DABA, 98%) and 3,4-diaminobenzoic acid (34DABA, 97%) were purchased from Aldrich. 2,3-diaminobenzoic acid (23DABA, 97%) was purchased from Fluorochem. 2,5-diaminobenzoic acid (25DABA, 98%) was purchased from Carbosynth.

Synthetic procedures

Synthesis of FA_mod: $ZrCl_4$ (5.83 g, 25.0 mmol) was dissolved in DMF (405.0 mL), followed by the addition of water (1.35 mL, 75.0 mmol), FA (94.0 mL, 2500.0 mmol) and BDC (4.35 g, 25.00 mmol). The mixture was sonicated until complete dissolution, divided into two 500 mL Schott bottles and kept for 24 hours at 120 °C. The solid was subsequently filtered and washed with DMF (2 × 250 mL, two-hour soaking), water (2 × 150 mL, two-hour soaking) and acetone (150 mL, two-hour soaking). The solid was dried in air at 80 °C for two hours. Yield: 6.6 g.

Synthesis of defect-engineered MOFs by post-synthetic defect exchange (PSDE): FA_mod-2ABA, FA_mod-3ABA, FA_mod-4ABA, FA_mod-35DABA and FA_mod-BA resulted from the suspension of FA_mod (0.50 g) in the respective solution of 2ABA, 3ABA, 4ABA, 35DABA and BA (0.1 M) in DMF (30.0 mL) for 24 hours at 80 °C. Afterwards, the solids were centrifuged and washed with DMF (2 × 7 mL, one-hour soaking), water (2 × 5 mL, two-hour soaking) and acetone (10 mL, two-hour soaking). The solids were dried in air at 80 °C for two hours. Yields: 479 mg (FA_mod-2ABA); 477 mg (FA_mod-3ABA); 495 mg (FA_mod-4ABA); 495 mg (FA_mod-35DABA); 480 mg (FA_mod-BA).

Synthesis of defect-engineered MOFs by modulation method: $ZrCl_4$ (233 mg, 1.0 mmol) was dissolved in DMF (10.0 mL) in a 20 mL glass vial, followed by the addition of water (0.054 mL, 3.0 mmol). The desired ABA modulator was then added (2ABA, 3ABA, 4ABA: 2.1 g, 15.0 mmol; 35DABA: 3.82 g, 25.0 mmol) and the mixture was sonicated until complete dissolution. Finally, BDC (166 mg, 1.0 mmol) was added, the mixture was sonicated until complete dissolution and kept for 24 hours at 120 °C. The solid was subsequently centrifuged and washed with DMF (2 × 10 mL, two-hour soaking), water (2 × 10 mL, two-hour soaking) and acetone (10 mL, two-hour soaking). The solids were dried in air at 80 °C for two hours. Yields: 333 mg (2ABA_mod); 403 mg (3ABA_mod); 331 mg (4ABA_mod); 311 mg (35DABA_mod).

Synthesis of UiO-66-NH_2_33%: $ZrCl_4$ (233 mg, 1.0 mmol) was dissolved in DMF (10.0 mL) in a 20 mL glass vial, followed by the addition of water (0.054 mL, 3.0 mmol) and the mixture was sonicated until complete dissolution. Finally, BDC (116 mg, 0.7 mmol) and ABDC (54 mg, 0.3 mmol) were added, the mixture was sonicated until complete dissolution and kept for 24 hours at 120 °C. The solid was subsequently filtered and washed with DMF (2 × 10 mL, two-hour soaking), water (2 × 10 mL, two-hour soaking) and acetone (10 mL, two-hour soaking). The solid was dried in air at 80 °C for two hours. Yield: 341 mg.

Analytical procedures

Powder X-ray diffraction (PXRD) patterns were collected in the 4-30° 2θ range with a Bruker D8 Avance diffractometer working in reflection geometry and equipped with a LYNXEYE XE detector, using the Cu Kα radiation. The X-ray tube was operated at 40 kV and 40 mA.

N_2 sorption isotherms at 77 K were measured with a Quantachrome Nova 2000e analyzer. The samples (about 30-50 mg) were activated for four hours under vacuum at 120 °C prior to analysis. BET surface areas were calculated in the 0.001-0.043 P/P_0 range. Pore volume was determined at $P/P_0 = 0.90$. Pore size distribution was determined using the Density Functional theory (DFT) method implemented in the Quantachrome NovaWin software. The kernel implemented in NovaWin software was Non Local DFT (NLDFT)- N_2 – carbon equilibrium transition kernel at 77 K based on a slit pore model.

Thermogravimetric analysis (TGA) was performed with a TA Instruments SDT-Q600 instrument using alumina cups at and a 5 °C min^{-1} heating rate up to 700 °C in air.

Quantitative NMR analysis of hydrolysed solids was performed with a Bruker AV-500 Avance III spectrometer. About 10-15 mg of solid was introduced in a pre-weighed glass vial and kept at 120 °C for two hours. Afterwards, the vial was capped while still hot and weighed to determine the mass of the desolvated solid (the cap had previously been weighed alongside the vial). 0.8 mL of 1 M NaOH in D_2O, spiked with 0.1 M acetic acid as an internal standard, was then added to the vial and the mixture briefly sonicated and left to digest overnight. The NMR tubes were then loaded with the solution, taking care to avoid transferring solid particles in the tubes.

Optical properties of each material were assessed using a spring-loaded powder cell in an Agilent Cary 100 UV-Vis spectrophotometer. The spectra were referenced to a Labsphere Spectralon diffuse reflectance standard. The spectra were recorded between wavelengths of 200 nm and 800 nm, using an increment size of 1 nm and an integration time of 1 s. A custom MATLAB code was used to produce Tauc plots from which the band gap extrapolated by a line-of-best-fit through the point of steepest gradient within the absorption cut-off curve.

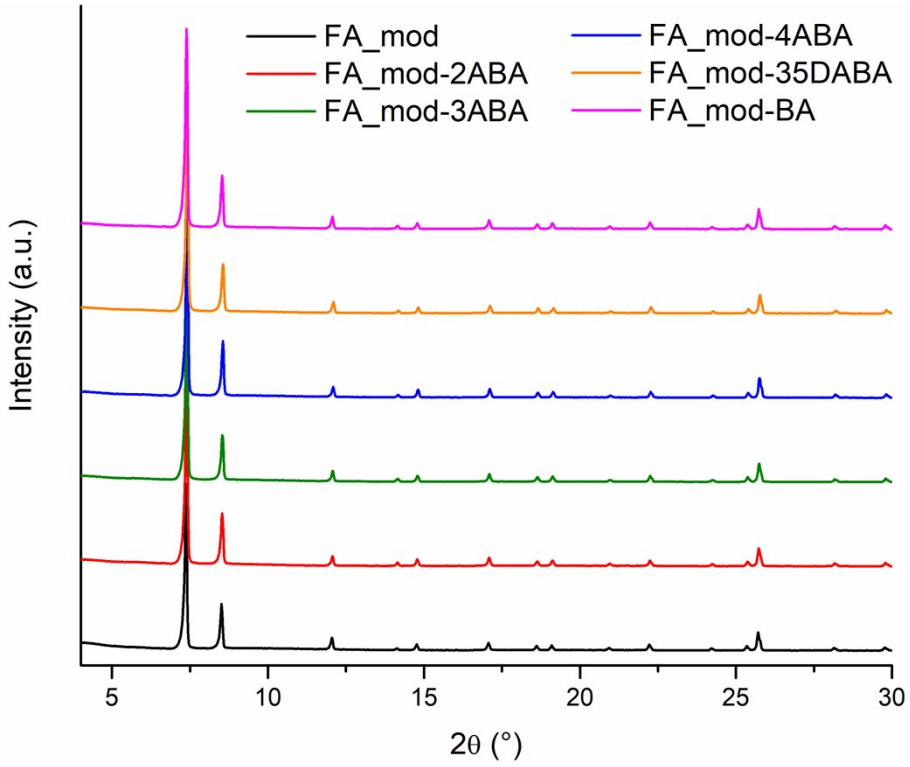

Figure S3. PXRD patterns of FA_mod (black), FA_mod-2ABA (red), FA_mod-3ABA (olive), FA_mod-4ABA (blue), FA_mod-35DABA (orange) and FA_mod-BA (magenta).

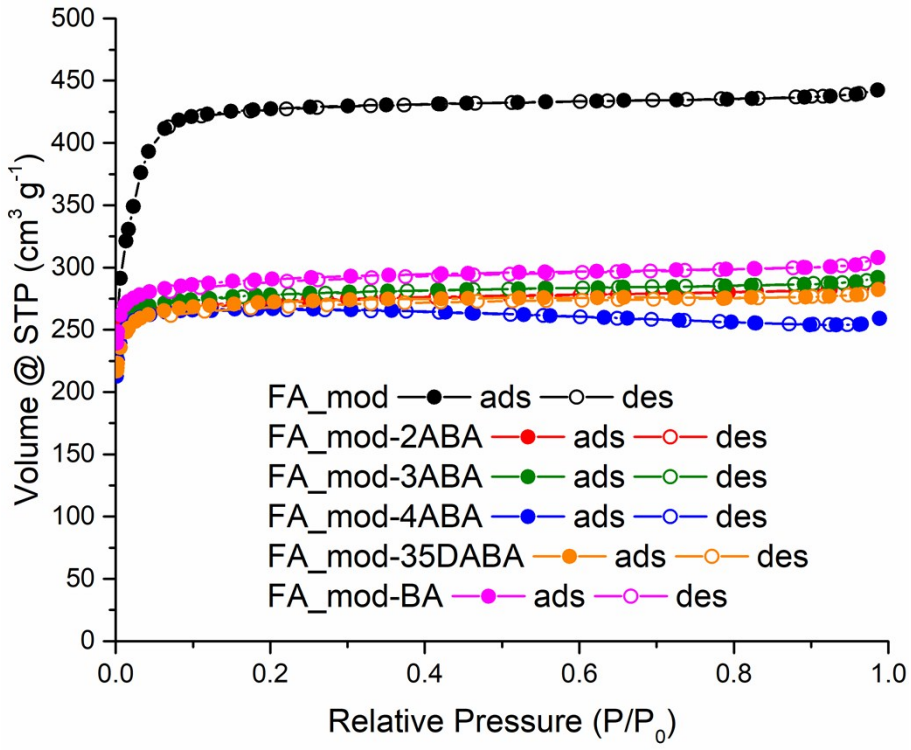

Figure S4. N_2 sorption isotherms at 77 K of FA_mod (black), FA_mod-2ABA (red), FA_mod-3ABA (olive), FA_mod-4ABA (blue), FA_mod-35DABA (orange) and FA_mod-BA (magenta).

Table S1. BET surface area and pore volume values extracted from the isotherms in Figure S4.

Sample	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
FA_mod	1524.6	0.68
FA_mod-2ABA	1115.4	0.44
FA_mod-3ABA	1135.1	0.44
FA_mod-4ABA	1105.1	0.42
FA_mod-35DABA	1103.0	0.43
FA_mod-BA	1180.8	0.47

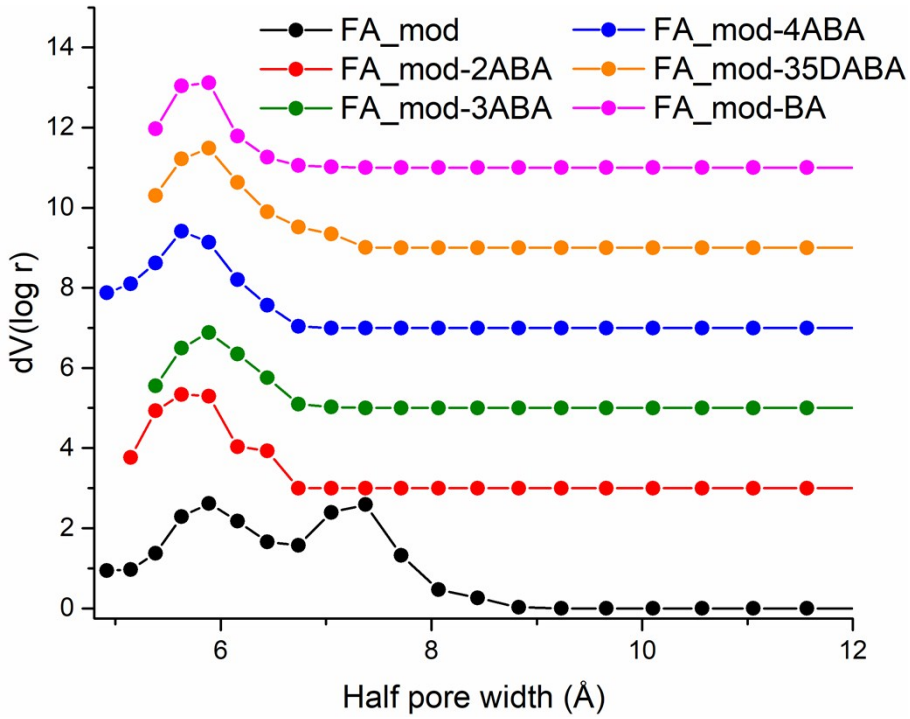

Figure S5. Pore size distribution of FA_mod (black), FA_mod-2ABA (red), FA_mod-3ABA (olive), FA_mod-4ABA (blue), FA_mod-35DABA (orange) and FA_mod-BA (magenta).

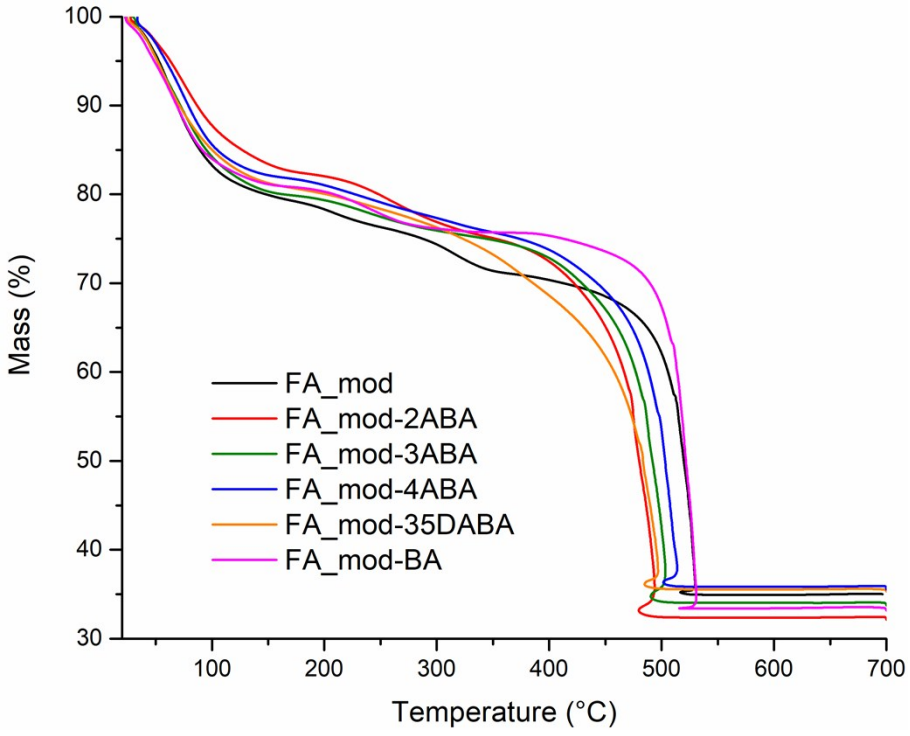

Figure S6. TGA curves of FA_mod (black), FA_mod-2ABA (red), FA_mod-3ABA (olive), FA_mod-4ABA (blue), FA_mod-35DABA (orange) and FA_mod-BA (magenta).

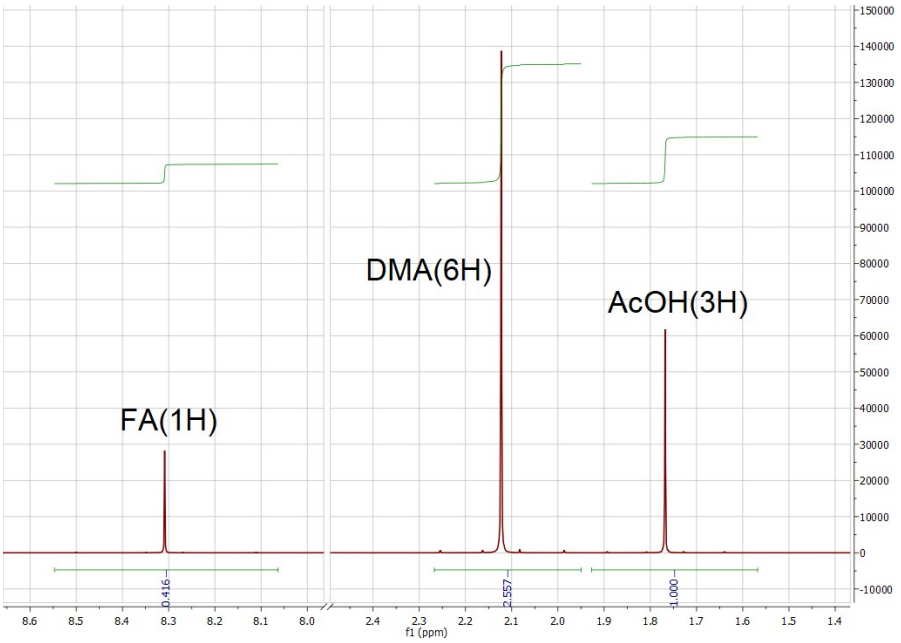

Figure S7. ^{1}H-NMR spectrum of DMF (10 µL, 0.13 mmol) digested in 1.0 mL of 0.1 M NaOH in D_2O, spiked with 0.1 M AcOH as internal standard. No signals of DMF are visible, whereas dimethylamine (DMA) and formic acid (FA), the products of hydrolysis of DMF, are observed. The signal of DMA accounts for six protons belonging to two methyl groups, while the one of FA accounts for one formyl proton. By dividing the integral of DMA (2.557) by six, a value of 0.426 is obtained, which closely matches the integral of FA (0.416). In order to determine the concentration of DMF, the integral of AcOH (1.000) is divided by three (giving 0.333), the integral of FA is divided by this number (giving 1.249), and finally multiplied by 0.1, returning 0.125 M, a value in good agreement with the expected figure of 0.130 M. These results suggest that trace DMF present in the MOFs is completely hydrolysed in the conditions employed to digest the solids. In addition, the amount of DMF can be derived from the integral of DMA, which is fully retained in solution despite its low boiling point. In addition, the use of AcOH as internal standard allows to accurately determine the absolute concentration of species in solution.

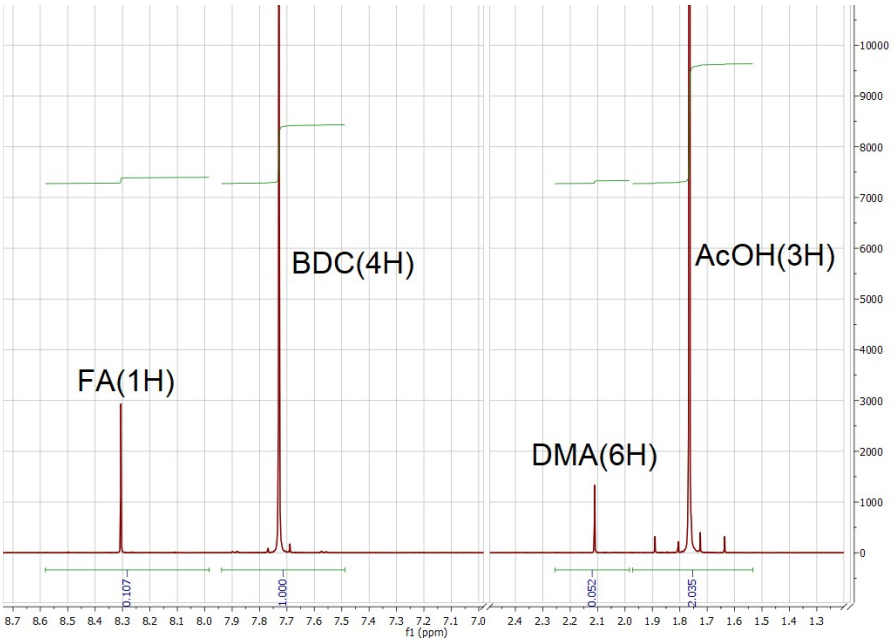

Figure S8. ^{1}H NMR spectrum of FA_mod. The signal of DMA suggests that a little amount of DMF is present in the solid. As a consequence, the integral of FA is the combination of FA derived from DMF and FA present in the MOF. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.107) is subtracted of the value determined by dividing the integral of DMA by six (0.009), giving a value of 0.098. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with that of FA. This leads to calculate a BDC/FA ratio of 2.55. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x}(FA)_{2x}$, the following can be written:

$$\frac{6-x}{2x} = 2.55$$

Solving the equation, a value of 0.98 is found for *x*. The proposed formula unit for FA_mod is therefore $Zr_6O_4(OH)_4(BDC)_{5.02}(FA)_{1.96}$. The absolute concentration of BDC and FA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (2.035) and multiplying the result by 0.1, obtaining 0.037 M for BDC and 0.014 M for FA. The weight % of BDC and FA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA) and dividing the obtained values (4.84 mg for BDC, 0.52 mg for FA) by the mass of the desolvated MOF digested (9 mg), resulting in 53.7% for BDC and 5.8% for FA. Table S2 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

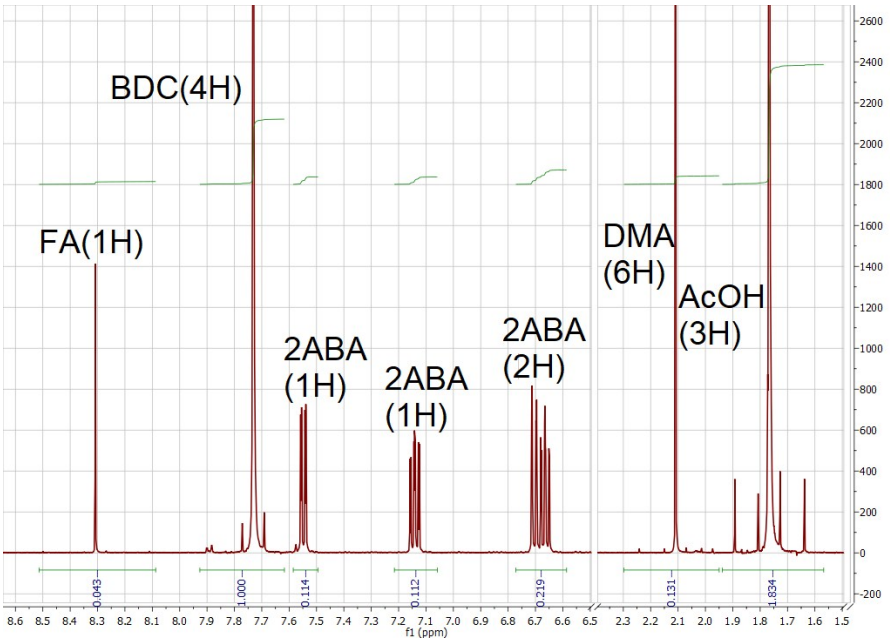

Figure S9. ^{1}H NMR spectrum of FA_mod-2ABA. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.043) is subtracted of the value determined by dividing the integral of DMA by six (0.022), giving a value of 0.021. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 2ABA (0.111, average of three signals accounting for one, one and two aromatic protons each). This leads to calculate a BDC/FA ratio of 11.28 and a BDC/2ABA ratio of 2.21. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(2ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 11.28$$

$$\frac{6-x-y}{2y} = 2.21$$

Solving the equation, a value of 0.21 is found for *x* and a value of 1.07 is found for *y*. The proposed formula unit for FA_mod-2ABA is therefore $Zr_6O_4(OH)_4(BDC)_{4.72}(FA)_{0.42}(2ABA)_{2.14}$. The absolute concentration of BDC, FA and 2ABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.834) and multiplying the result by 0.1, obtaining 0.041 M for BDC, 0.004 M for FA and 0.019 M for 2ABA. The weight % of BDC, FA and 2ABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 136 for 2ABA) and dividing the obtained values (5.37 mg for BDC, 0.13 mg for FA, 2.01 mg for 2ABA) by the mass of the desolvated MOF digested (12.5 mg), resulting in 42.9% for BDC, 1.0% for FA and 16.1% for 2ABA. Table S2 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

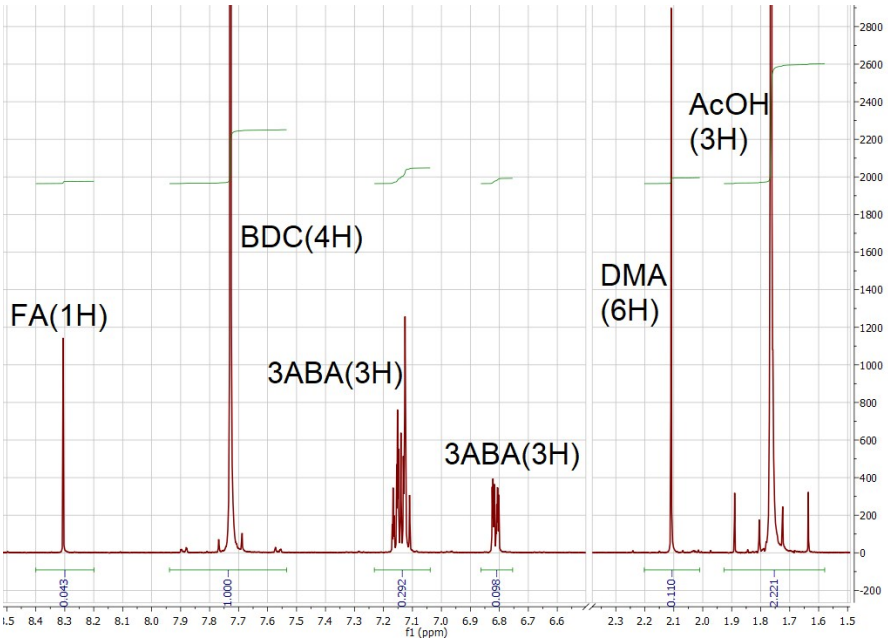

Figure S10. ^{1}H NMR spectrum of FA_mod-3ABA. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.043) is subtracted of the value determined by dividing the integral of DMA by six (0.018), giving a value of 0.025. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 3ABA (0.098, average of two signals accounting for three and one aromatic protons each). This leads to calculate a BDC/FA ratio of 10.34 and a BDC/3ABA ratio of 2.45. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(3ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 10.34$$

$$\frac{6-x-y}{2y} = 2.45$$

Solving the equation, a value of 0.23 is found for *x* and a value of 0.98 is found for *y*. The proposed formula unit for FA_mod-3ABA is therefore $Zr_6O_4(OH)_4(BDC)_{4.79}(FA)_{0.46}(3ABA)_{1.96}$. The absolute concentration of BDC, FA and 3ABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.834) and multiplying the result by 0.1, obtaining 0.034 M for BDC, 0.003 M for FA and 0.014 M for 3ABA. The weight % of BDC, FA and 3ABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 136 for 3ABA) and dividing the obtained values (5.37 mg for BDC, 0.13 mg for FA, 2.01 mg for 3ABA) by the mass of the desolvated MOF digested (10.0 mg), resulting in 44.3% for BDC, 1.2% for FA and 15.0% for 3ABA. Table S2 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

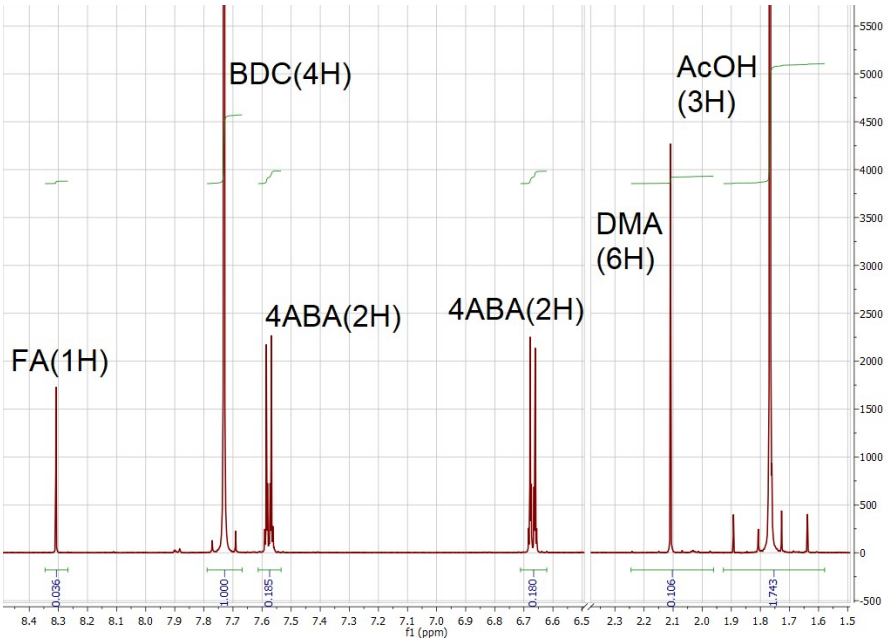

Figure S11. ^{1}H NMR spectrum of FA_mod-4ABA. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.036) is subtracted of the value determined by dividing the integral of DMA by six (0.018), giving a value of 0.018. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 4ABA (0.091, average of two signals accounting for two aromatic protons each). This leads to calculate a BDC/FA ratio of 13.89 and a BDC/4ABA ratio of 2.78. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(4ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 13.89$$

$$\frac{6-x-y}{2y} = 2.78$$

Solving the equation, a value of 0.17 is found for *x* and a value of 0.86 is found for *y*. The proposed formula unit for FA_mod-4ABA is therefore $Zr_6O_4(OH)_4(BDC)_{4.97}(FA)_{0.34}(4ABA)_{1.72}$. The absolute concentration of BDC, FA and 4ABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.743) and multiplying the result by 0.1, obtaining 0.043 M for BDC, 0.003 M for FA and 0.016 M for 4ABA. The weight % of BDC, FA and 4ABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 136 for 4ABA) and dividing the obtained values (5.65 mg for BDC, 0.11 mg for FA, 1.69 mg for 4ABA) by the mass of the desolvated MOF digested (12.0 mg), resulting in 47.1% for BDC, 0.9% for FA and 14.0% for 4ABA. Table S2 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

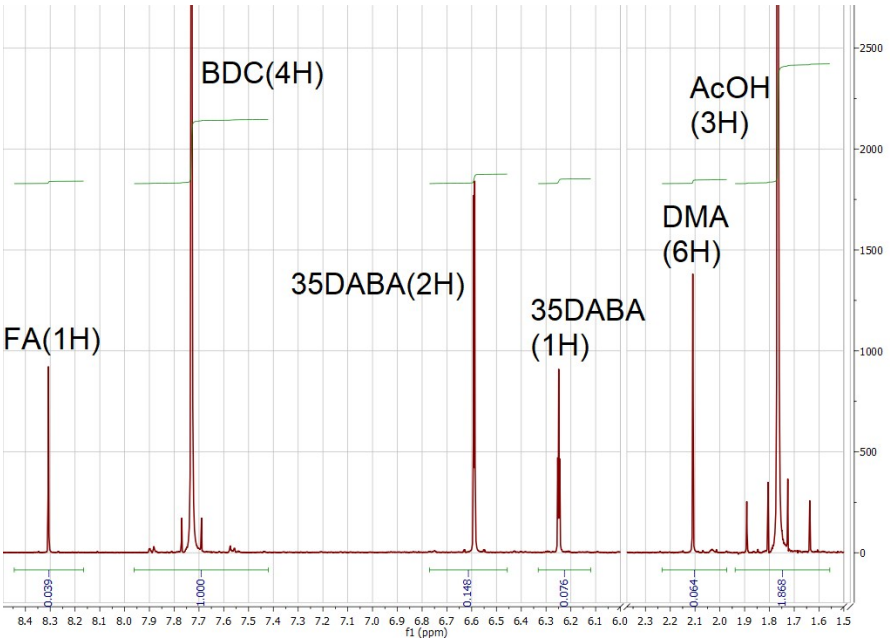

Figure S12. ^{1}H NMR spectrum of FA_mod-35DABA. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.039) is subtracted of the value determined by dividing the integral of DMA by six (0.011), giving a value of 0.028. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 35DABA (0.075, average of two signals accounting for two and one aromatic protons each). This leads to calculate a BDC/FA ratio of 8.93 and a BDC/35DABA ratio of 3.29. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(35DABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 8.93$$

$$\frac{6-x-y}{2y} = 3.29$$

Solving the equation, a value of 0.28 is found for *x* and a value of 0.74 is found for *y*. The proposed formula unit for FA_mod-35DABA is therefore $Zr_6O_4(OH)_4(BDC)_{4.98}(FA)_{0.56}(35DABA)_{1.48}$. The absolute concentration of BDC, FA and 35DABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.868) and multiplying the result by 0.1, obtaining 0.040 M for BDC, 0.004 M for FA and 0.012 M for 35DABA. The weight % of BDC, FA and 35DABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 151 for 35DABA) and dividing the obtained values (5.27 mg for BDC, 0.16 mg for FA, 1.47 mg for 35DABA) by the mass of the desolvated MOF digested (12.0 mg), resulting in 43.9% for BDC, 1.4% for FA and 12.3% for 35DABA. Table S2 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

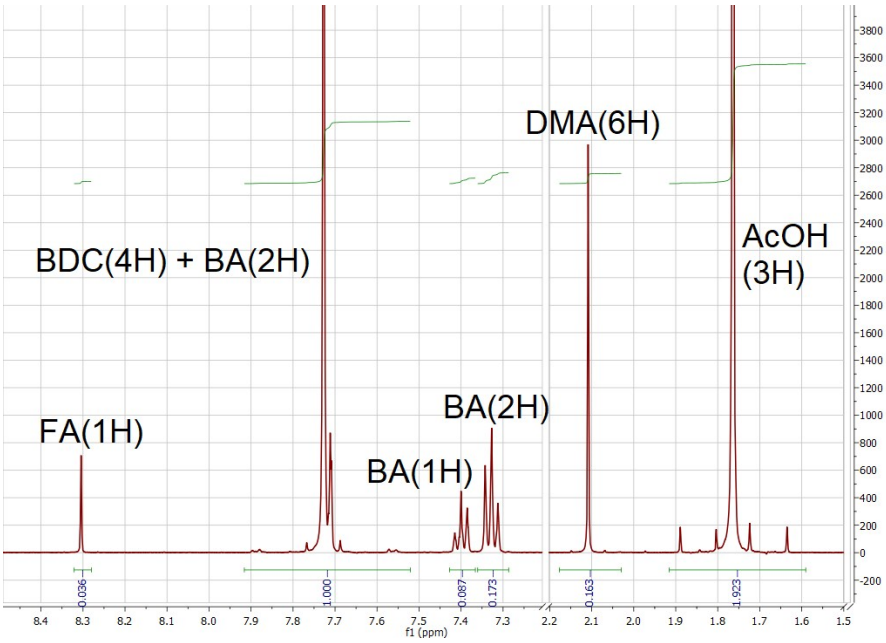

Figure S13. ^{1}H NMR spectrum of FA_mod-BA. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.036) is subtracted of the value determined by dividing the integral of DMA by six (0.027), giving a value of 0.009. The signal of BDC superimposes with one of the signals of BA (accounting for two aromatic protons), therefore the value of the integral of BDC (0.216) is derived by subtracting that of BA (0.173, average of two signals accounting for one and two aromatic protons each) from 1.000 and dividing the result (0.863) by four. This leads to calculate a BDC/FA ratio of 25.88 and a BDC/BA ratio of 2.41. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(BA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 25.88$$

$$\frac{6-x-y}{2y} = 2.41$$

Solving the equation, a value of 0.09 is found for *x* and a value of 1.06 is found for *y*. The proposed formula unit for FA_mod-BA is therefore $Zr_6O_4(OH)_4(BDC)_{4.85}(FA)_{0.18}(BA)_{2.12}$. The absolute concentration of BDC, FA and BA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.923) and multiplying the result by 0.1, obtaining 0.032 M for BDC, 0.001 M for FA and 0.013 M for BA. The weight % of BDC, FA and BA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 121 for BA) and dividing the obtained values (4.25 mg for BDC, 0.05 mg for FA, 1.30 mg for BA) by the mass of the desolvated MOF digested (9.0 mg), resulting in 47.2% for BDC, 0.5% for FA and 14.5% for BA. Table S2 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

Table S2. Compositional analysis of the MOFs prepared by PSDE, based on NMR data.

Sample	Proposed formula unit	BDC wt%		FA wt%		Benzoic acid analogue wt%	
		Exp[a]	Calc[b]	Exp[a]	Calc[b]	Exp[a]	Calc[b]
FA_mod	$Zr_6O_4(OH)_4(BDC)_{5.02}(FA)_{1.96}$	53.7%	51.8.7%	5.8%	5.6%	-	-
FA_mod-2ABA	$Zr_6O_4(OH)_4(BDC)_{4.72}(FA)_{0.42}(2ABA)_{2.14}$	42.9%	43.9%	1.0%	1.1%	16.2%	16.5%
FA_mod-3ABA	$Zr_6O_4(OH)_4(BDC)_{4.79}(FA)_{0.46}(3ABA)_{1.96}$	44.9%	44.3%	1.2%	1.2%	15.0%	15.2%
FA_mod-4ABA	$Zr_6O_4(OH)_4(BDC)_{4.97}(FA)_{0.34}(4ABA)_{1.72}$	47.1%	46.8%	0.9%	0.9%	13.6%	13.3%
FA_mod-35DABA	$Zr_6O_4(OH)_4(BDC)_{4.98}(FA)_{0.56}(35DABA)_{1.48}$	43.9%	46.9%	1.4%	1.4%	12.1%	12.8%
FA_mod-BA	$Zr_6O_4(OH)_4(BDC)_{4.85}(FA)_{0.18}(BA)_{2.12}$	47.1%	45.8%	0.5%	0.5%	14.5%	14.8%

[a] The mass of each acid was derived starting from the integral ratio with respect to internal standard AcOH; [b] On the basis of the proposed formula unit

Table S3. Comparison of the weight loss observed above 400 °C in the TGA with the expected one derived from the proposed formula unit on the basis of NMR analysis.

Sample	Calculated weight loss at framework decomposition (from formula unit)[a]	Observed weight loss at framework decomposition (from TGA)[b]	Difference
FA_mod	663.0	753.2	12.0%
FA_mod-2ABA	892.5	958.1	6.9%
FA_mod-3ABA	879.8	873.9	-0.7%
FA_mod-4ABA	875.7	823.9	-6.3%
FA_mod-35DABA	871.6	840.2	-3.7%
FA_mod-BA	877.4	932.5	5.9%

[a] Calculated assuming dehydroxylated clusters and removal of FA; [b] Determined assuming ZrO_2 as final decomposition product

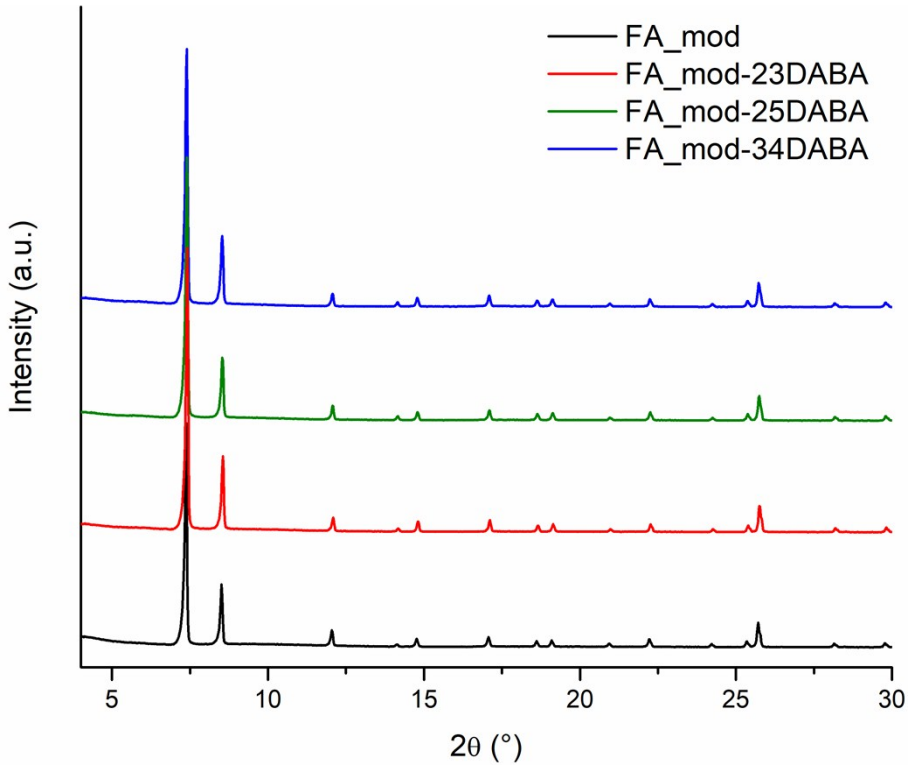

Figure S14. PXRD patterns of FA_mod (black), FA_mod-23DABA (red), FA_mod-25DABA (olive) and FA_mod-34DABA (blue).

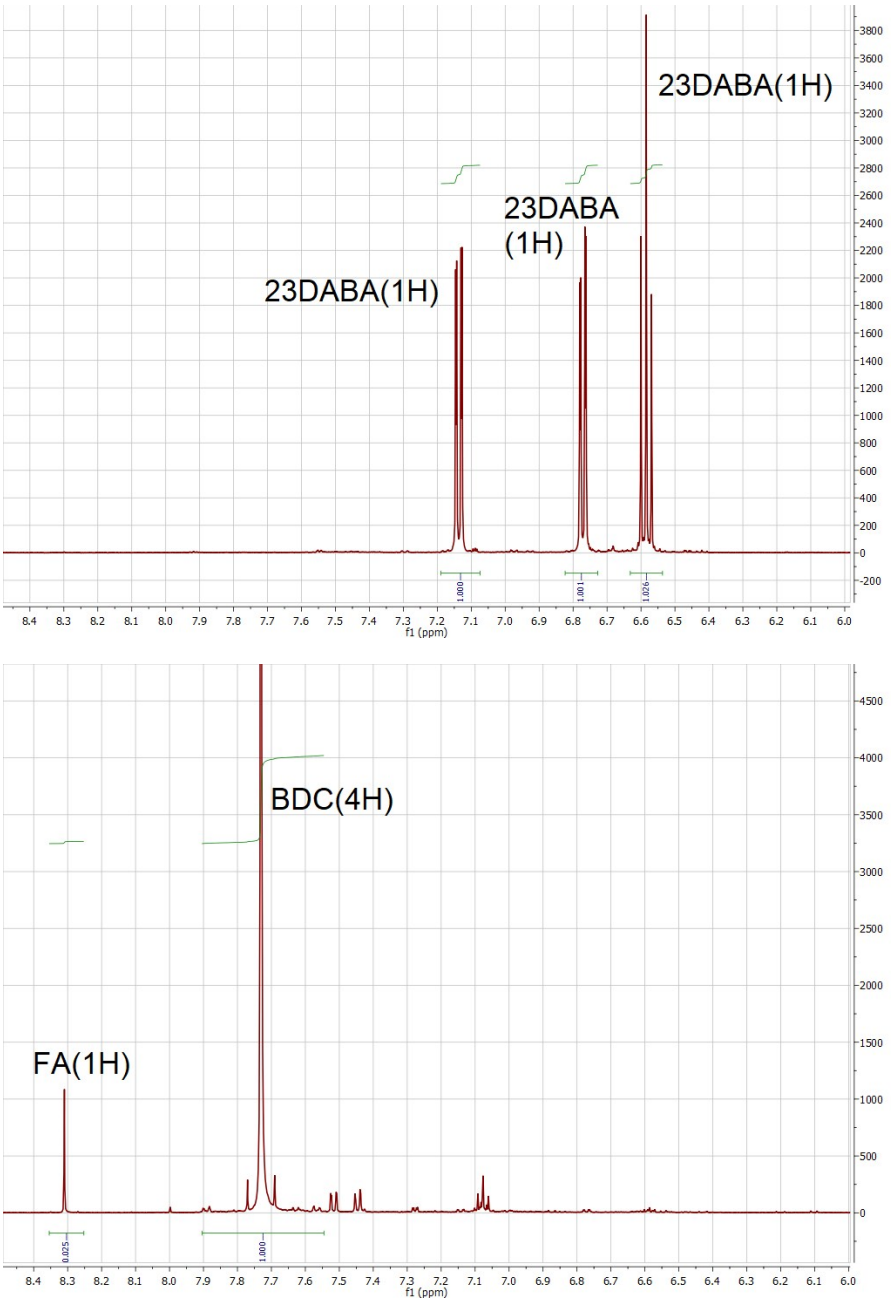

Figure S15. ^{1}H NMR spectrum of 23DABA (top) and FA_mod-23DABA (bottom) in the 8.5 to 6.0 ppm region. The signals of 23DABA are not visible in the bottom spectrum, suggesting that it was not introduced in the framework, despite the BDC/FA ratio grew from 2.55 in FA_mod to 10.00 in FA_mod-23DABA and the solid had turned dark red in colour. Some minor signals of unknown origin can be seen in the bottom spectrum, which might derive from decomposition of 23DABA during the exchange process.

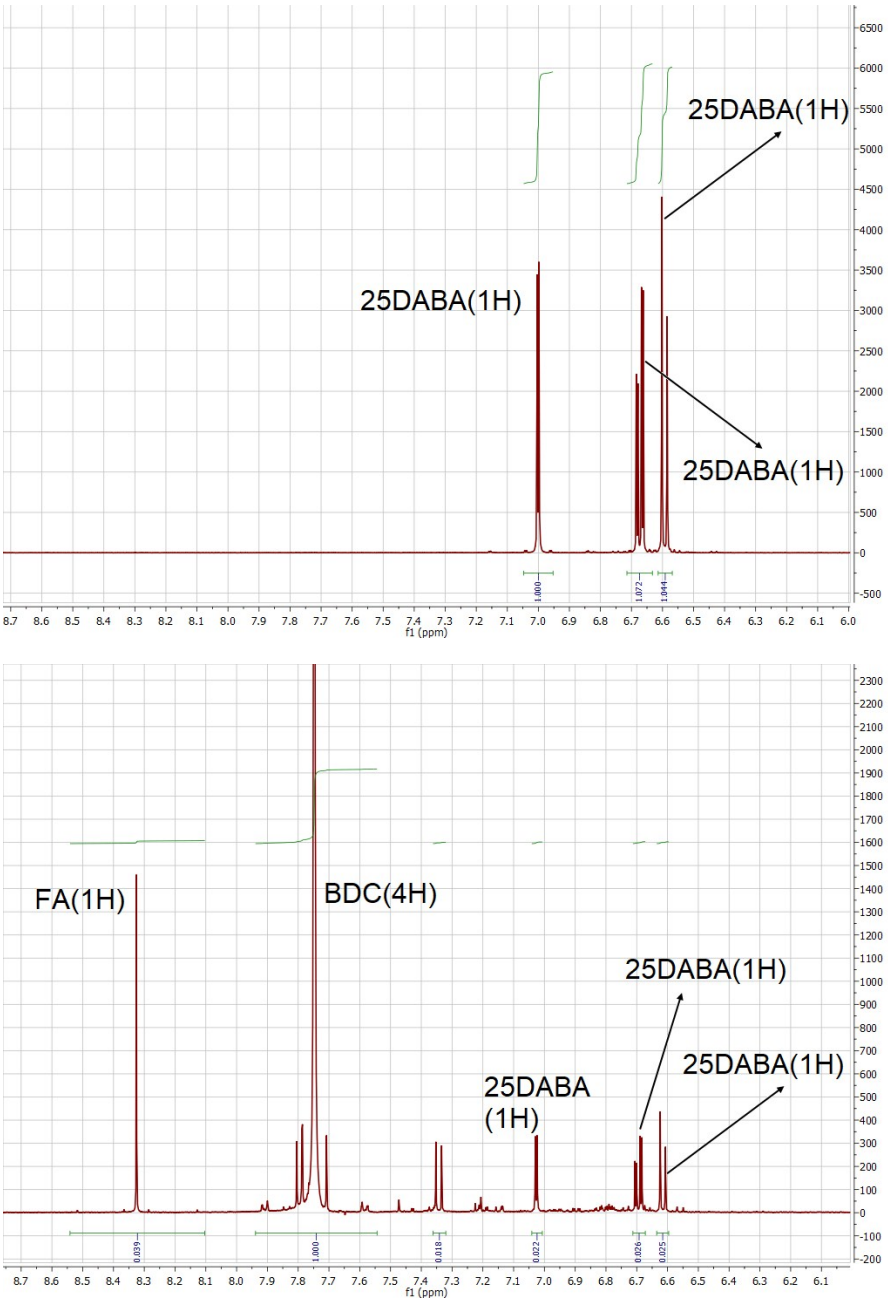

Figure S16. ^{1}H NMR spectrum of 25DABA (top) and FA_mod-25DABA (bottom) in the 8.75 to 6.0 ppm region. The signals of 25DABA are visible in the bottom spectrum, but the average integral of 0.024 suggests that it was introduced in the framework only in very little amount, despite the BDC/FA ratio grew from 2.55 in FA_mod to 6.41 in FA_mod-25DABA and the solid had turned deep purple in colour. Some minor signals of unknown origin can be seen in the bottom spectrum, which might derive from decomposition of 25DABA during the exchange process.

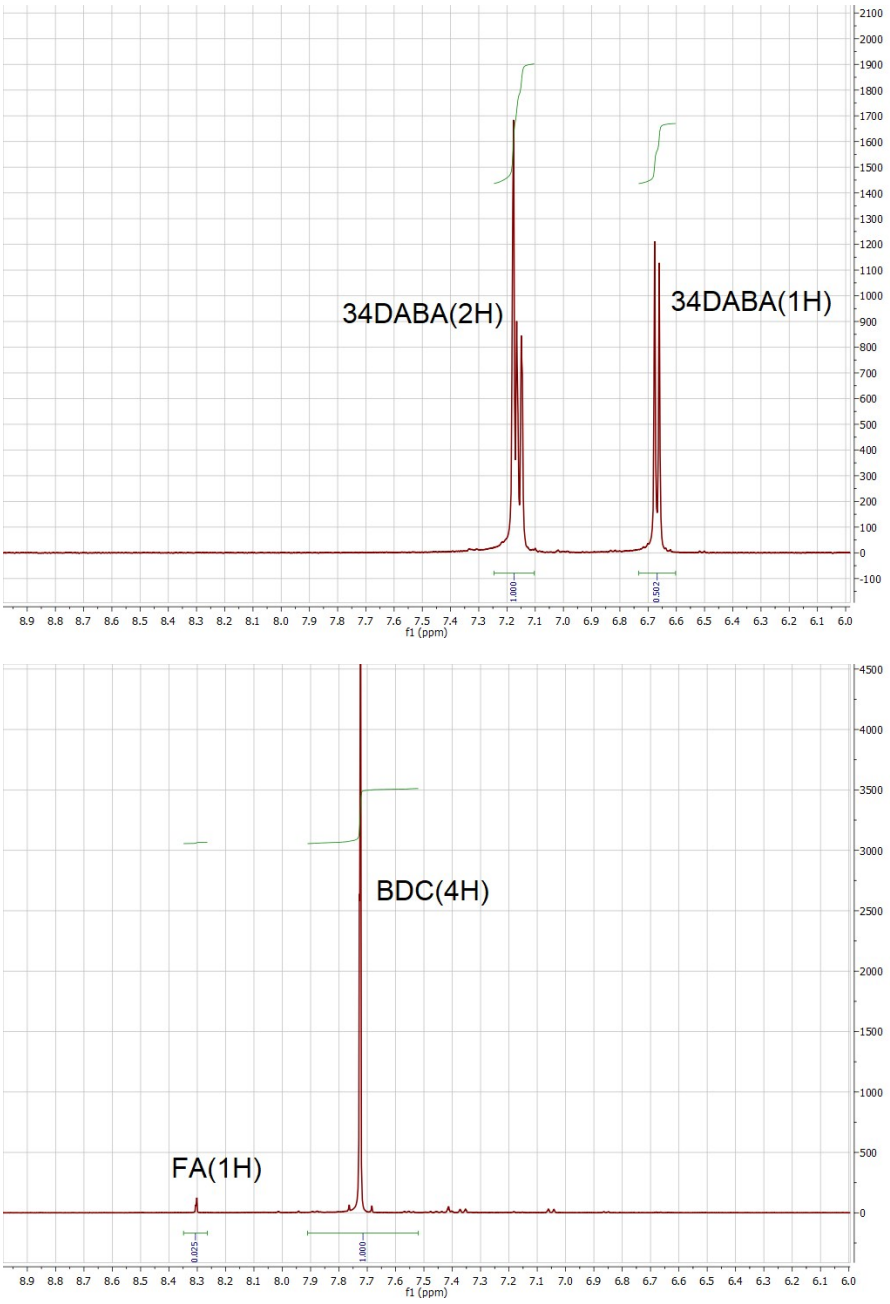

Figure S17. ^{1}H NMR spectrum of 34DABA (top) and FA_mod-34DABA (bottom) in the 9.0 to 6.0 ppm region. The signals of 34DABA are not visible in the bottom spectrum, suggesting that it was not introduced in the framework, despite the BDC/FA ratio grew from 2.55 in FA_mod to 10.00 in FA_mod-34DABA and the solid had turned beige in colour. Some minor signals of unknown origin can be seen in the bottom spectrum, which might derive from decomposition of 34DABA during the exchange process.

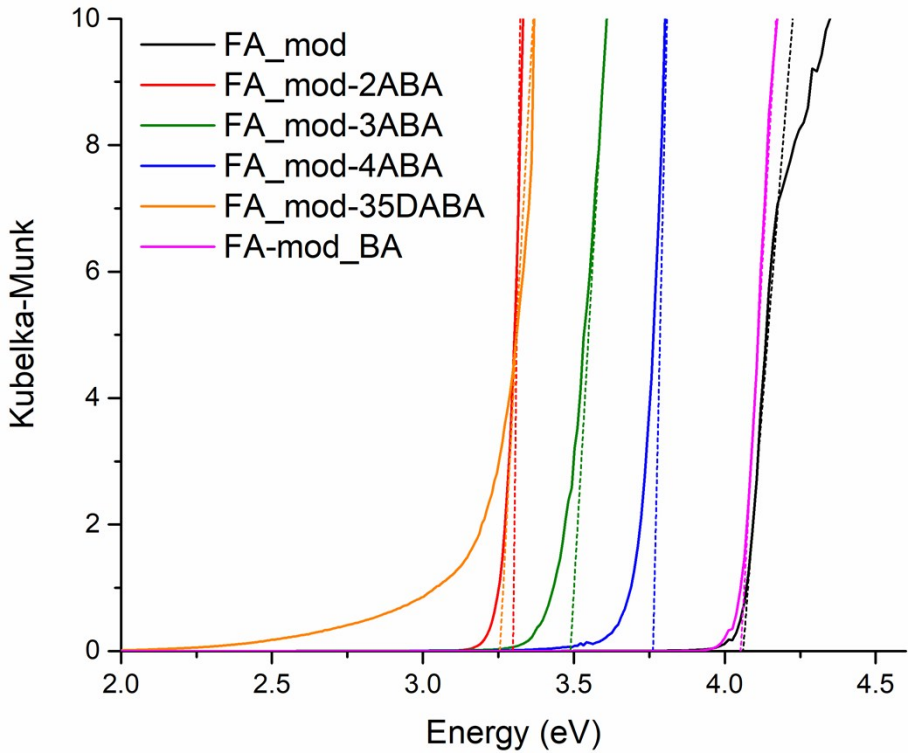

Figure S18. Tauc plots (solid lines) derived from the diffuse reflectance UV-Vis spectra in Figure 2 and relative fittings (dashed lines) for FA_mod (black), FA_mod-2ABA (red), FA_mod-3ABA (olive), FA_mod-4ABA (blue), FA_mod-35DABA (orange) and FA_mod-BA (magenta).

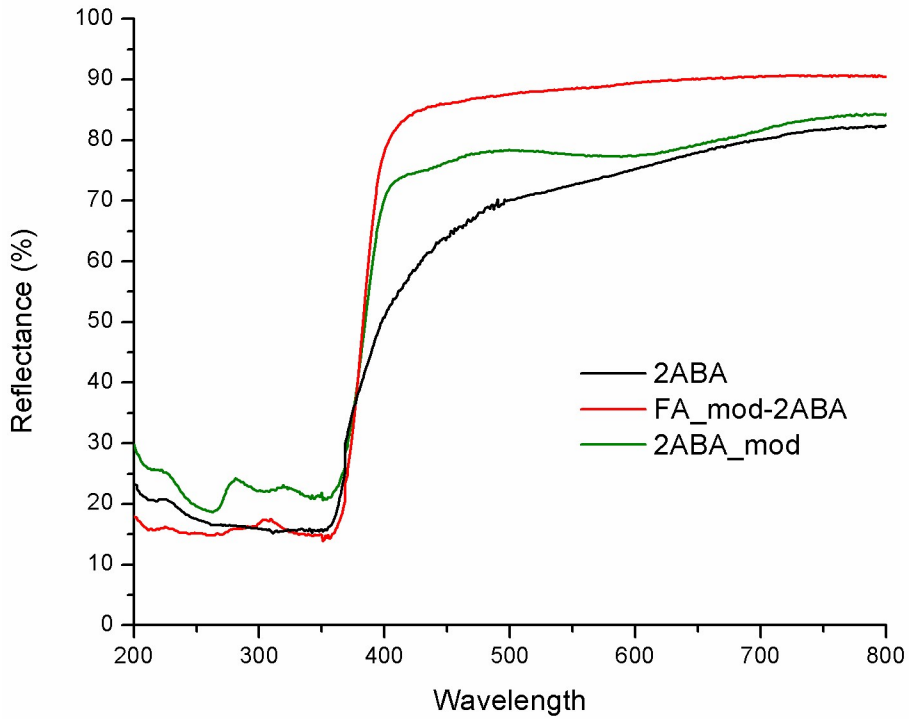

Figure S19. Diffuse reflectance UV-Vis spectra for 2ABA (black), FA_mod-2ABA (red) and 2ABA_mod (olive).

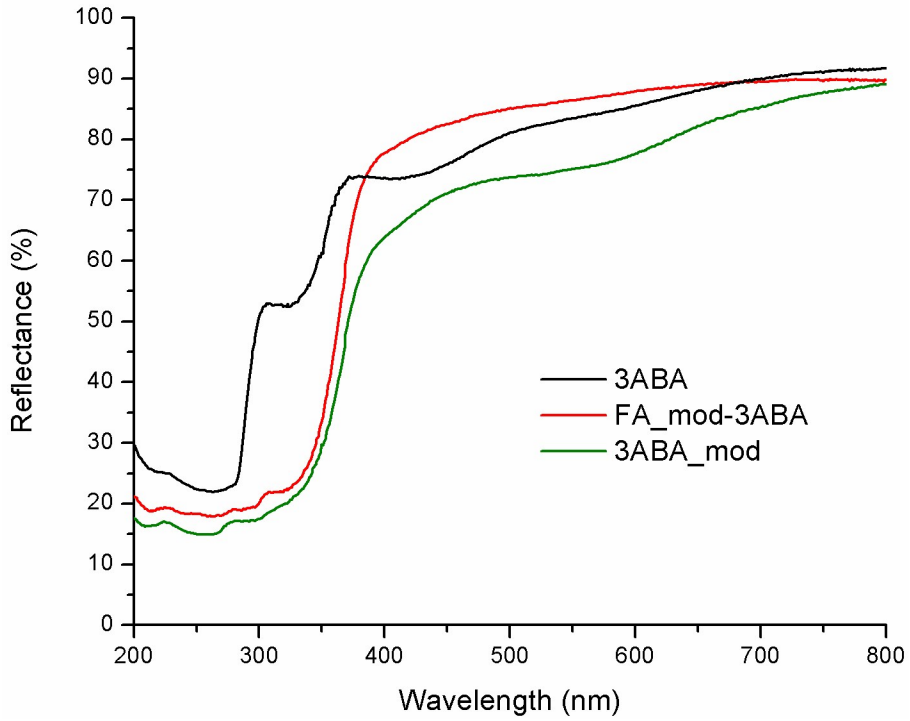

Figure S20. Diffuse reflectance UV-Vis spectra for 3ABA (black), FA_mod-3ABA (red) and 3ABA_mod (olive).

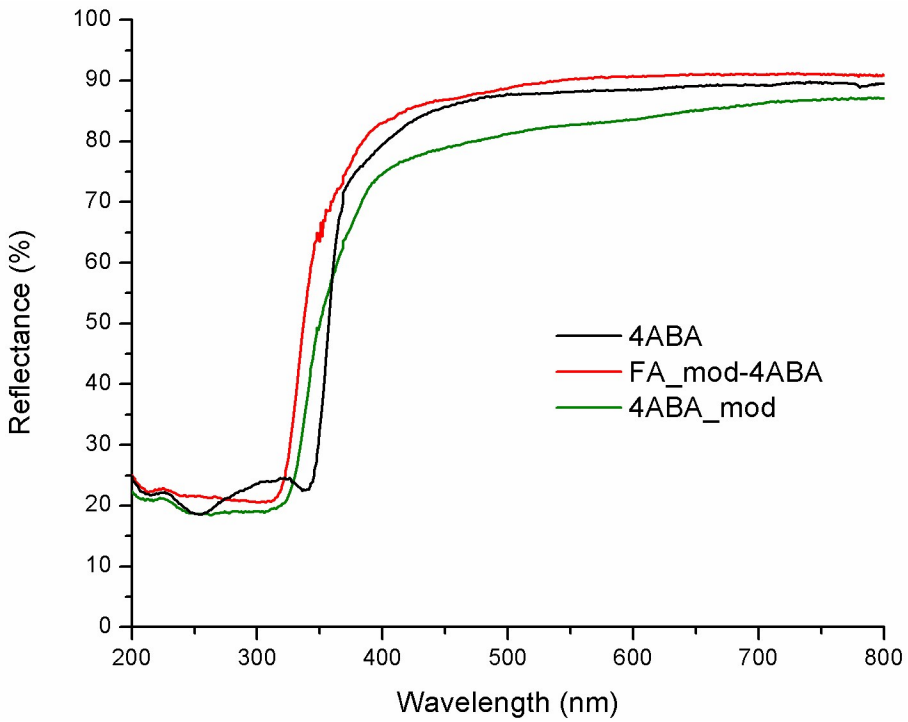

Figure S21. Diffuse reflectance UV-Vis spectra for 4ABA (black), FA_mod-4ABA (red) and 4ABA_mod (olive).

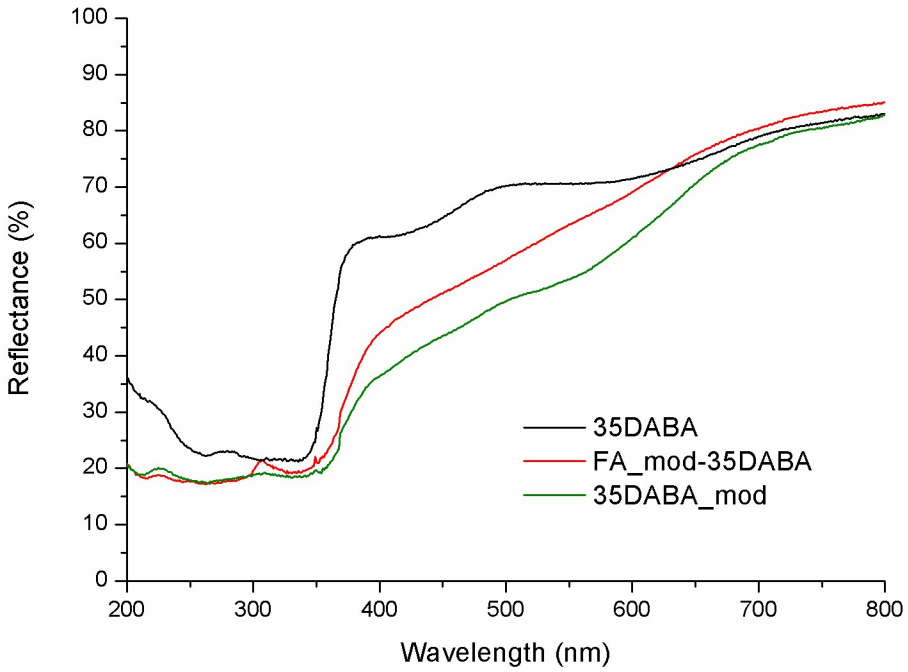

Figure S22. Diffuse reflectance UV-Vis spectra for 35DABA (black), FA_mod-35DABA (red) and 35DABA_mod (olive).

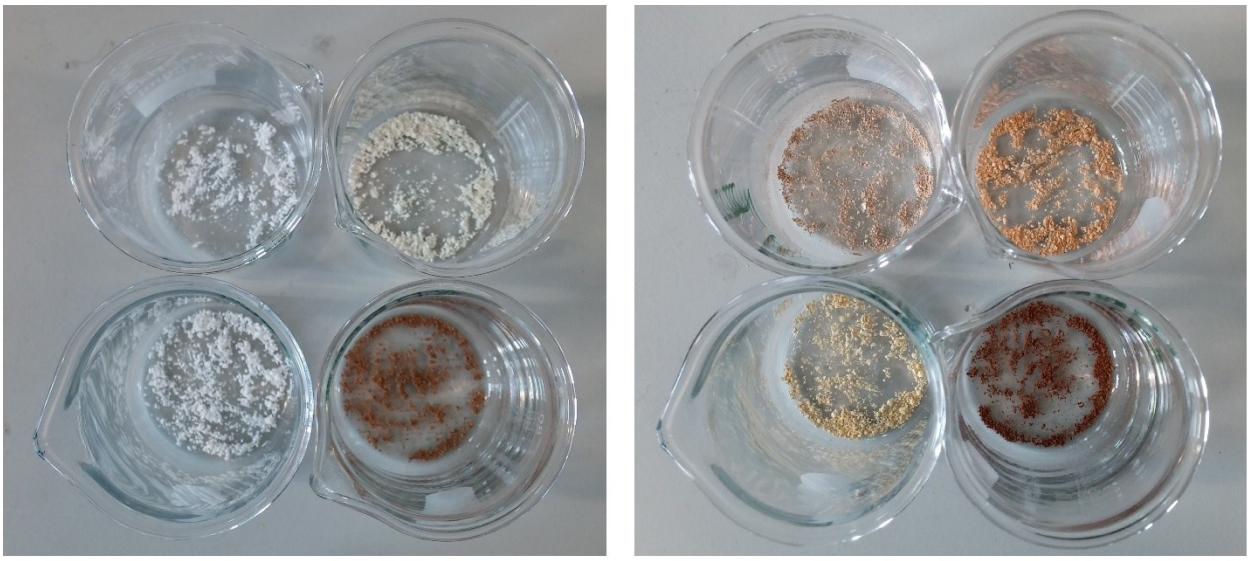

Figure S23. Powders of FA_mod-2ABA (top left beaker), FA_mod-3ABA (top right beaker), FA_mod-4ABA (bottom left beaker) and FA_mod-35DABA (bottom right beaker) before (left picture) and after irradiation (right picture) for 18 hours under visible light and UV light (365 nm).

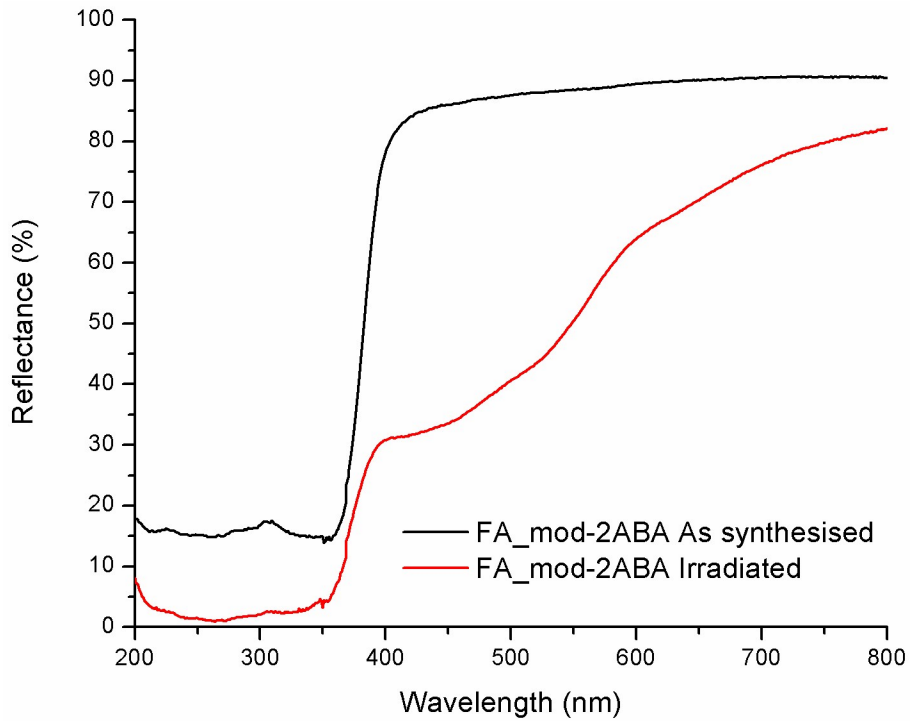

Figure S24. Diffuse reflectance UV-Vis spectra of FA_mod-2ABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

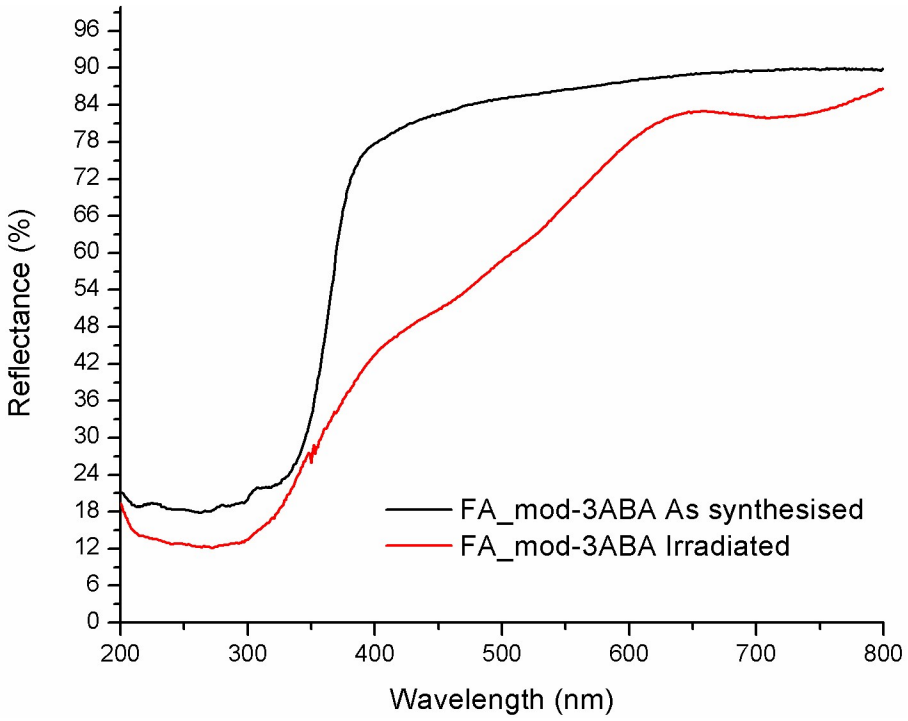

Figure S25. Diffuse reflectance UV-Vis spectra of FA_mod-3ABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

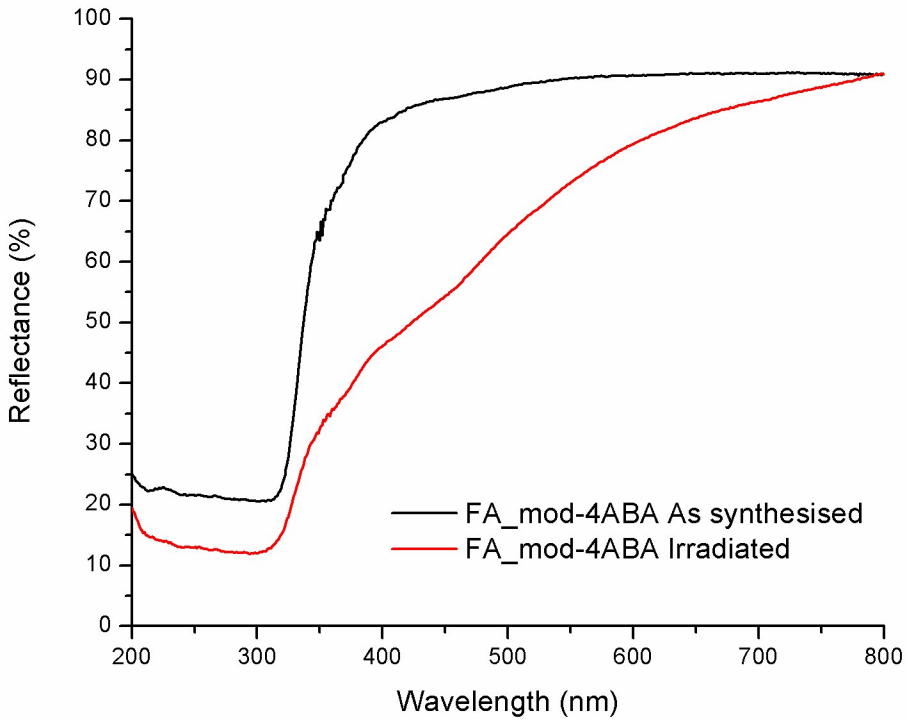

Figure S26. Diffuse reflectance UV-Vis spectra of FA_mod-4ABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

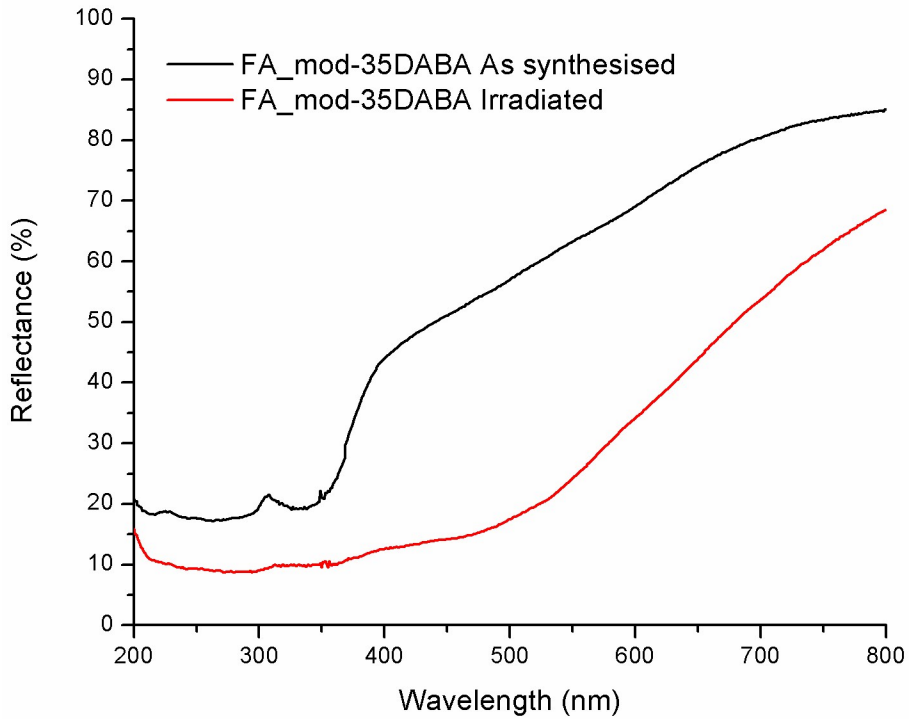

Figure S27. Diffuse reflectance UV-Vis spectra of FA_mod-35DABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

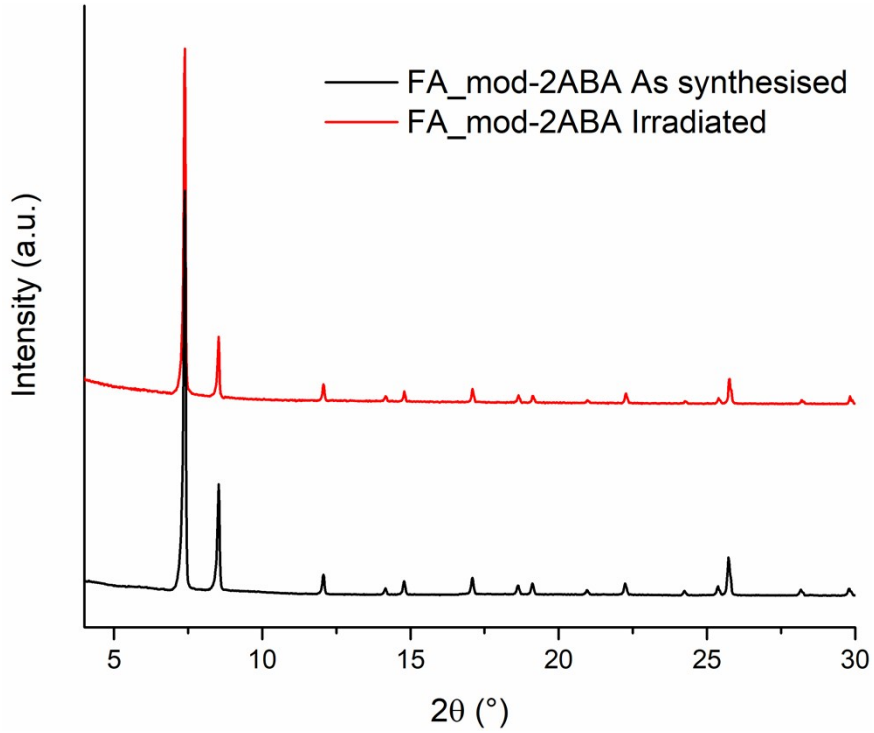

Figure S28. PXRD patterns of FA_mod-2ABA of FA_mod-2ABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

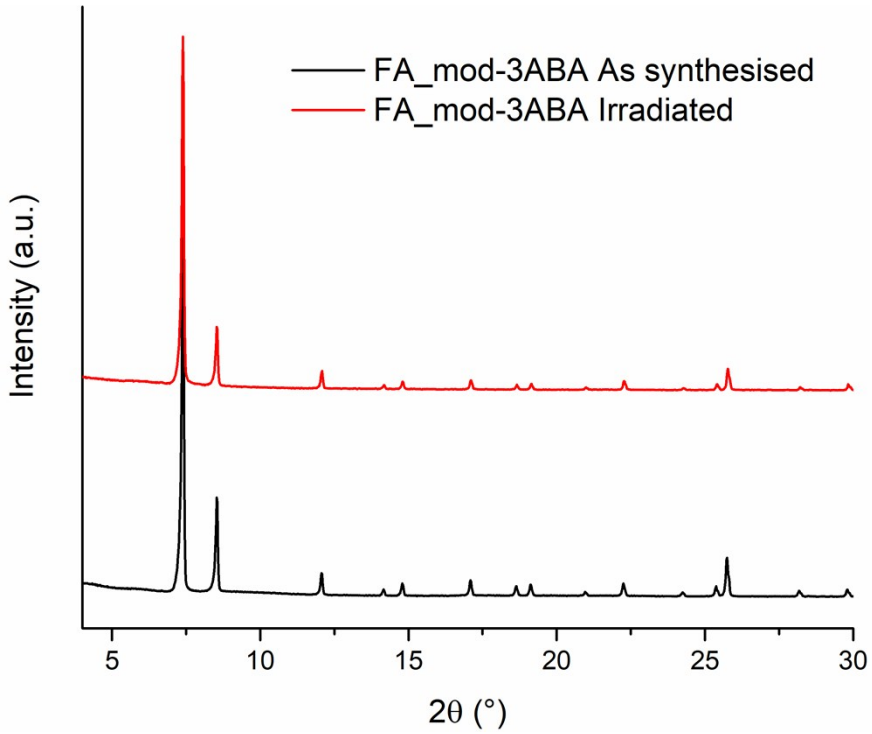

Figure S29. PXRD patterns of FA_mod-3ABA of FA_mod-2ABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

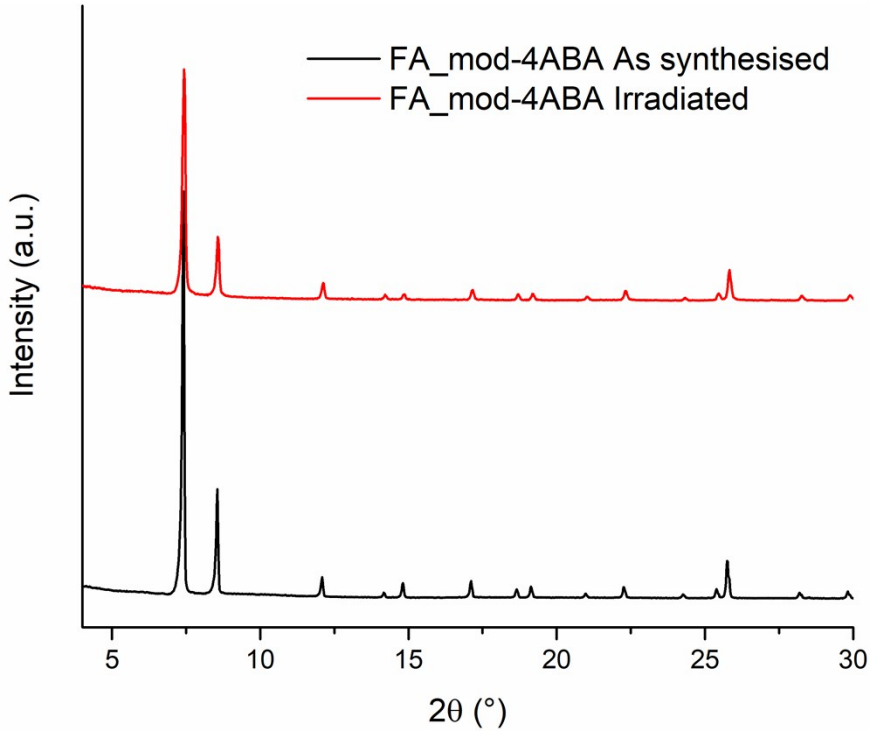

Figure S30. PXRD patterns of FA_mod-4ABA of FA_mod-2ABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

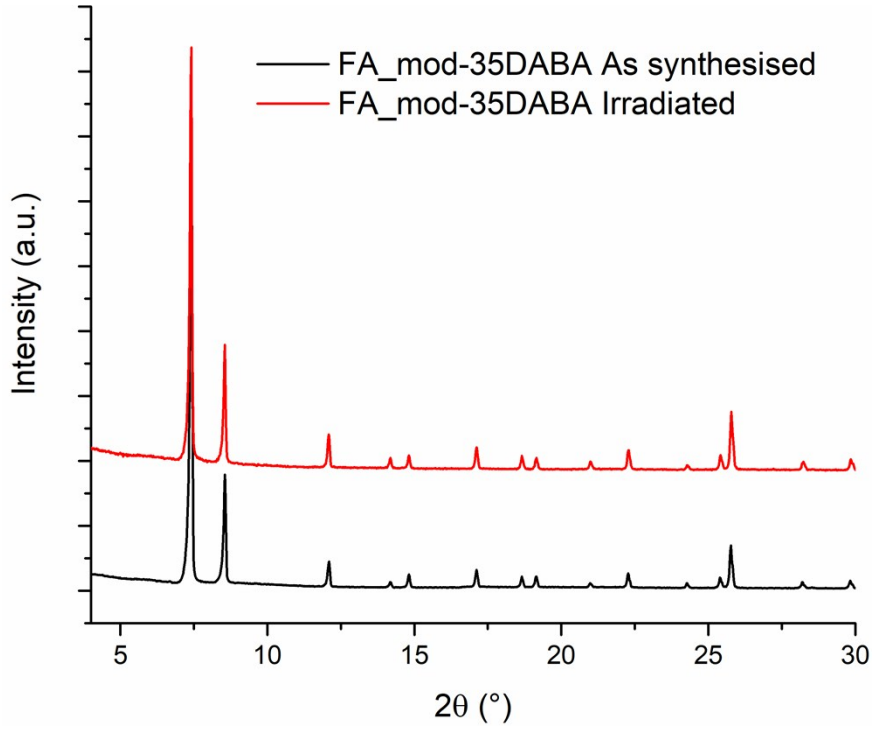

Figure S31. PXRD patterns of FA_mod-2ABA of FA_mod-35DABA as synthesised (black) and after irradiation for 18 hours under visible light and UV light (365 nm) (red).

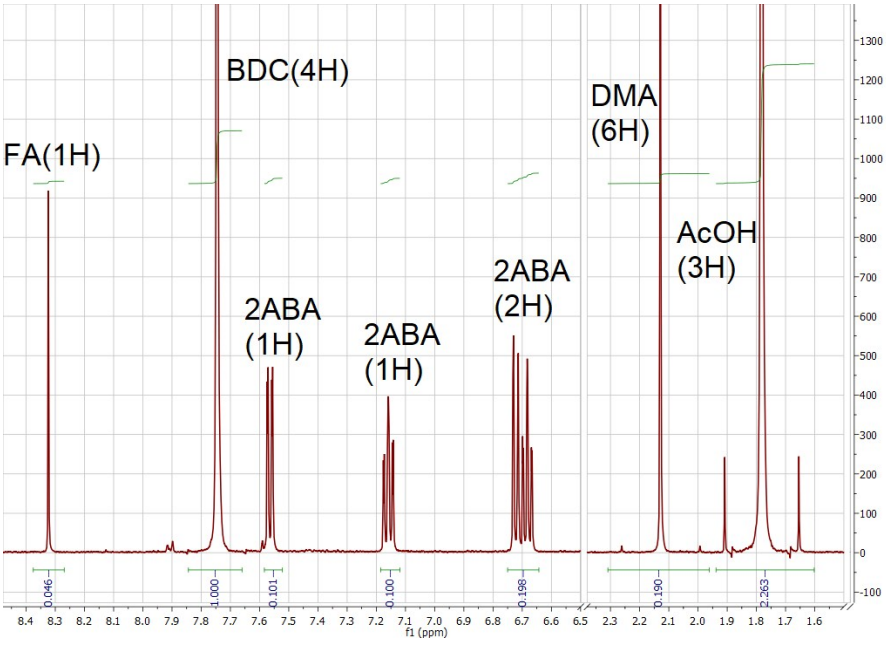

Figure S32. ^{1}H NMR spectrum of FA_mod-2ABA after irradiation for 18 hours under visible light and UV light (365 nm). Irradiation causes the BDC/2ABA ratio to increase to 2.50, from the original value of 2.21 in the as-synthesised MOF (Figure S9).

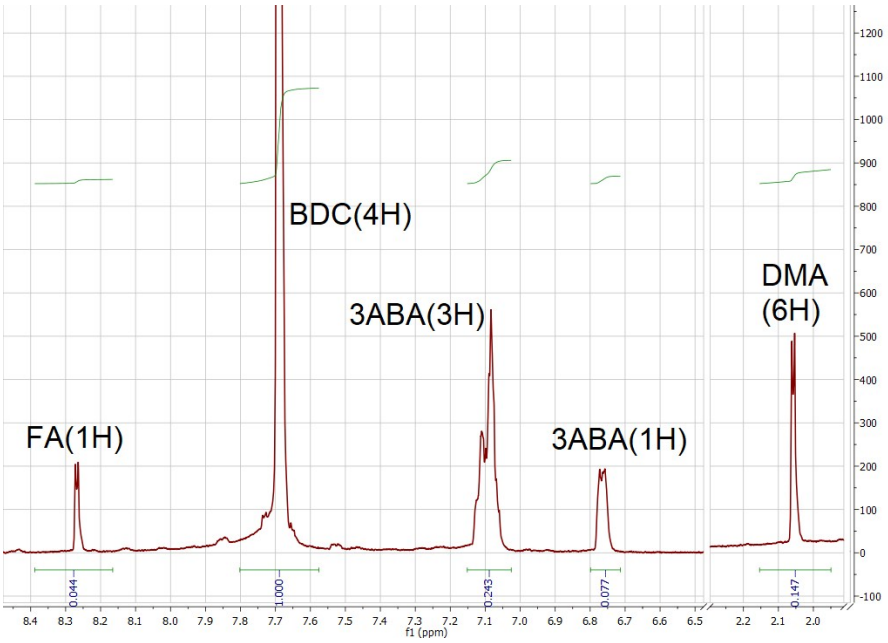

Figure S33. ^{1}H NMR spectrum of FA_mod-3ABA after irradiation for 18 hours under visible light and UV light (365 nm). Irradiation causes the BDC/3ABA ratio to increase to 3.25, from the original value of 2.45 in the as-synthesised MOF (Figure S10).

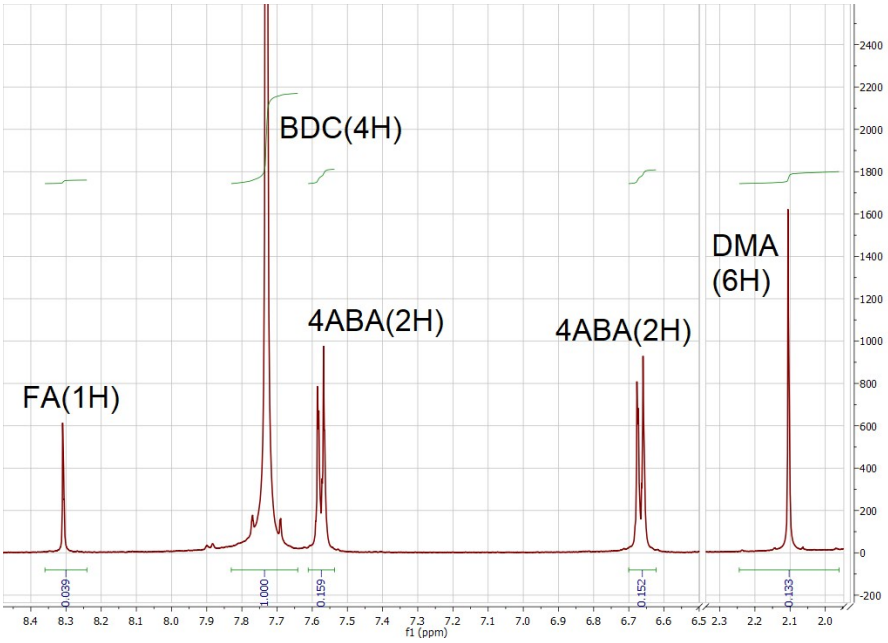

Figure S34. ^{1}H NMR spectrum of FA_mod-4ABA after irradiation for 18 hours under visible light and UV light (365 nm). Irradiation causes the BDC/3ABA ratio to increase to 3.33, from the original value of 2.78 in the as-synthesised MOF (Figure S11).

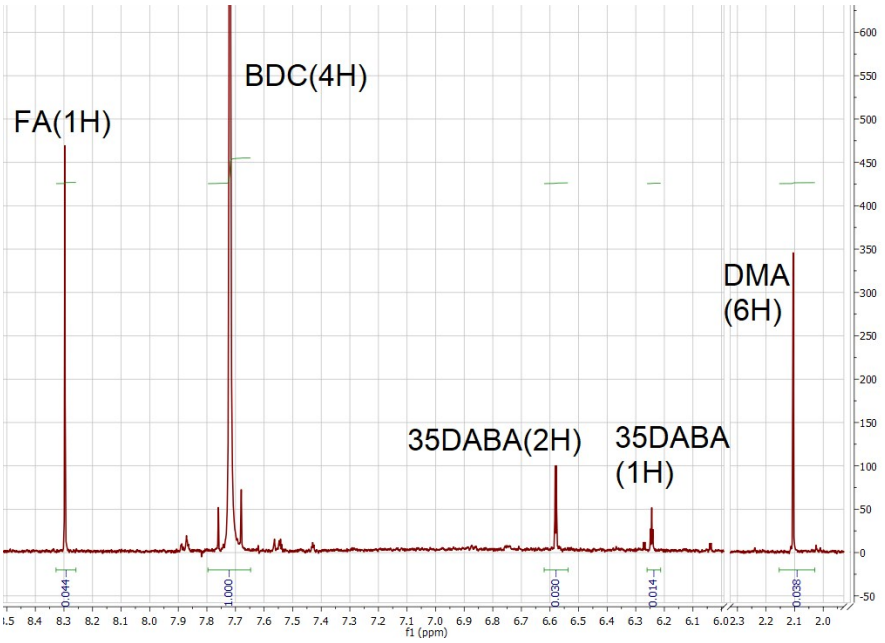

Figure S35. ^{1}H NMR spectrum of FA_mod-35DABA after irradiation for 18 hours under visible light and UV light (365 nm). Irradiation causes the BDC/35DABA ratio to increase to 17.86, from the original value of 3.29 in the as-synthesised MOF (Figure S12).

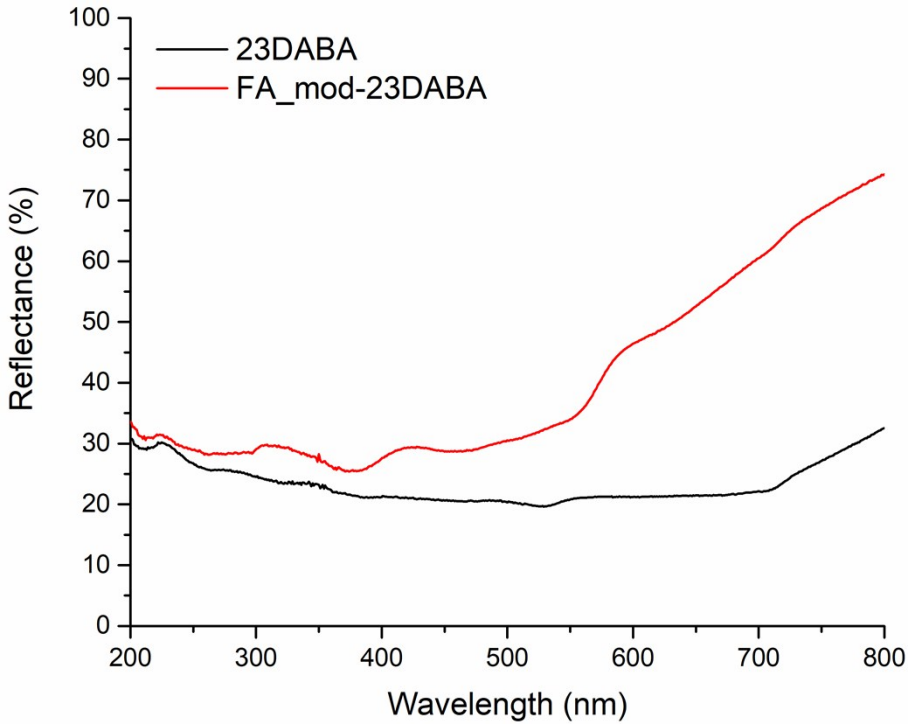

Figure S36. Diffuse reflectance UV-Vis spectra for 23DABA (black) and FA_mod-23DABA (red).

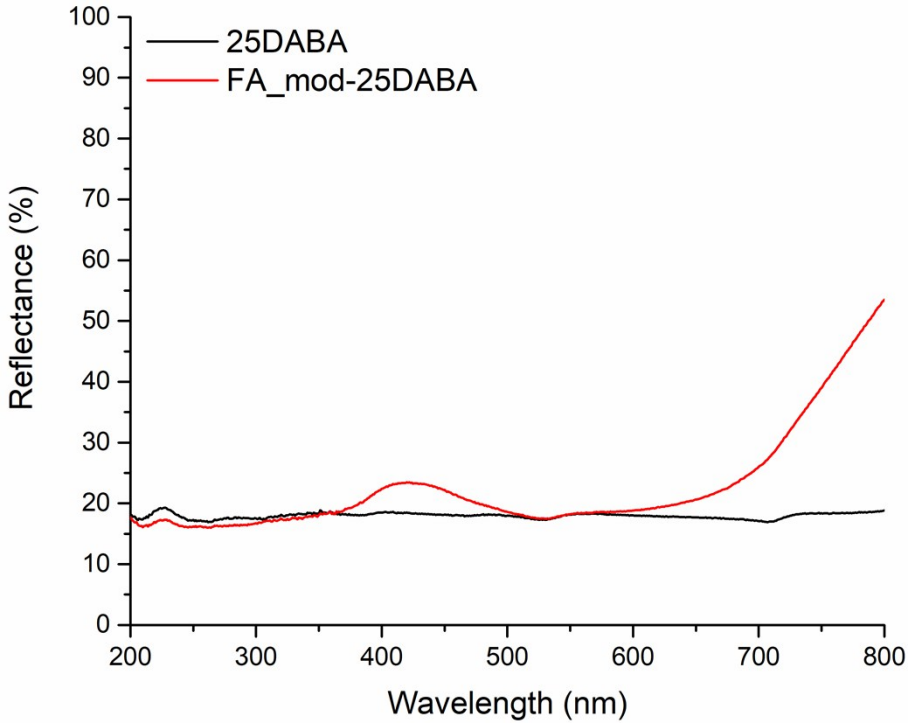

Figure S37. Diffuse reflectance UV-Vis spectra for 25DABA (black) and FA_mod-25DABA (red).

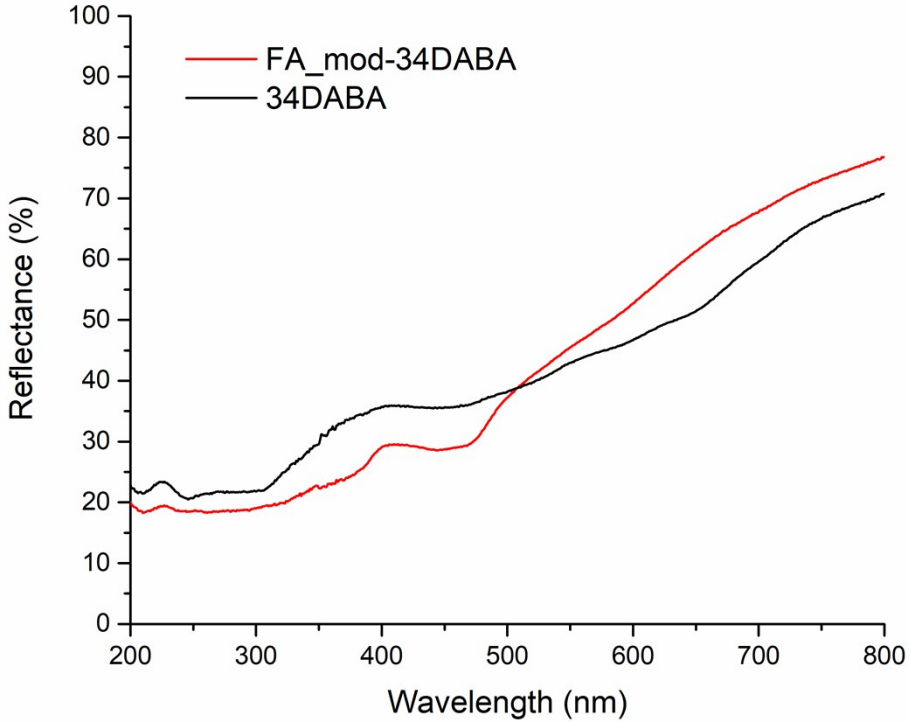

Figure S38. Diffuse reflectance UV-Vis spectra for 34DABA (black) and FA_mod-34DABA (red).

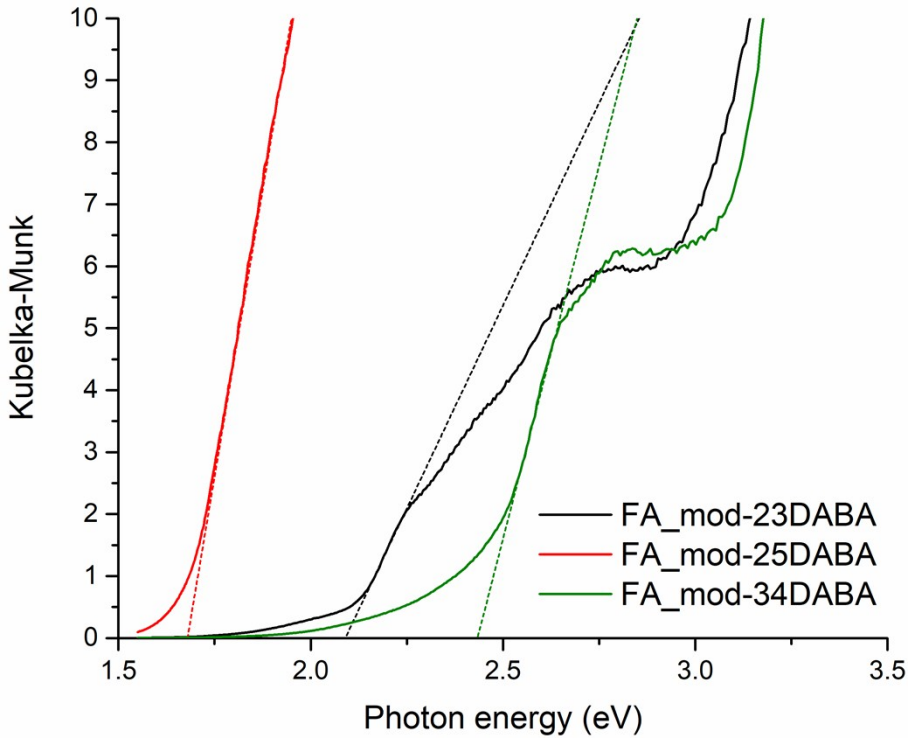

Figure S39. Tauc plots (solid lines) derived from the diffuse reflectance UV-Vis spectra in Figures S36-38 and relative fittings (dashed lines) for FA_mod-23DABA (black), FA_mod-25DABA (red) and FA_mod-34DABA (olive).

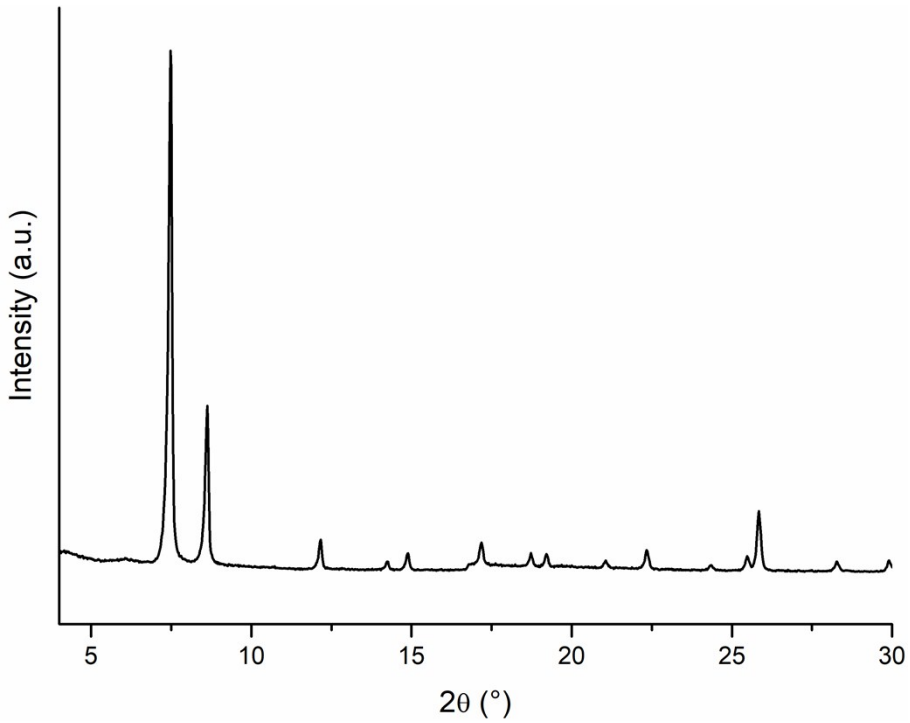

Figure S40. PXRD pattern of UiO-66-NH_2_33%.

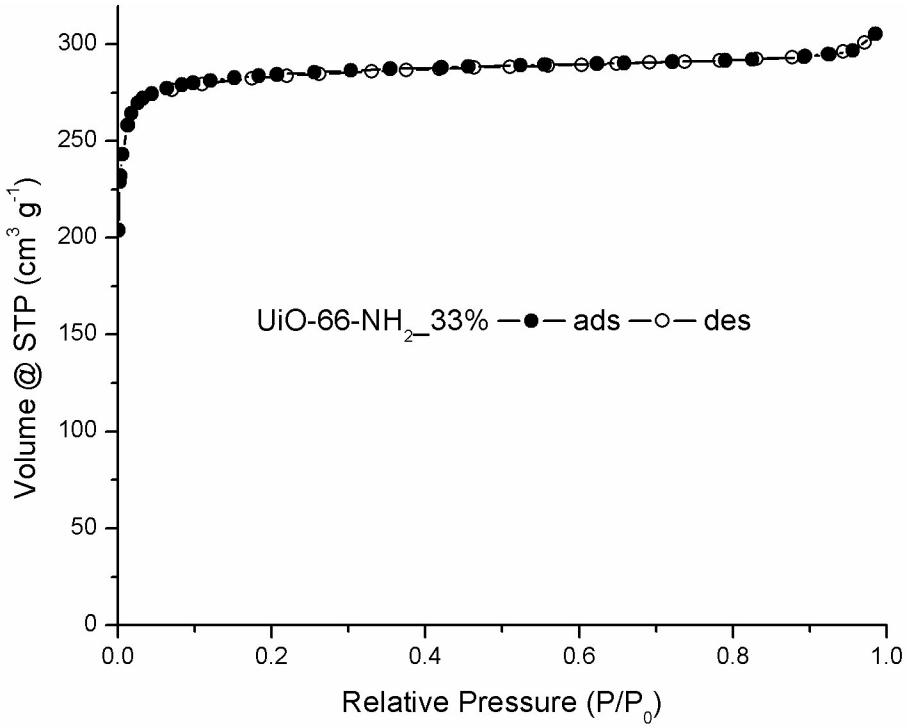

Figure S41. N_2 sorption isotherm of UiO-66-NH_2_33%. BET surface area = 1159.2 $m^2 g^{-1}$; pore volume = 0.46 $cm^3 g^{-1}$.

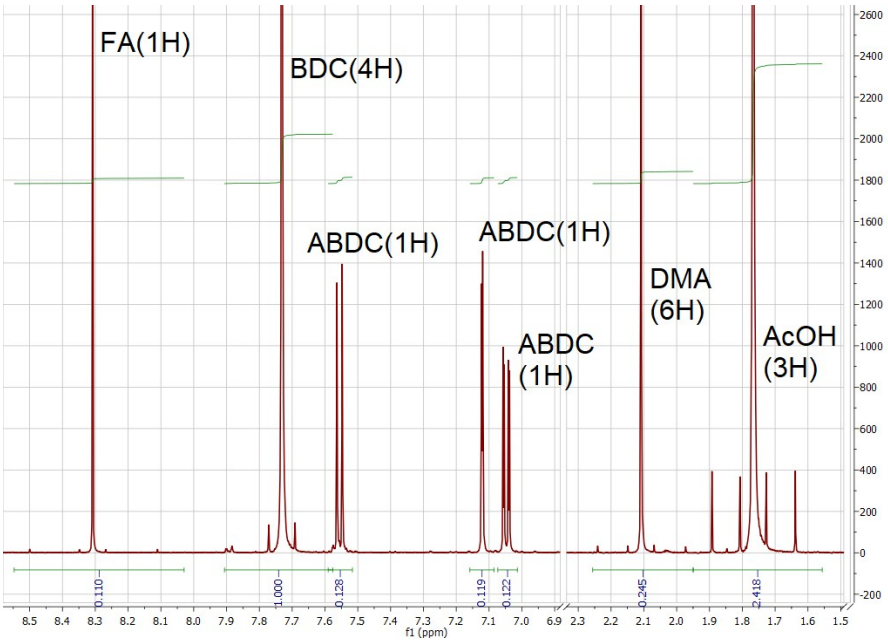

Figure S42. ^{1}H NMR spectrum of UiO-66-NH_2_33%. The signal of DMA suggests that a little amount of DMF is present in the solid. As a consequence, the integral of FA is the combination of FA derived from DMF and FA present in the MOF. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.110) is subtracted of the value determined by dividing the integral of DMA by six (0.041), giving a value of 0.069. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with that of FA. ABDC gives three signals at 7.56, 7.12 and 7.05 ppm, each accounting for one proton. The average integral is 0.122. This leads to calculate a BDC/FA ratio of 2.55 and a BDC/ABDC ratio of 2.05. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(ABDC)_x(FA)_{2y}$, the following can be written:

$$\frac{6-x-y}{x} = 2.05$$

$$\frac{6-x-y}{2y} = 2.55$$

Solving the equation, a value of 1.88 is found for *x* and a value of 0.51 is found for *y*. The proposed formula unit for UiO-66-NH_2_33% is therefore $Zr_6O_4(OH)_4(BDC)_{3.61}(ABDC)_{1.88}(FA)_{1.02}$. The absolute concentration of BDC, ABDC and FA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (2.418) and multiplying the result by 0.1, obtaining 0.031 M for BDC, 0.015 for ABDC and 0.009 M for FA. The weight % of BDC, ABDC and FA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 179 for ABDC, 45 for FA) and dividing the obtained values (4.07 mg for BDC, 2.17 mg for ABDC, 0.31 mg for FA) by the mass of the desolvated MOF digested (11.1 mg), resulting in 36.6% for BDC, 19.5% for ABDC and 2.8% for FA. These values are in good agreement with those expected from the proposed formula $Zr_6O_4(OH)_4(BDC)_{3.61}(ABDC)_{1.88}(FA)_{1.02}$ (35.8% for BDC, 20.4% for ABDC and 2.8% for FA).

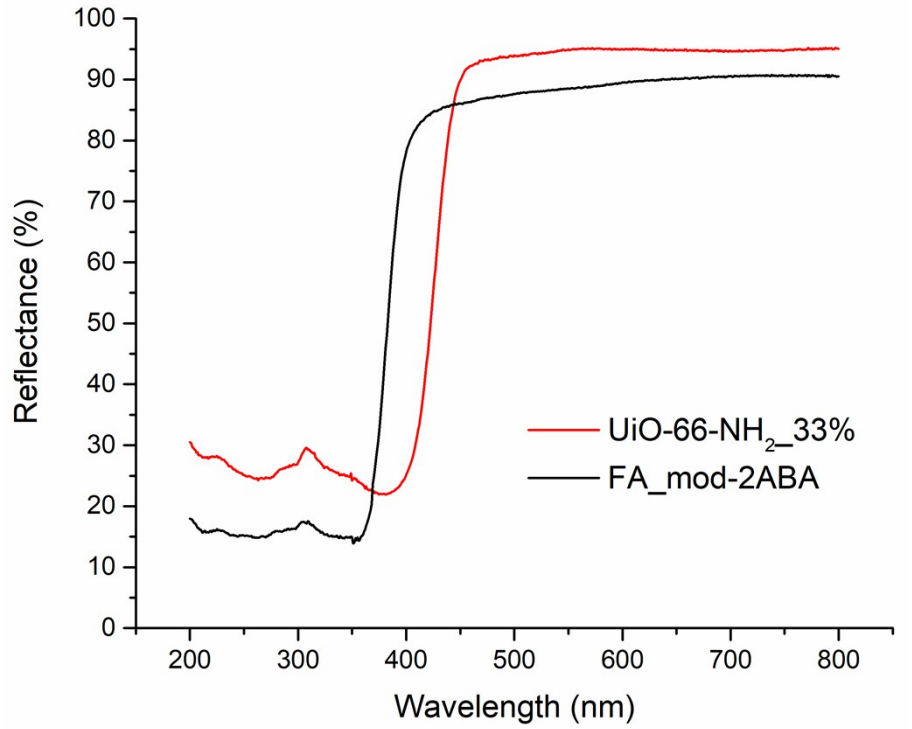

Figure S43. Diffuse reflectance UV-Vis spectra for FA_mod-2ABA (black) and UiO-66-NH_2_33% (red).

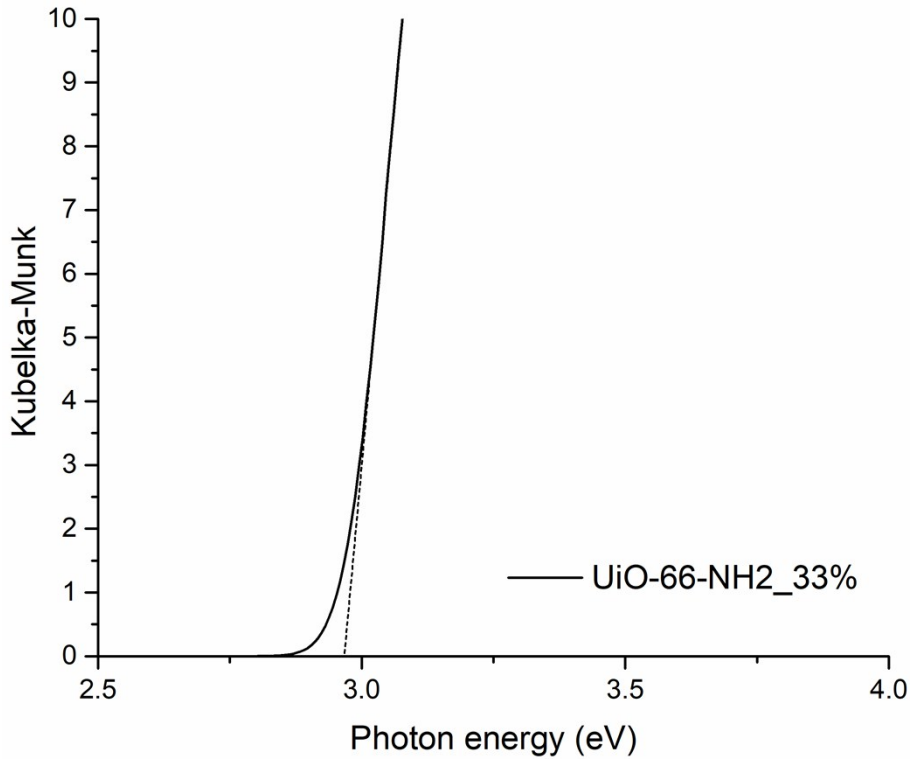

Figure S44. Tauc plot (solid line) derived from the diffuse reflectance UV-Vis spectra in Figure S43 and relative fitting (dashed lines) for UiO-66-NH_2_33%.

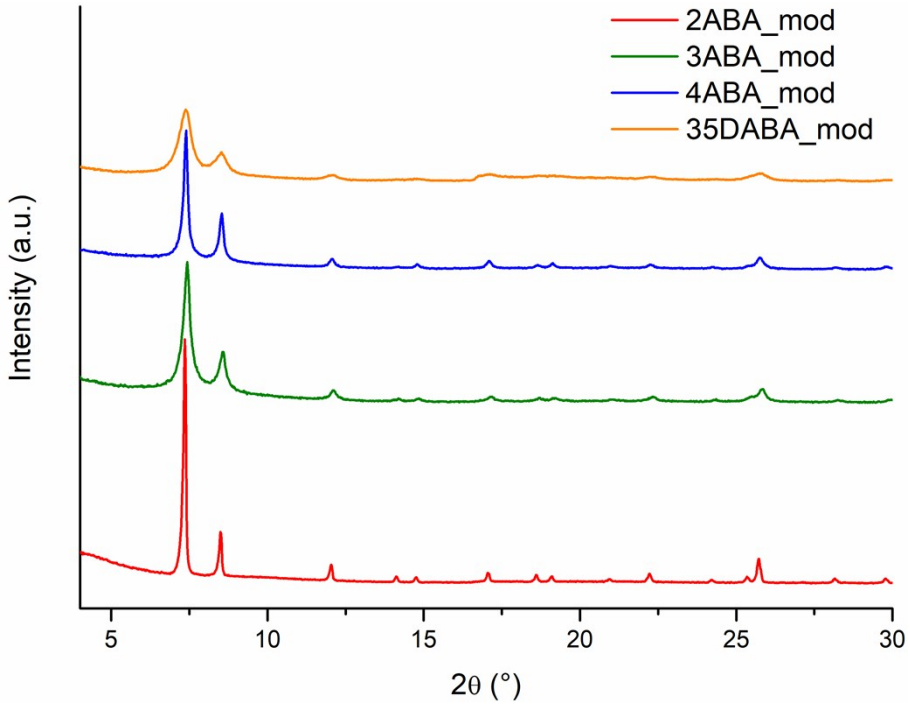

Figure S45. PXRD patterns of 2ABA_mod (red), 3ABA_mod (olive), 4ABA_mod (blue) and 35DABA_mod (orange).

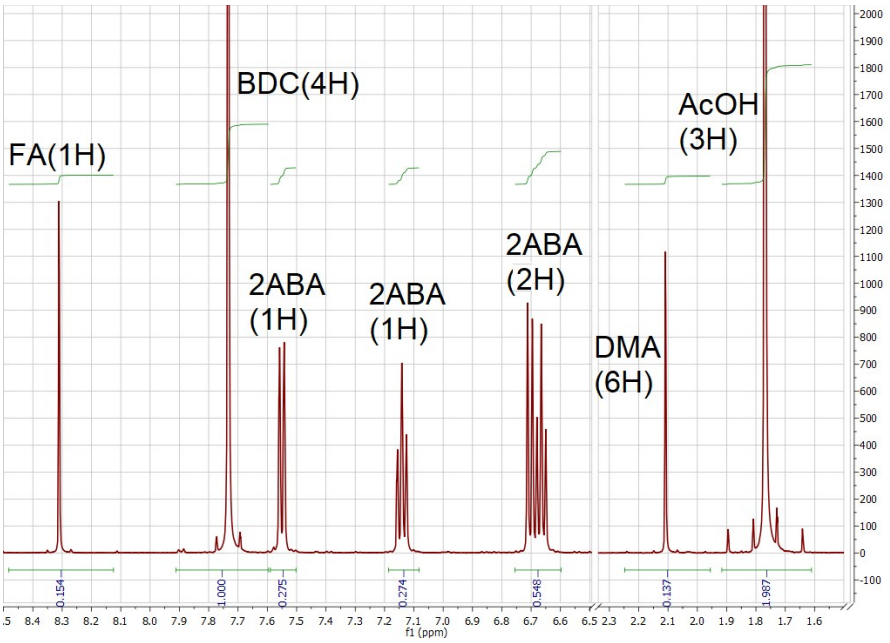

Figure S46. ^{1}H NMR spectrum of 2ABA_mod. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.154) is subtracted of the value determined by dividing the integral of DMA by six (0.023), giving a value of 0.131. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 2ABA (0.274, average of three signals accounting for one, one and two aromatic protons each). This leads to calculate a BDC/FA ratio of 1.88 and a BDC/2ABA ratio of 0.91. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(2ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 1.88$$

$$\frac{6-x-y}{2y} = 0.91$$

Solving the equation, a value of 0.90 is found for *x* and a value of 1.81 is found for *y*. The proposed formula unit for 2ABA_mod is therefore $Zr_6O_4(OH)_4(BDC)_{3.29}(FA)_{1.80}(2ABA)_{3.62}$. The absolute concentration of BDC, FA and 2ABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.987) and multiplying the result by 0.1, obtaining 0.038 M for BDC, 0.020 M for FA and 0.042 M for 2ABA. The weight % of BDC, FA and 2ABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 136 for 2ABA) and dividing the obtained values (4.95 mg for BDC, 0.72 mg for FA, 4.52 mg for 2ABA) by the mass of the desolvated MOF digested (17.0 mg), resulting in 29.1% for BDC, 4.3% for FA and 26.6% for 2ABA. Table S4 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

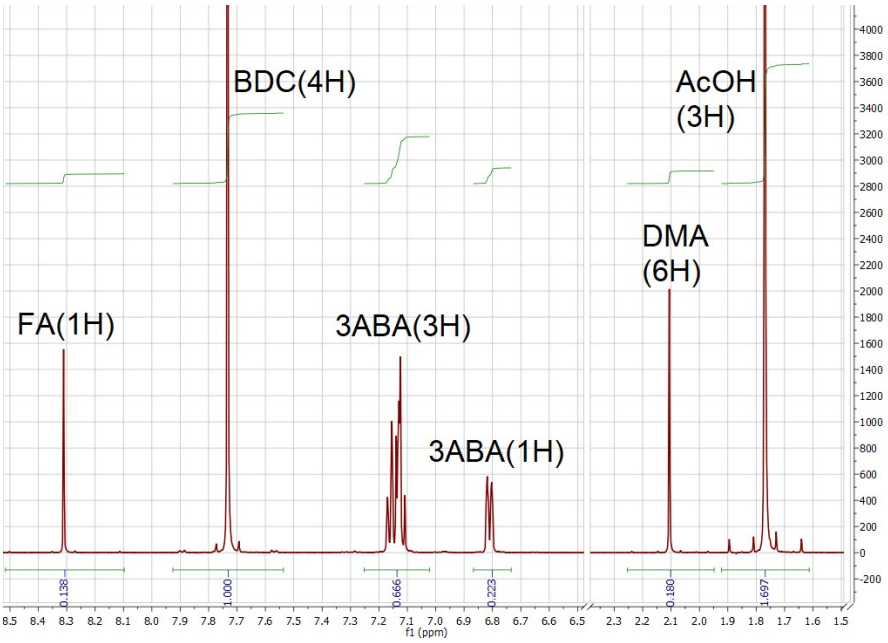

Figure S47. ^{1}H NMR spectrum of 3ABA_mod. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.138) is subtracted of the value determined by dividing the integral of DMA by six (0.030), giving a value of 0.108. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 3ABA (0.172, average of two signals accounting for three and one aromatic protons each). This leads to calculate a BDC/FA ratio of 2.31 and a BDC/3ABA ratio of 1.12. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(3ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 2.31$$

$$\frac{6-x-y}{2y} = 1.12$$

Solving the equation, a value of 0.77 is found for *x* and a value of 1.61 is found for *y*. The proposed formula unit for 3ABA_mod is therefore $Zr_6O_4(OH)_4(BDC)_{3.62}(FA)_{1.54}(3ABA)_{3.22}$. The absolute concentration of BDC, FA and 3ABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.697) and multiplying the result by 0.1, obtaining 0.044 M for BDC, 0.019 M for FA and 0.039 M for 3ABA. The weight % of BDC, FA and 3ABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 136 for 3ABA) and dividing the obtained values (5.80 mg for BDC, 0.69 mg for FA, 4.29 mg for 3ABA) by the mass of the desolvated MOF digested (17.3 mg), resulting in 33.5% for BDC, 4.0% for FA and 24.8% for 3ABA. Table S4 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

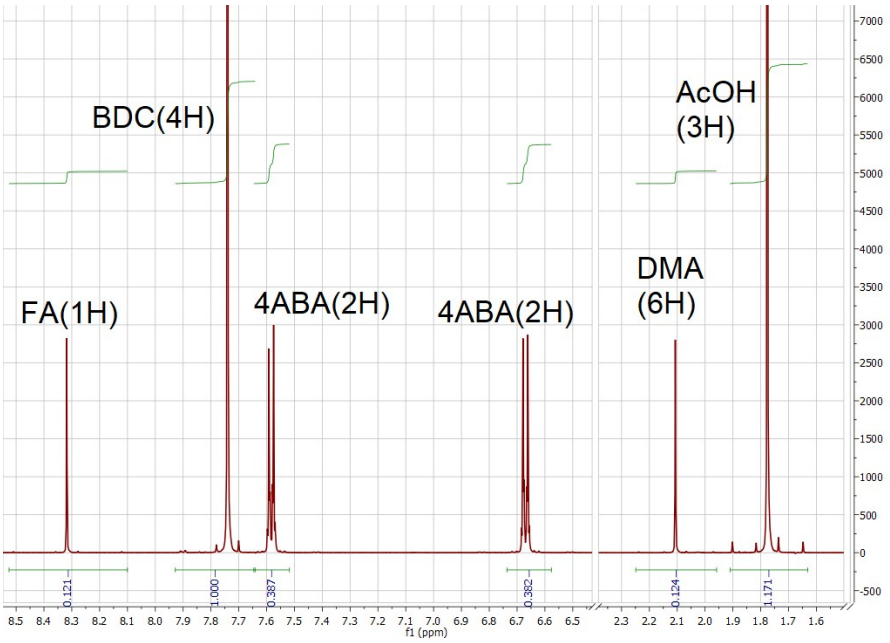

Figure S48. ^{1}H NMR spectrum of 4ABA_mod. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.121) is subtracted of the value determined by dividing the integral of DMA by six (0.021), giving a value of 0.100. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 4ABA (0.192, average of two signals accounting for two aromatic protons each). This leads to calculate a BDC/FA ratio of 2.50 and a BDC/4ABA ratio of 1.28. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(4ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 2.50$$

$$\frac{6-x-y}{2y} = 1.28$$

Solving the equation, a value of 0.75 is found for *x* and a value of 1.47 is found for *y*. The proposed formula unit for 4ABA_mod is therefore $Zr_6O_4(OH)_4(BDC)_{3.78}(FA)_{1.50}(4ABA)_{2.94}$. The absolute concentration of BDC, FA and 4ABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (1.171) and multiplying the result by 0.1, obtaining 0.064 M for BDC, 0.026 M for FA and 0.050 M for 4ABA. The weight % of BDC, FA and 4ABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 136 for 4ABA) and dividing the obtained values (8.41 mg for BDC, 0.92 mg for FA, 5.44 mg for 4ABA) by the mass of the desolvated MOF digested (25.9 mg), resulting in 32.5% for BDC, 3.6% for FA and 21.0% for 4ABA. Table S4 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

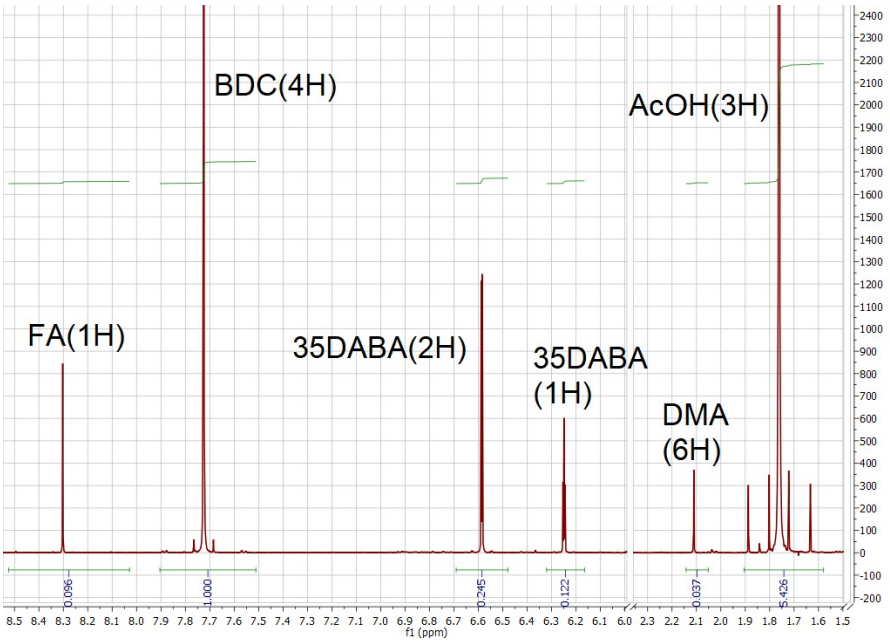

Figure S49. ^{1}H NMR spectrum of 35DABA_mod. The signal of DMA suggests that a little amount of DMF is present in the solid. In order to determine the amount of FA effectively present in the MOF, the integral of FA (0.096) is subtracted of the value determined by dividing the integral of DMA by six (0.006), giving a value of 0.090. The signal of BDC accounts for four aromatic protons, therefore its integral (1.000) must be divided by four to obtain a value (0.250) comparable with those of FA and 35DABA (0.122, average of two signals accounting for two and one aromatic protons each). This leads to calculate a BDC/FA ratio of 2.78 and a BDC/35DABA ratio of 2.05. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(35DABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 2.78$$

$$\frac{6-x-y}{2y} = 2.05$$

Solving the equation, a value of 0.76 is found for *x* and a value of 1.03 is found for *y*. The proposed formula unit for 35DABA_mod is therefore $Zr_6O_4(OH)_4(BDC)_{4.21}(FA)_{1.52}(35DABA)_{2.06}$. The absolute concentration of BDC, FA and 35DABA in solution can be derived by dividing each integral by one third of the value of the integral of AcOH (5.426) and multiplying the result by 0.1, obtaining 0.014 M for BDC, 0.005 M for FA and 0.007 M for 35DABA. The weight % of BDC, FA and 35DABA can be derived by multiplying these values by 0.8 (volume of the solution) and the molecular weight of the respective anions (164 for BDC, 45 for FA, 151 for 35DABA) and dividing the obtained values (1.81 mg for BDC, 0.18 mg for FA, 0.81 mg for 35DABA) by the mass of the desolvated MOF digested (5.4 mg), resulting in 33.6% for BDC, 3.3% for FA and 15.1% for 35DABA. Table S4 reports the comparison of the weight % experimentally determined and that calculated based on the proposed formula unit.

Table S4. Compositional analysis of the MOFs prepared by modulated synthesis, based on NMR data.

Sample	Proposed formula unit	BDC wt%		FA wt%		Benzoic acid analogue wt%	
		Exp[a]	Calc[b]	Exp[a]	Calc[b]	Exp[a]	Calc[b]
2ABA_mod	$Zr_6O_4(OH)_4(BDC)_{3.29}(FA)_{1.80}(2ABA)_{3.62}$	29.1	30.1	4.3	4.5	26.6	27.5
3ABA_mod	$Zr_6O_4(OH)_4(BDC)_{3.62}(FA)_{1.54}(3ABA)_{3.22}$	33.5	33.1	4.0	3.8	24.8	25.0
4ABA_mod	$Zr_6O_4(OH)_4(BDC)_{3.78}(FA)_{1.50}(4ABA)_{2.94}$	32.5	35.1	3.6	3.9	21.0	22.5
35DABA_mod	$Zr_6O_4(OH)_4(BDC)_{4.21}(FA)_{1.52}(35DABA)_{2.06}$	33.6	39.4	3.3	3.9	15.1	18.0

[a] The mass of each acid was derived starting from the integral ratio with respect to internal standard AcOH; [b] On the basis of the proposed formula unit

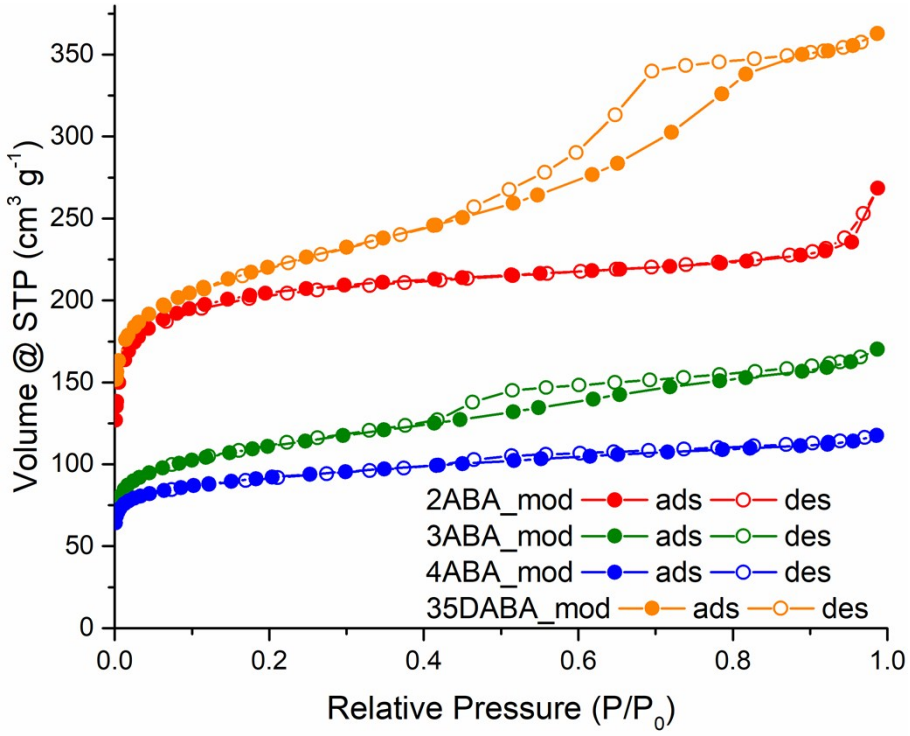

Figure S50. N_2 sorption isotherms at 77 K of 2ABA_mod (red), 3ABA_mod (olive), 4ABA_mod (blue) and 35DABA_mod (orange).

Table S5. BET surface area values for the samples in Figure S38.

Sample	BET surface area ($m^2\ g^{-1}$)
2ABA_mod	770.5
3ABA_mod	399.4
4ABA_mod	342.0
35DABA_mod	803.0

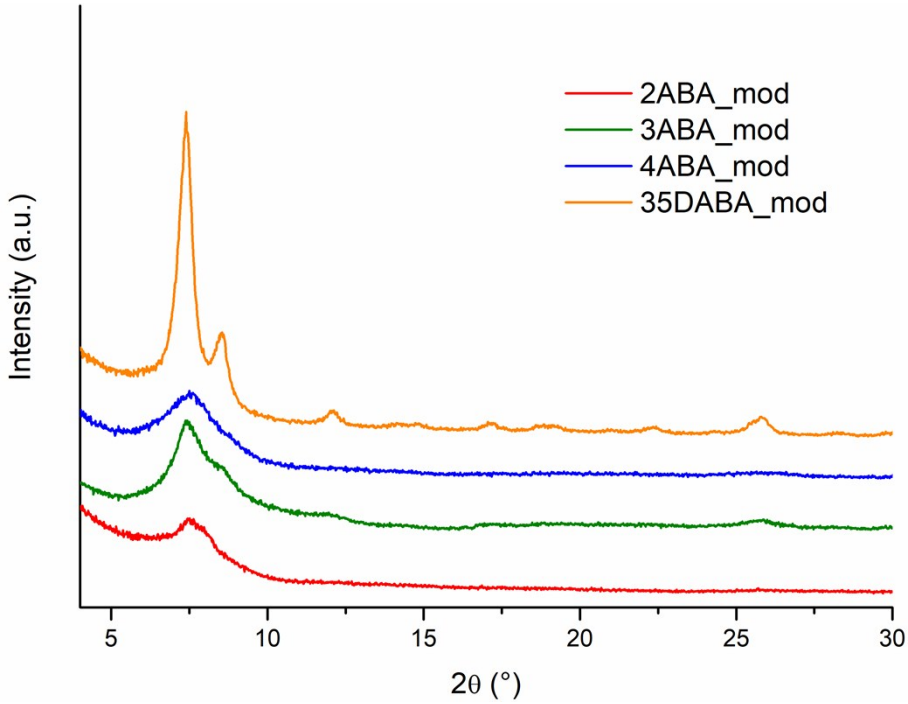

Figure S51. PXRD patterns of 2ABA_mod (red), 3ABA_mod (olive), 4ABA_mod (blue) and 35DABA_mod (orange) after N_2 sorption analysis.

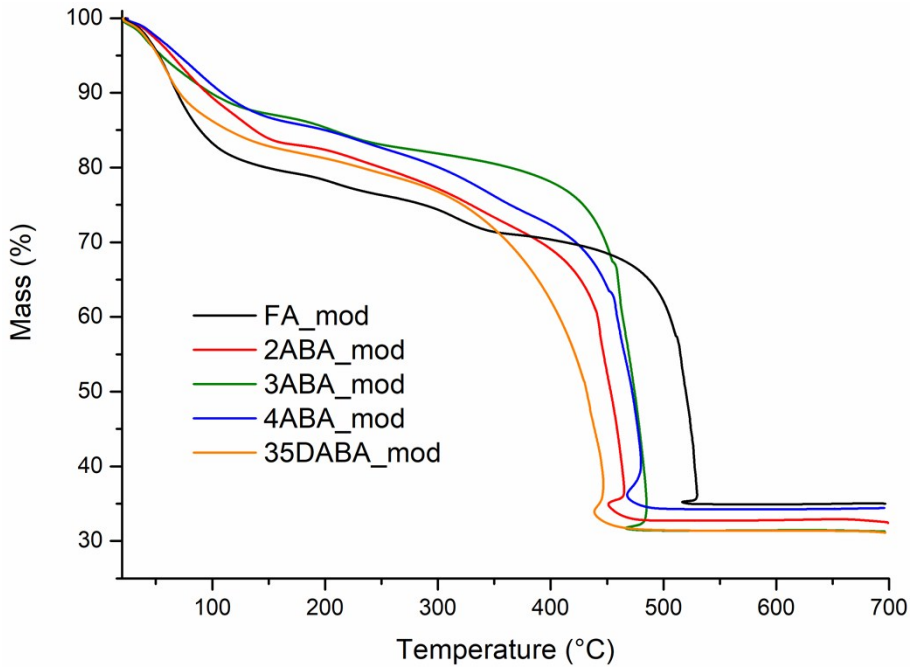

Figure S52. TGA curves of FA_mod (black), 2ABA_mod (red), 3ABA_mod (olive), 4ABA_mod (blue) and 35DABA_mod (orange).

COMPUTATIONAL STUDY

All the calculations were done using the code CP2K v6.1.[1] The systems were simulated constructing single cluster capped with H atoms (Figure S53). The DZP-MOLPLOT-SR-GTH basis-set was adopted for all atoms. The plane-wave part was described using the GTH-PBE potential with a cut-off of 500 Ry. The SCF convergence was set to 1.0×10^{-6}. The calculations were performed in two steps. Firstly, the geometry was optimised using standard density functional theory. Then, to analyse the excited states, single point calculation was performed on the optimised geometry using time dependent density functional theory. The calculations were done at using the GGA PBE functional,[2] which is a common DFT functional used when studying MOFs electronic properties. It should be noted that GGA functionals tend to underestimate the HOMO-LUMO gap (i.e. it cannot provide quantitative descriptions). However, they can be used to provide a qualitative picture,[3] as they correctly reproduce trends for HOMO-LUMO gap and molecular orbitals composition.[4-6] Attempts to use hybrid functional PBE0 were performed, but could not be concluded because of the too high computational effort required (each cluster was composed of ca 220 atoms, ca 850 electrons).

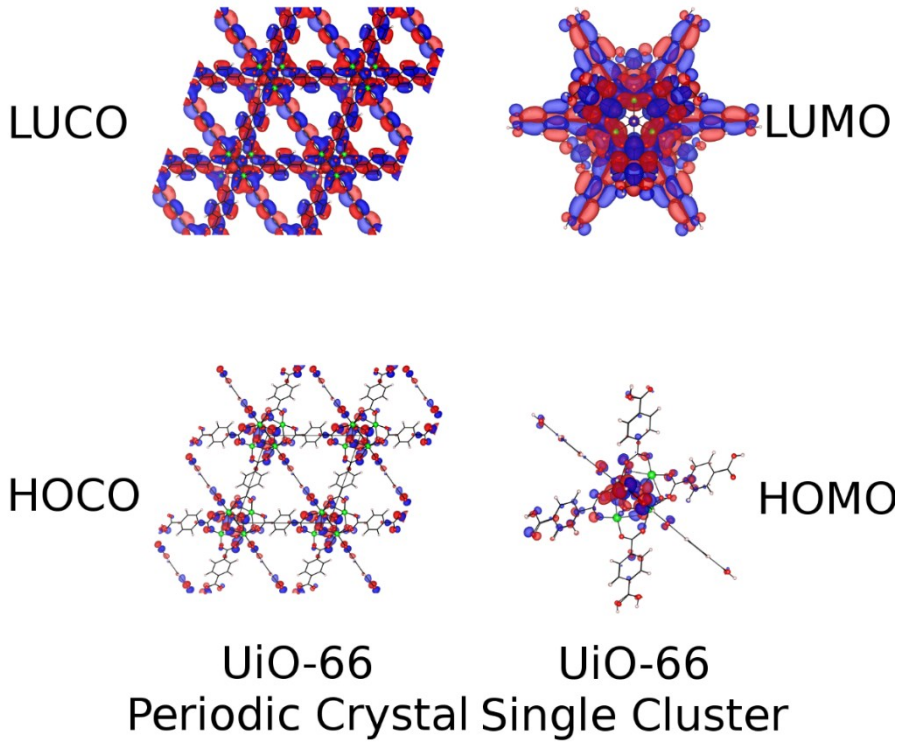

Figure S53. Validation of the cluster approximation. On the left, periodic calculation of pristine UiO-66 showing the Highest Occupied and the Lowest Unoccupied Crystalline Orbitals. On the right, single molecule calculation of its cluster approximation showing the Highest Occupied and Lowest Unoccupied Molecular Orbitals, respectively.

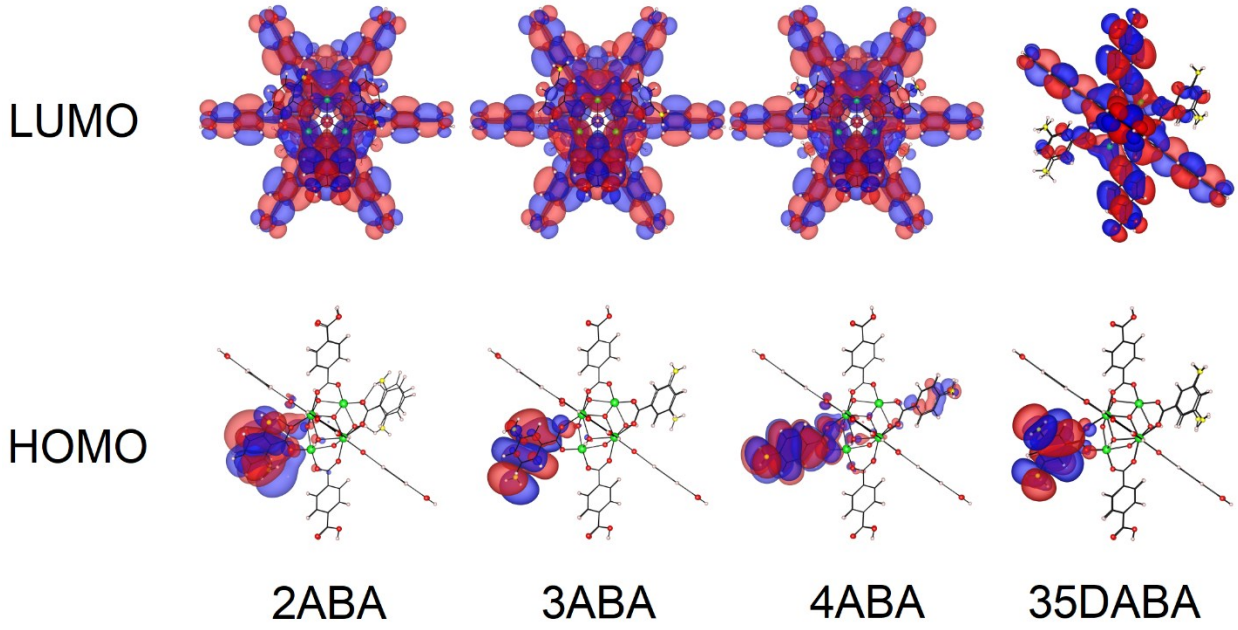

Figure S54. Calculated HOMO (bottom) and LUMO (top) for FA_mod -2ABA (leftmost), FA_mod-3ABA (centre-left), FA_mod-4ABA (centre-right) and FA_mod-35DABA (rightmost).

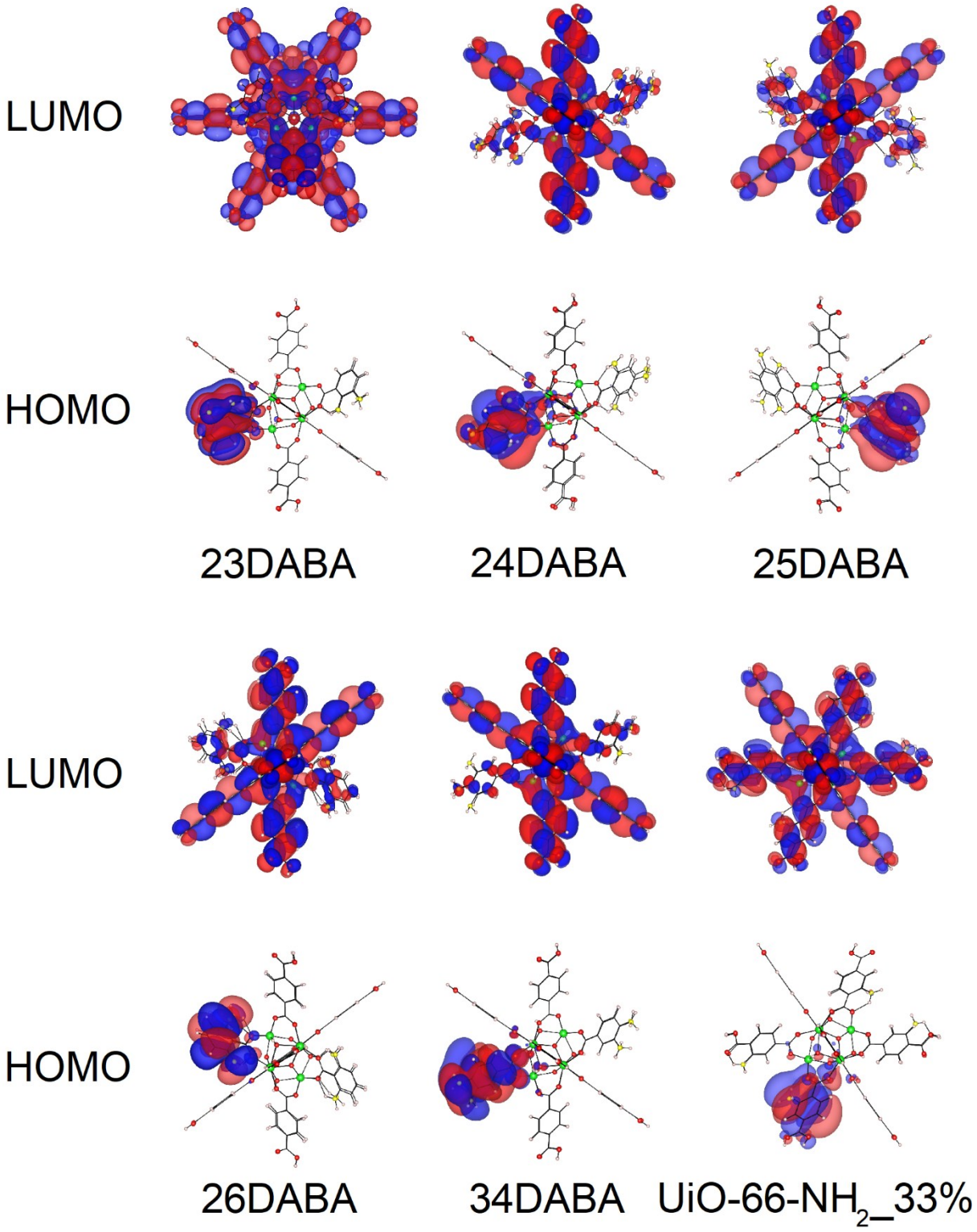

Figure S55. Calculated HOMO and LUMO for FA_mod-23DABA (top left), FA_mod-24DABA (top centre), FA_mod-25DABA (top right), FA_mod-26DABA (bottom left), FA_mod-34DABA (bottom centre) and UiO-66-NH_2_33% (bottom right). In the case of UiO-66-NH_2_33%, we assumed that the aminoterephthalate

linkers be randomly arranged, therefore the cluster was simulated with two linkers having the amino group in *ortho* position to the coordinating carboxylate and two linkers having the amino group in *meta* position to the coordinating carboxylate

Table S6. Calculated HOMO-LUMO gaps for all the simulated cluster models.

Sample	Calculated HOMO-LUMO gap (eV)
UiO-66	3.2
UiO-66-NH_2_33%	2.0
FA_mod	3.2
FA_mod-2ABA	1.8
FA_mod-3ABA	1.9
FA_mod-4ABA	2.2
FA_mod-23DABA	1.7
FA_mod-24DABA	1.8
FA_mod-25DABA	1.2
FA_mod-26DABA	1.2
FA_mod-34DABA	1.8
FA_mod-35DABA	1.6

In the attempt to rationalise the observed and predicted band gap trends, we note that the amino group is a strong mesomeric electron donor, but also a moderate electron-withdrawing group by induction. The mesomeric effect is strongest when the amino group is in either *ortho* or *para* position and weakest when it is in *meta*, whereas the inductive effect becomes weaker as the amino group moves from *ortho* to *meta* to *para*. Furthermore, there could be steric factors playing a role as well.

If the observed positional effect were predominantly of mesomeric nature, we should expect that the band gap decreases in the order FA_mod-3ABA < FA_mod-4ABA ≈ FA_mod-2ABA. This is clearly not the case, thus directing us towards considering inductive and steric effects. In considering sterics, we note that the so-called "*ortho* effect" is commonly invoked to explain the peculiar acid-base properties of *ortho*-substituted benzoic acids. This is attributed to the steric hindrance existing between the carboxylic group and the *ortho* substituent, which forces the former out of the plane of the aromatic ring, reducing the stabilising resonance effect and making the carboxylic acid group more acidic. In our case, the *ortho* effect should only affect FA_mod-2ABA, but the fact that the decrease in experimental band gap from FA_mod-3ABA to

FA_mod-2ABA (0.2 eV) is slightly smaller than that from FA_mod-4ABA to FA_mod-3ABA (0.3 eV) suggests that this is not the main factor determining the positional dependence of the band gap. This leaves us with inductive effects. As mentioned above, the amino group is a moderate electron-withdrawing group by induction. The same applies for the carboxylic group, which also exerts a mesomeric electron-withdrawing effect. This means that the ring C atoms bonded to both the amine and the carboxylic group have a little positive charge. The closer the amine and carboxylic acid are, the higher is the electrostatic repulsion between the slightly positive C atoms, which destabilises the system by pushing the HOMO to higher energies. This is consistent with the observed band gap order FA_mod-4ABA < FA_mod-3ABA < FA_mod-2ABA, which leads us to propose inductive effects as the main factor responsible for the band gap shrinkage.

Shifting the attention to the models involving difunctionalised benzoic acids, we find calculated HOMO-LUMO gaps ≤ 1.8 eV, which is the value we obtain for FA_mod-2ABA, suggesting that addition of a further amino group is an effective method of lowering the band gap below that of FA_mod-2ABA. We attribute this effect to the additional mesomeric electron-donating contribution of the second amino group, which further increases the electron density of the aromatic π system and its ability to interact with light and promote electrons to the conduction band, in an analogous way to what observed for UiO-66-NH_2 and UiO-66-$(NH_2)_2$ (see ref 18 in manuscript, *Inorg. Chem.* 2015, 54, 10701-10710). We observe that 24DABA and 34DABA display very similar gap to 2ABA and 3ABA, respectively, suggesting that the effect of an additional amino group in *para* position is little. On the other hand, 26DABA and 25 DABA display the lowest gap, proving that proximity of the amino groups to the carboxylate is key to maximise the effect.

PHOTOCATALYTIC CO_2 REDUCTION

The photocatalytic activity of the samples to reduce CO_2 were performed using the gas/solid reactor setup (Figure S56). At first, 30 mg of the photocatalysts was dissolved into 2 mL of water. The solution was sonicated for 30 seconds and was then deposited on a round stainless steel metal disc with a fixed area of 9.6 cm^2. Research grade (99.999%) CO_2 and H_2 (99.9995%, Peak Scientific PH200 hydrogen generator) were flowed at controlled rates using mass flow controllers (Omega Engineering, 0–50 mL/min). Isotopic tracing experiments were performed with $^{13}CO_2$ (BOC, >98% atom $^{13}CO_2$ compared to $^{12}CO_2$, >99%). The photoreactor (132 mL) was vacuumed and replenished with the reactant gases five times. A CO_2/H_2 ratio of 1.5 (vol/vol) was used for experiments. The reactants gases were passed over the catalyst bed in the photoreactor for 10 minutes before sealing the reactor at 1.25 bar. A xenon arc lamp (300 W, λ > 325 nm, LOT Quantum Design), equipped with a water filter was used as the irradiation source (Figure S57). After 6 h irradiation the evolved gases were detected by a gas chromatograph (GC, Agilent Technologies) coupled with a thermal conductivity (TCD) and flame ionization (FID) detectors.

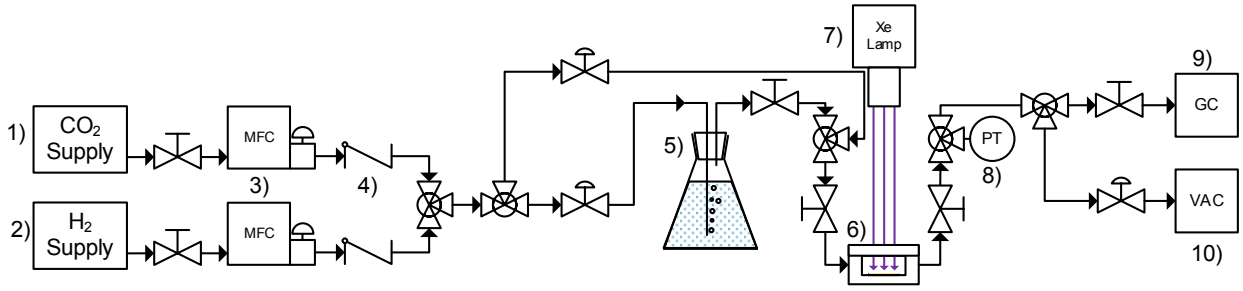

Figure S56. Photocatalytic gas-solid reactor setup used to evaluate photocatalytic CO_2 reduction: 1) CO_2 cylinder, 2) H_2 generator, 3) mass flow controllers, 4) non-return valves, 5) H_2O saturator, 6) photoreactor, 7) Xe arc lamp, 8) pressure transducer, 9) gas chromatograph, 10) vacuum pump.

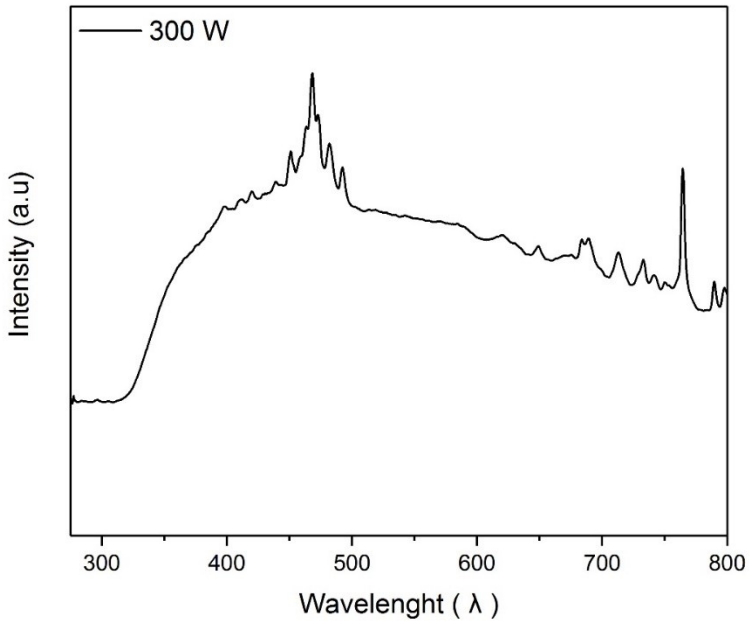

Figure S57. Xenon arc lamp emission spectrum, 300 W (LOT Quantum Design), equipped with a water filter.

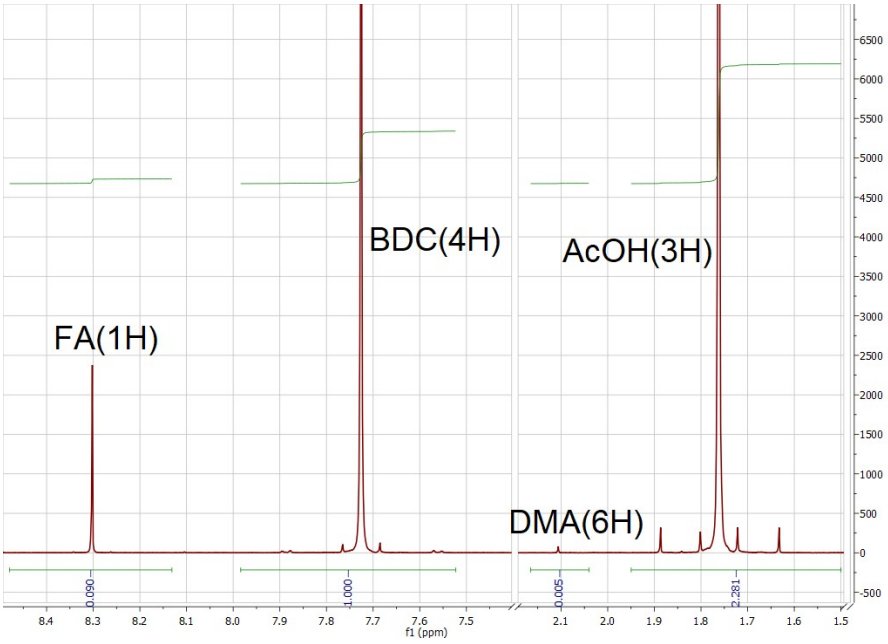

Figure S58. ^{1}H-NMR spectrum of FA_mod after further washing in water and acetone, showing nearly complete absence of the signal of DMA, originated by hydrolysis of DMF.

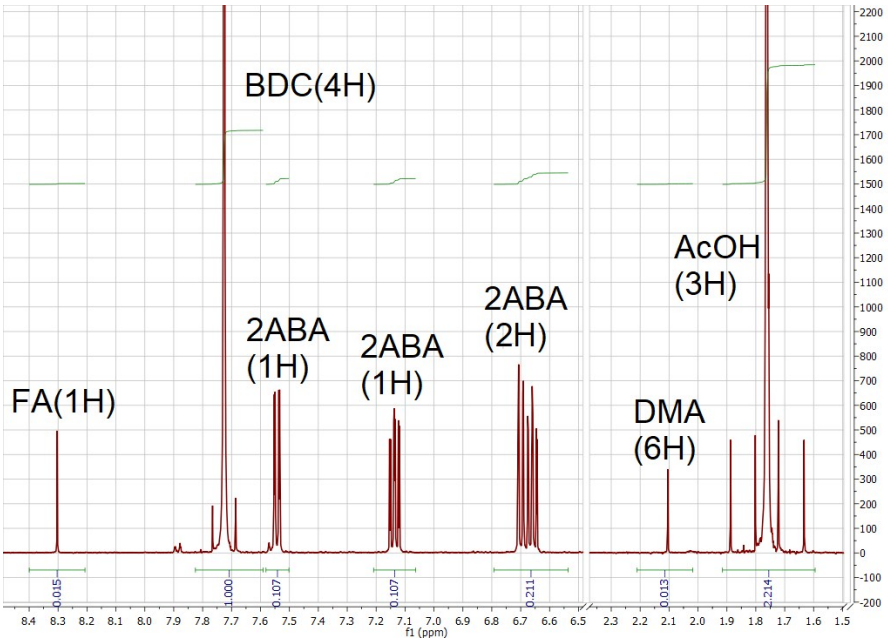

Figure S59. ^{1}H-NMR spectrum of FA_mod-2ABA after further washing in water and acetone, showing nearly complete absence of the signal of DMA, originated by hydrolysis of DMF.

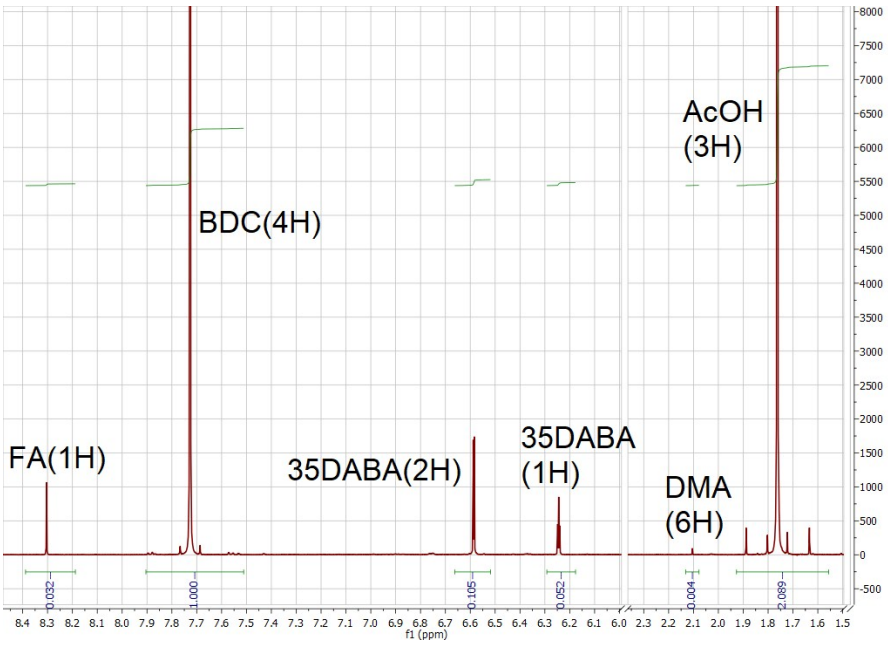

Figure S60. ^{1}H-NMR spectrum of FA_mod-35DABA after further washing in water and acetone, showing nearly complete absence of the signal of DMA, originated by hydrolysis of DMF.

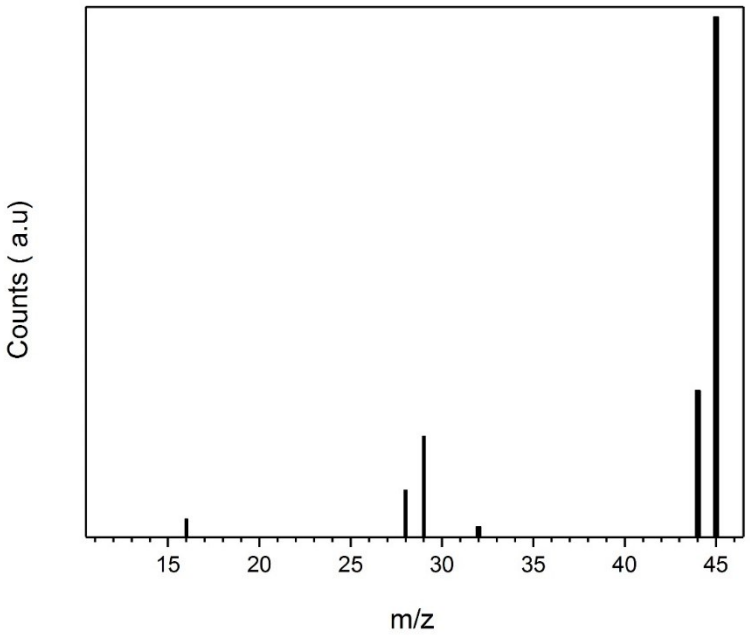

Figure S61. Mass spectrometer chromatographs (full scan) of evolved gases using $^{13}CO_2$. The following assignments can be made: m/z 16: O (due to O_2 from air or to CO_2); m/z 28: N_2 (due to an air leak in the system); m/z 29: ^{13}CO; m/z 32: O_2 (due to an air leak in the system); m/z 44: $^{12}CO_2$ (likely from cylinder not being pure); m/z 45: $^{13}CO_2$. Ratio 28/32 is 4.6 vs 3.7 for air, which suggests possible presence of ^{12}CO (m/z 28), originated either from the material or from $^{12}CO_2$ present as impurity in the cylinder.

PHOTOCATALYTIC DYE DEGRADATION

Photocatalytic dye degradation assessment was carried out using a custom built mirrored light box containing 10 neon tubes at a colour temperature of 6500 K with power rating of 18 W and an average light intensity of 23200 lux. In addition, UV radiation was supplied at 365 nm using an 8 W Thermo Scientific Pierce UVP 3UV ultraviolet lamp positioned for side on illumination. 20 mg of sample was suspended in 20 mL of 0.008 mM Rhodamine B solution. Samples were run in parallel, with one kept in the dark as a control to allow for the assessment of dye adsorption effects. Samples were stirred throughout experiments. Periodically, 6 mL aliquots of the suspensions were centrifuged and the visible spectrum between 400 – 650 nm was recorded on the supernatant to measure reduction in absorption at 554 nm to assess the degradation of Rhodamine B. After testing, the solution was resuspended and returned to the bulk test sample. At the end of the tests, the suspensions were centrifuged, the solids soaked in 5 mL of ethanol for two hours and centrifuged again. The solids were then dried in an oven at 80 °C and dissolved in 0.8 mL of 1M NaOH in D_2O for NMR analysis.

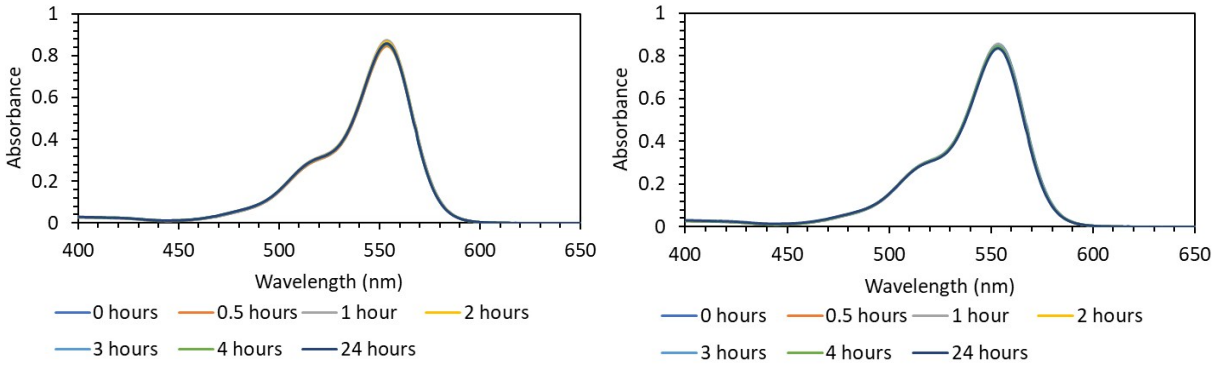

Figure S62. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right).

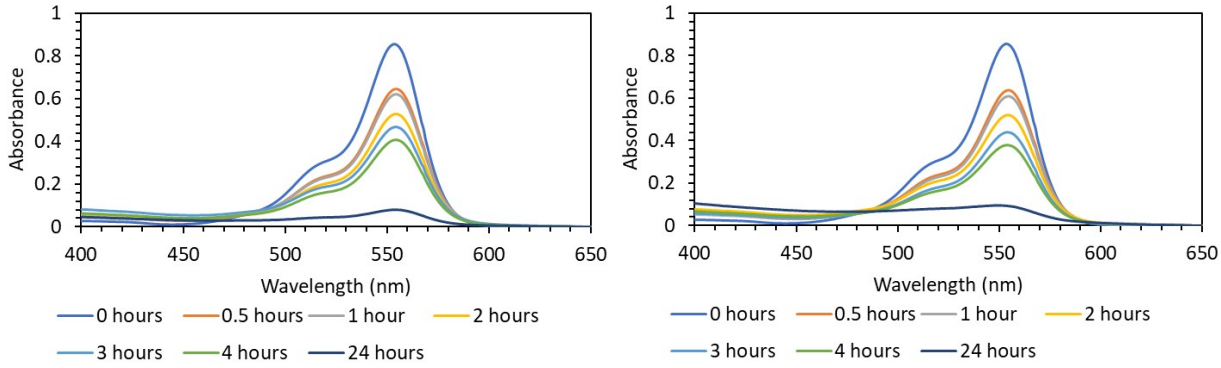

Figure S63. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 20 mg of FA_mod.

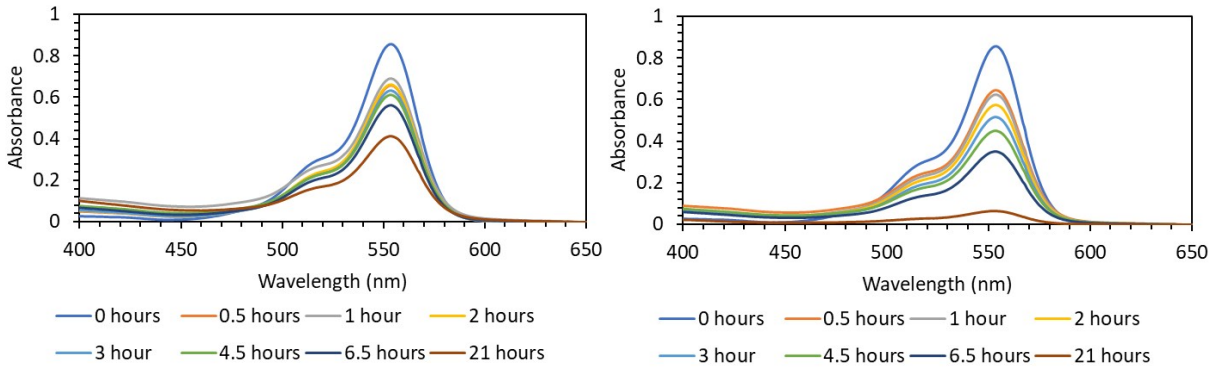

Figure S64. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 20 mg of FA_mod-35DABA.

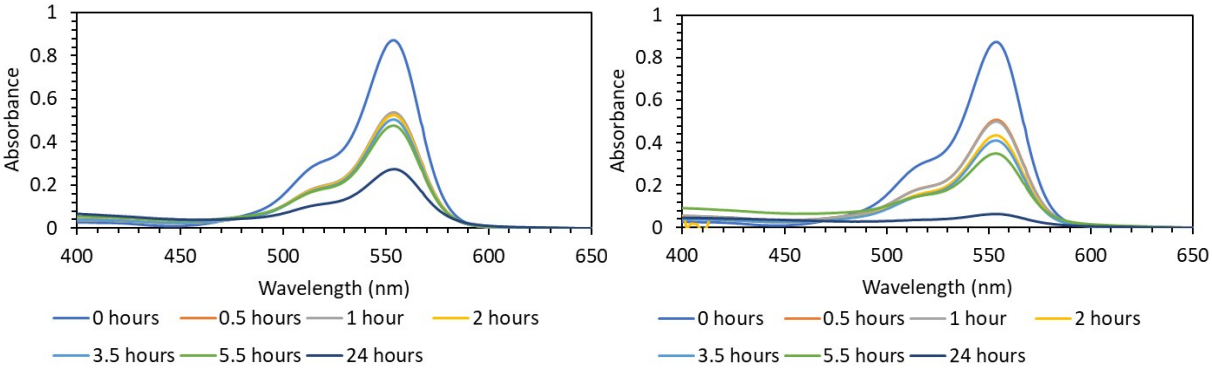

Figure S65. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 20 mg of FA_mod-2ABA.

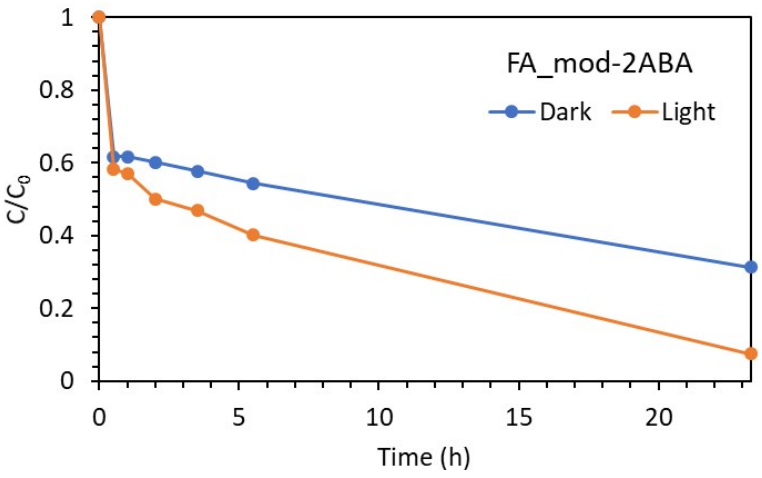

Figure S66. Evolution of the concentration of Rhodamine B in solution (expressed as C/C_0) during experiments carried out in the dark (blue) and under light irradiation (orange) using 20 mg of FA_mod-2ABA.

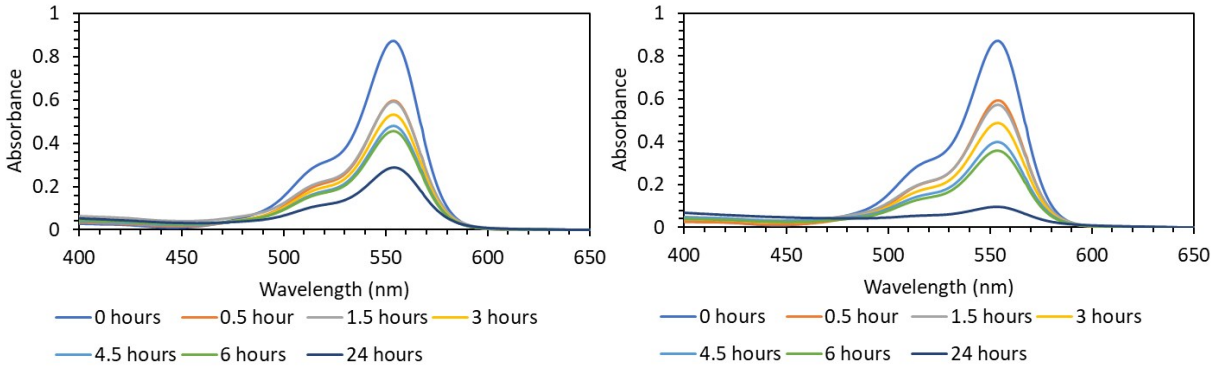

Figure S67. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 20 mg of FA_mod-3ABA.

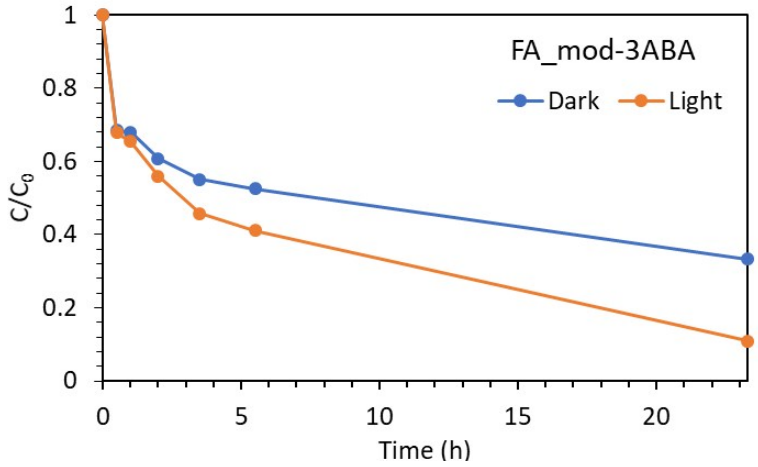

Figure S68. Evolution of the concentration of Rhodamine B in solution (expressed as C/C_0) during experiments carried out in the dark (blue) and under light irradiation (orange) using 20 mg of FA_mod-3ABA.

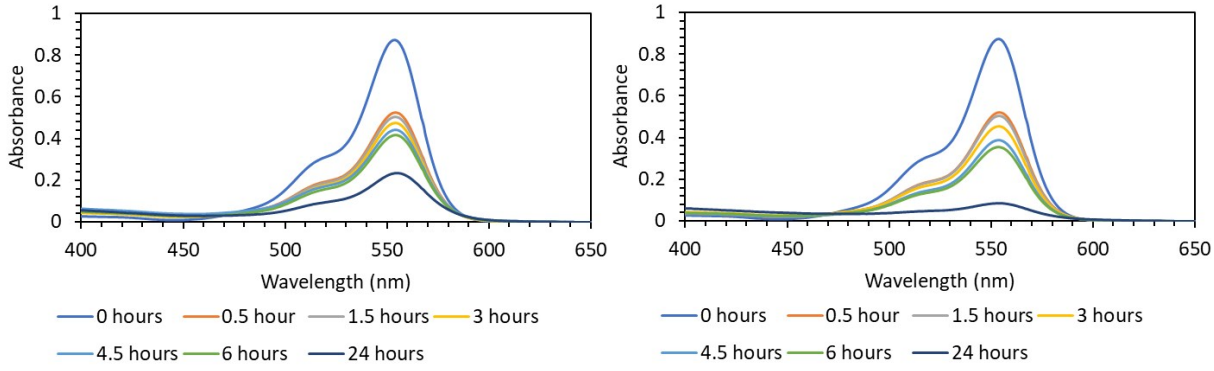

Figure S69. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 20 mg of FA_mod-4ABA.

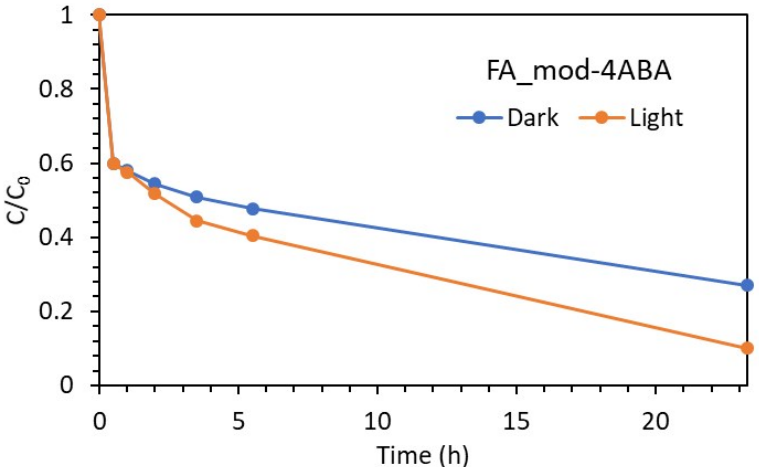

Figure S70. Evolution of the concentration of Rhodamine B in solution (expressed as C/C_0) during experiments carried out in the dark (blue) and under light irradiation (orange) using 20 mg of FA_mod-4ABA.

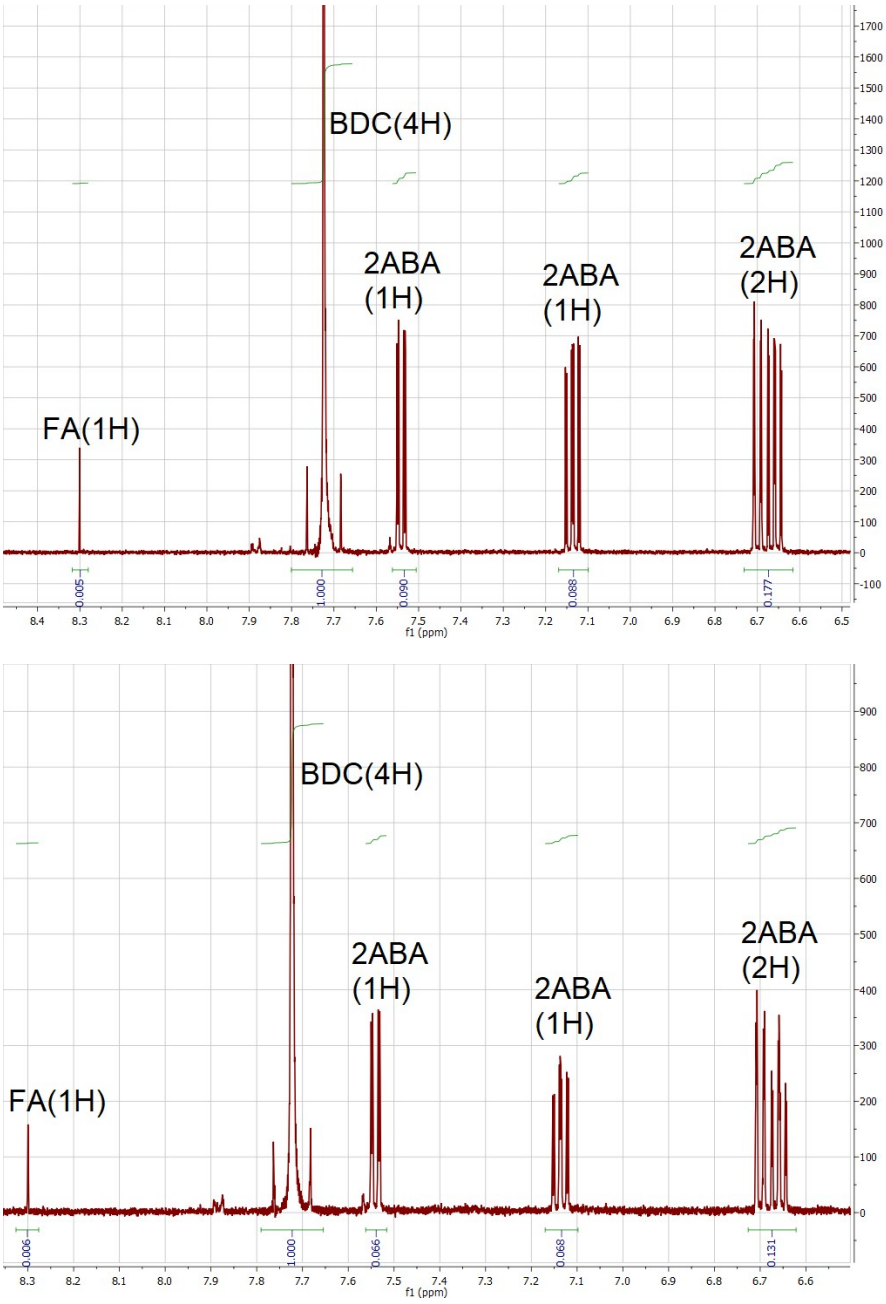

Figure S71. ^{1}H-NMR spectra of recovered FA_mod-2ABA after dye degradation tests in the dark (top) and under irradiation (bottom). The BDC/2ABA ratio increases from 2.21 in the as-synthesised sample to 2.78 and 3.79 for the samples tested in the dark and under irradiation, respectively.

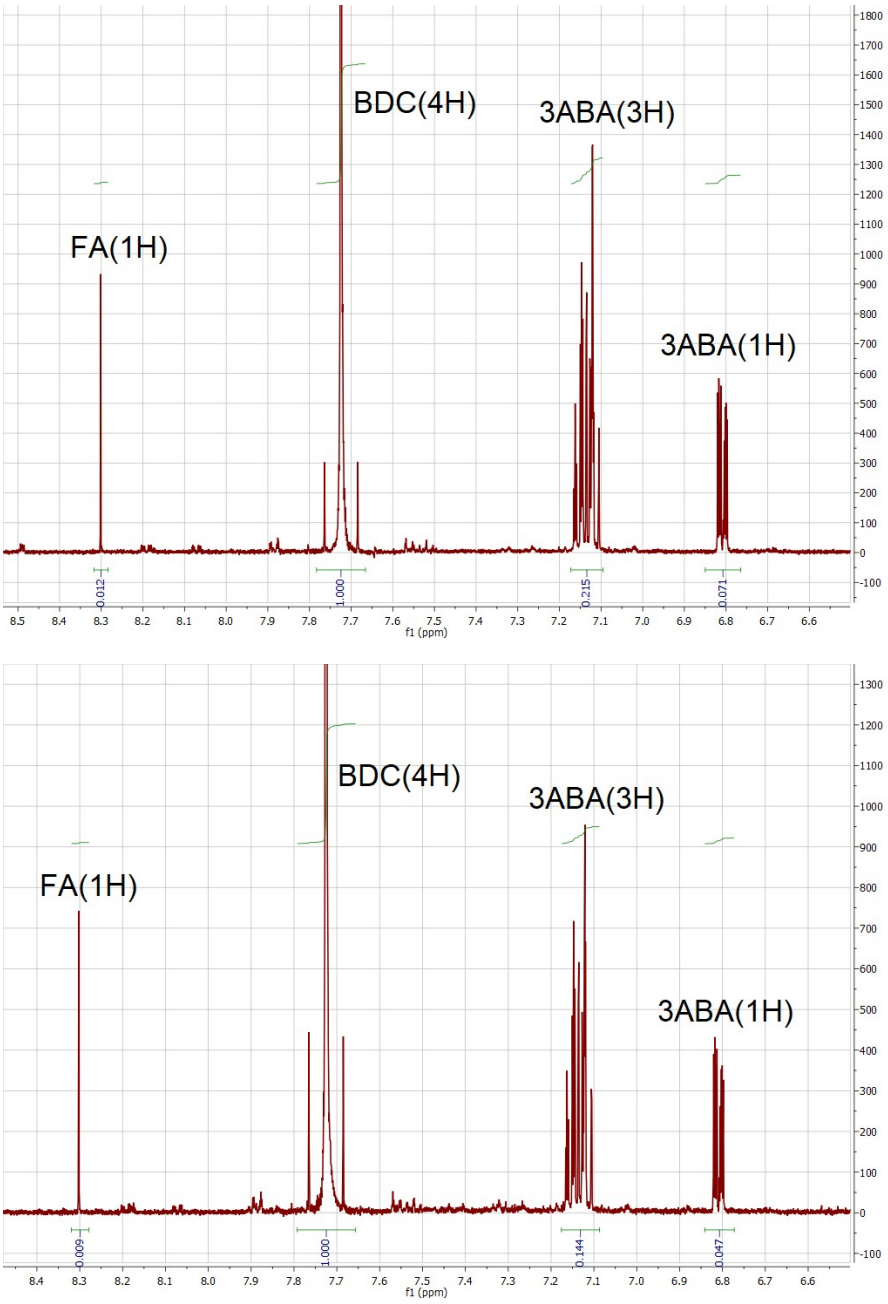

Figure S72. ^{1}H-NMR spectra of recovered FA_mod-3ABA after dye degradation tests in the dark (top) and under irradiation (bottom). The BDC/3ABA ratio increases from 2.45 in the as-synthesised sample to 3.52 and 5.32 for the samples tested in the dark and under irradiation, respectively.

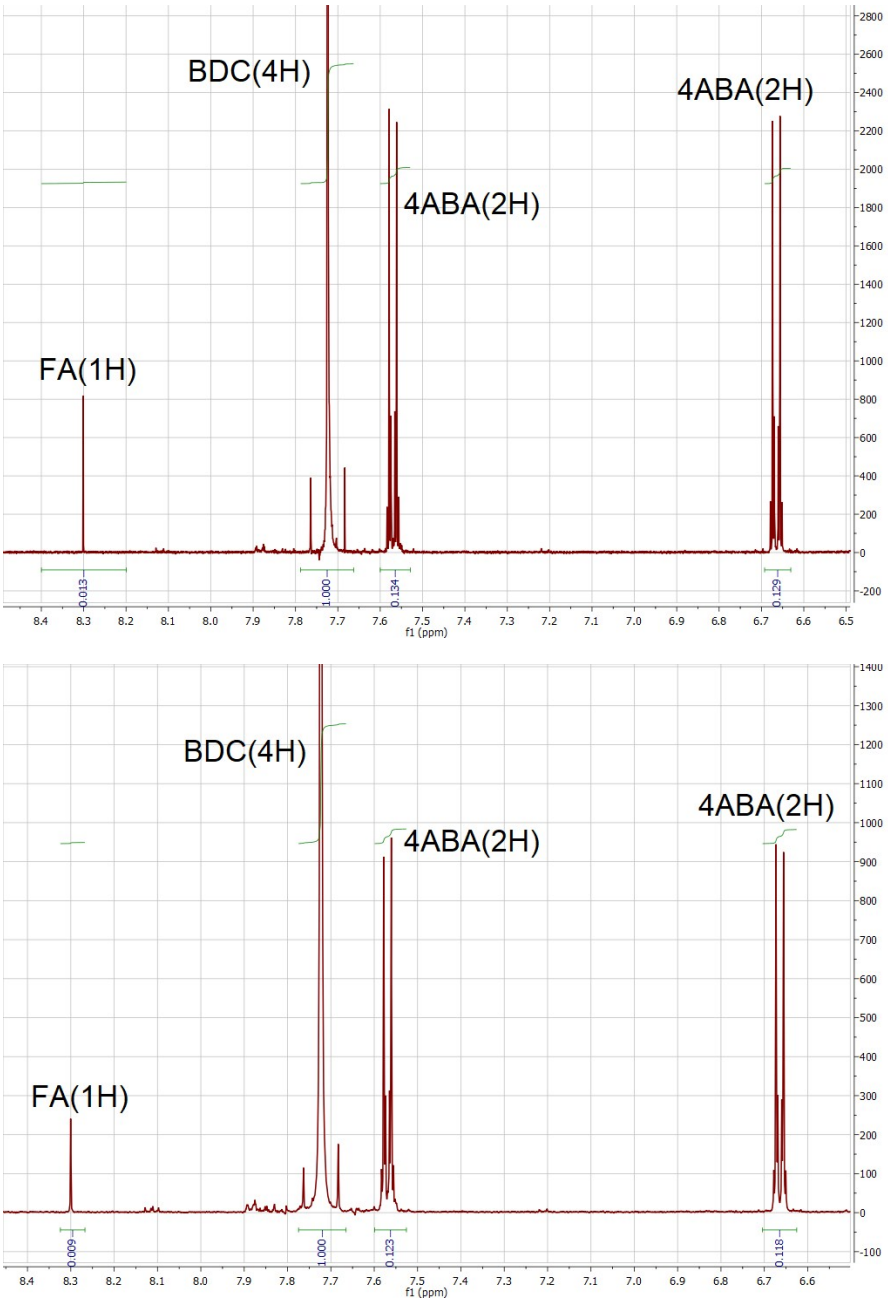

Figure S73. ^{1}H-NMR spectra of recovered FA_mod-4ABA after dye degradation tests in the dark (top) and under irradiation (bottom). The BDC/4ABA ratio increases from 2.78 in the as-synthesised sample to 3.33 and 4.17 for the samples tested in the dark and under irradiation, respectively.

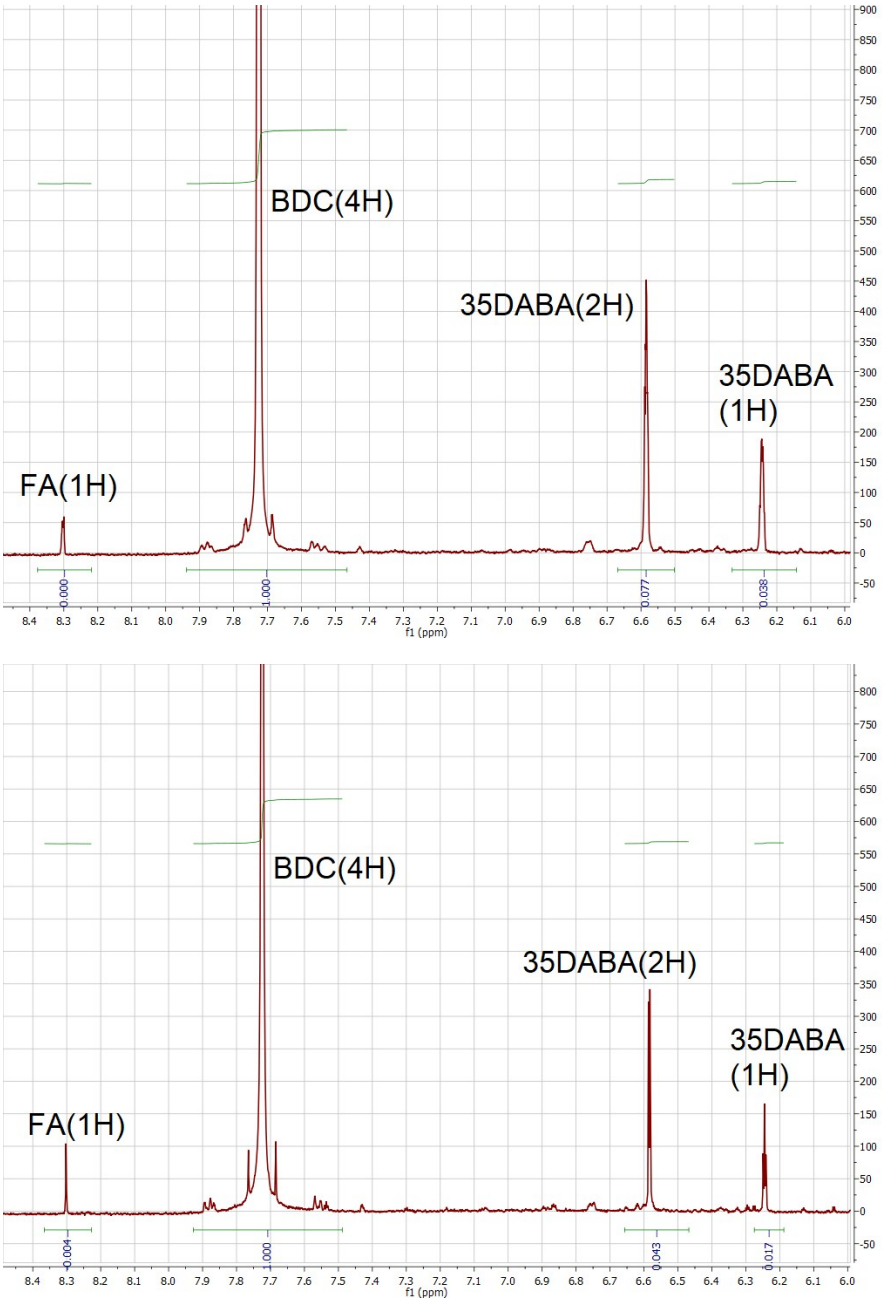

Figure S74. ^{1}H-NMR spectra of recovered FA_mod-35DABA after dye degradation tests in the dark (top) and under irradiation (bottom). The BDC/35DABA ratio increases from 3.29 in the as-synthesised sample to 5.43 and 11.36 for the samples tested in the dark and under irradiation, respectively.

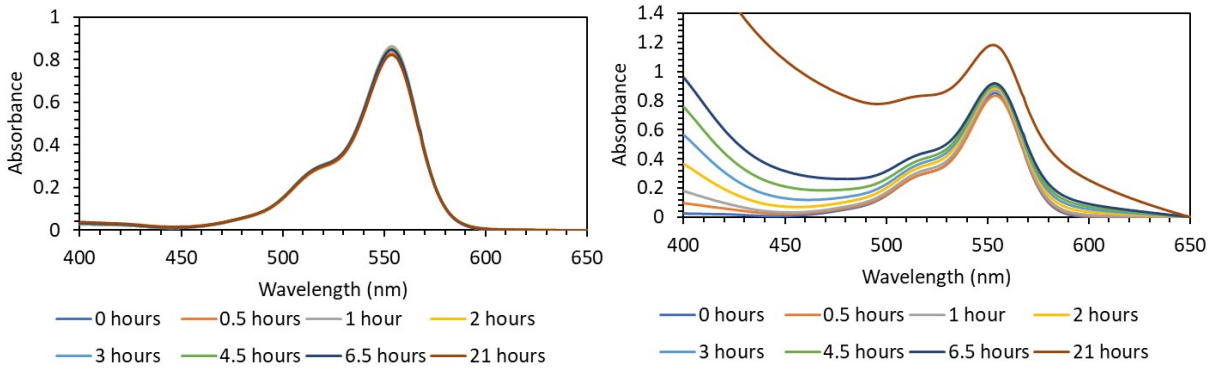

Figure S75. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 5 mg of the free 35DABA ligand. The tail at low wavelength is probably due to light-induced degradation of 35DABA, which gets more severe as the experiments proceeds and heavily affects the background.

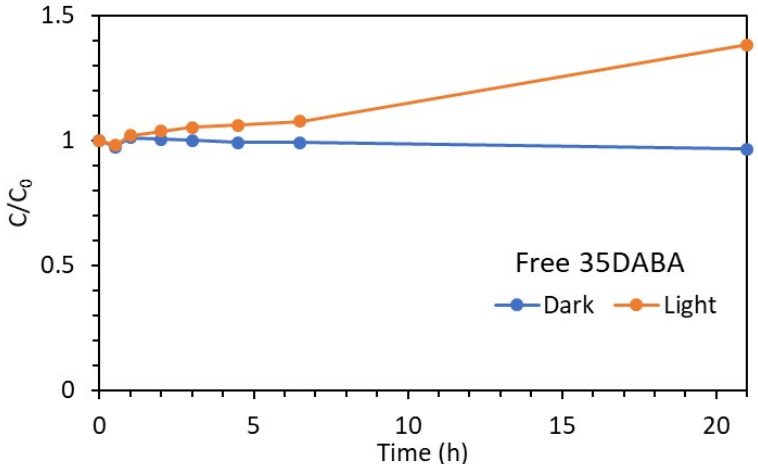

Figure S76. Evolution of the concentration of Rhodamine B in solution (expressed as C/C_0) during experiments carried out in the dark (blue) and under light irradiation (orange) using 5 mg of the free 35DABA ligand. The higher values of C/C_0 observed for the experiment under light irradiation are mainly due to increased background contribution to absorbance.

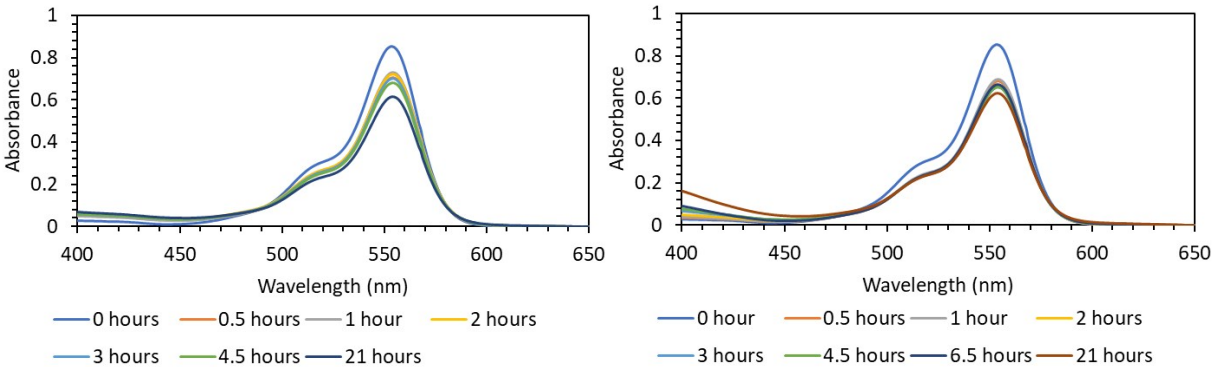

Figure S77. UV-Vis spectra, measured at different times, of a 0.008 M Rhodamine B solution (20 mL) stirred in the dark (left) and under light irradiation (right) in the presence of 15 mg of FA_mod and 5 mg

of the free 35DABA ligand. The tail appearing at low wavelength in the graph on the right hand side is probably due to light-induced degradation of the free 35DABA ligand (see Figure S63). Importantly, this tail is not visible in Figure S51, suggesting that there is little leaching of 35DABA in solution.

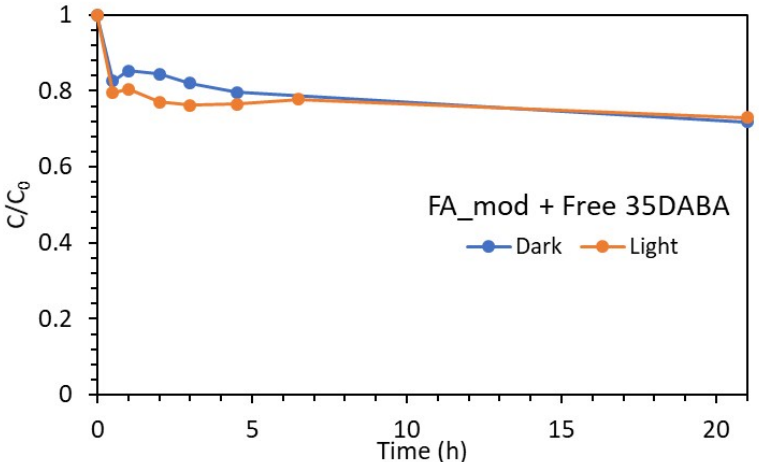

Figure S78. Evolution of the concentration of Rhodamine B in solution (expressed as C/C_0) during experiments carried out in the dark (blue) and under light irradiation (orange) using 15 mg of FA_mod and 5 mg of the free 35DABA ligand. There is very little difference between the two curves, suggesting that no photodegradation is taking place.

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