Supporting Information

A nanoporous graphene analog for superfast heavy metal removal and continuous-flow visible-light photoredox catalysis

Ran Xiao, John M. Tobin, Meiqin Zha, Yunlong Hou, Jun He, Filipe Vilela,* Zhengtao Xu*

General Procedure. All reagents and starting materials employed in this work are purchased from commercial sources (Aldrich, Acros, TCI, Riedel-de Haën, Fluorochem, and J&K; solvents from Merck, RCI, and ACS), and used without further purification. ¹H NMR and ¹³C NMR measurements were performed on a 400 and a 300 MHz Bruker superconducting-magnet high-field NMR spectrometer at room temperature. Solid State ¹³C CP-MAS measurements were carried out using a Bruker Avance 400 spectrometer operating at 100.6 MHz using a Bruker 4 mm double resonance probe-head operating at a spinning rate of 7 kHz. Elemental Analysis (CHN) was obtained with an Elementar VARIO Micro Cube Carbon-Hydrogen-Nitrogen Analyzer. Infrared Spectroscopy (FT-IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. Powder X-ray Diffraction (PXRD) data for the polymer solid were collected in reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with a CPS 180 detector using monochromated Cu-Ka1 $(\lambda = 1.5406 \text{ Å})$ radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA. Solid State UV/Vis absorption spectra were measured on a PerkinElmer Lambda 25 system using a Labsphere RSA-PE-20 reflectance spectroscopy integration sphere. Thermogravimetric analysis (TGA) of the HOTT-HATN was carried out with a PerkinElmer STA6000 under nitrogen flow (20 mL·min⁻¹). A heating rate of 2 °C·min⁻¹ was applied and an empty Al_2O_3 crucible being used as the reference. Gas sorption and porosity analysis were carried out using a Quantachrome Autosorb iQ gas sorption analyser. Scanning electron microscopy (SEM) was carried out on Philips XL30 Esem-FEG, (FEI Company, The Netherlands) equipped with an energy-dispersive x-ray microanalysis (EDX) system (EDAX Phoenix system, EDAX Inc., Mahwah NJ, USA). Transmission electronic microscopy (TEM) was conducted on a Philips Technai 12 Transmission Electron Microscope with an accelerating voltage of 120 KV.



Scheme S1. Synthetic procedure of HOTT-HATN polymer.

Synthesis of 2,3,8,9,14,15-Hexachloro-5,6,11,12,17,18-hexaazatrinaphthylene (HATN-Cl₆). Hexaketocyclohexane octahydrate (529 mg, 1.69 mmol), 4,5-dichloro-1,2-

phenylenediamine (900 mg, 5.08 mmol) and a magnetic stirrer were loaded into a 25ml twoneck round-bottom flask fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N₂ (three times for purging). Glacial acetic acid and ethanol (12 mL, 1:1 v/v), previously bubbled with N₂ for 5 min, was then transferred into the flask under N₂ *via* cannula. After refluxed under N₂ at 140 °C for 24 hours, the reaction mixture was filtered and washed with 20 mL hot glacial acetic acid. The solid was then refluxed with 15 mL of 30% nitric acid for 3 hours at 140 °C. The solid of the reaction mixture was filtered, washed with 10 mL deionized water and ethanol, and dried under vacuum. The product HATN-Cl₆ is yellowgreen solid (780 mg, 78% yield). ¹H NMR (300 MHz, CDCl₃): δ 8.80 (6H, s, Ar). ^{1,2}



Fig. S1. ¹H NMR spectrum of HATN-Cl₆ with a singlet at 8.80 ppm corresponding to the aromatic hydrogen nuclei.

Synthesis of HOTT-HATN polymer. 2,3,6,7,10,11-Hexahydroxytriphenylene (HOTT) (130 mg, 0.40 mmol), HATN-Cl₆ (236 mg, 0.40 mmol), potassium carbonate (1.66 g, 12.0 mmol) and a magnetic stirrer were loaded into a 50 mL two-neck round bottom flask fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N₂ (three times for purging). N,N-dimethylacetamide (10 mL) was bubbled with N₂ for 5 min before injected into the flask *via* cannula under N₂. The reaction was heated to 170 °C in an oil bath under reflux for 5 days. The reaction mixture were then poured into 300 mL deionized water and stirred at 50 °C for 2h before collection by centrifuge. The polymer was washed for several cycles until a pH of 7 was obtained. The mixture was filtered and washed with deionized water (50 mL), ethanol (50 mL) and CH₂Cl₂ (50 mL). A dark reddish brown powder were obtained after drying.³

Activation of HOTT-HATN polymer. A thimble (e.g., made from folding filter paper) containing the HOTT-HATN solid sample (400 mg) was loaded into the main chamber of a Soxhlet extractor. The Soxhlet extractor was connected onto a 250-mL round bottom flask

containing methanol (150 mL), and then equipped with a condenser. The flask was heated to 130 °C with a heating block for 2 days. The solvent was then replaced by clean tetrahydrofuran and extract heated at 130 °C for 1 day. The filter paper was then taken out and the solid was dried in air to give the activated HOTT-HATN sample (248 mg, 89.2% yield). Solid state ¹³C NMR CP-MAS (100 MHz): δ 147.07, 142.45, 126.27, 110.68.

Elemental analysis. A very small amount of Cl can be detected by EDX with atom number ratio lower than 0.2%. CHN elemental analysis of the activated sample found [C (57.14%), H (4.72%), N (10.70%)]. A fitting formula $(C_{42}H_{12}O_6N_6) \cdot (H_2O)_{10}$ gives a calculated profile as [C (57.54%), H (3.68%), N (9.59%)], which is largely consistent with the formation of the HOTT-HATN polymer as depicted in Fig. S2. The presence of water guests is also consistent with the TGA plot, which features significant weight loss at the low temperature region (e.g., <200 °C); however, the water content is likely to be rather variable due to the porous nature of the polymer solid, as well as air humidity and other experimental conditions.

Entry	N [%]	C [%]	H [%]	C/N ratio	C/H ratio		
1	10.72	57.11	4.724	5.3272	12.0899		
2	10.67	57.17	4.725	5.3579	12.0978		
Averag							
е	10.70	57.14	4.72	5.34	12.09		

Table S1. CHN analysis of activated HOTT-HATN sample.



Fig. S2. A repeating unit of the HOTT-HATN polymer framework, with the composition shown also in a condensed formula.



Fig. S3. An EDX spectrum of an activated HOTT-HATN polymer.



Fig. S4. A thermogravimetric analysis (TGA) plot of an activated sample of HOTT-HATN under N₂ stream (flow rate: 20 ml·min⁻¹). The heating rate is 2 °C·min⁻¹.



Fig. S5. FT-IR spectra of HATN-Cl₆ and the polymer solid HOTT-HATN.



Fig. S6. A solid state ¹³C NMR spectrum of HOTT-HATN. Peaks denoted by (*) indicate the presence of side bands.



Fig. S7. A solid-state UV-Vis spectrum of the HOTT-HATN polymer.



Fig. S8. An X-ray powder pattern (Cu K α λ =1.5418 Å) of an activated HOTT-HATN sample.



Fig. S9. Two SEM images of the activated HOTT-HATN polymer (with the magnification factors included).



Fig. S10. Two TEM images of the activated HOTT-HATN polymer.

Gas sorption. Pore analysis of the activated HOTT-HATN sample was performed both using N_2 at 77 K (P/P₀ range of 1×10⁻⁵ to 0.995). Initial data analysis was done using AS1Win and QuadraWin 5.05 software. The activated HOTT-HATN sample displayed a typical type-II gas adsorption isotherm for N_2 with a Brunauer-Emmett-Teller (BET) surface area of 526 m²·g⁻¹ (Fig. 2). QSDFT analysis (Pore Size Distribution and Pore Volume) of the N_2 adsorption isotherm (77 K) was performed using a commercialized model (N_2 at 77K on silica; cylinder pore; QSDFT equilibrium model). The PSD and pore volume analysis of N_2 showed an average pore width of 0.52 nm and a micropore volume of 0.579 cm³·g⁻¹ (Fig. S11).



Fig. S11. Pore size distribution and pore volume of an activated HOTT-HATN solid.

Removal of lead from water - kinetic and isotherm studies.

Kinetics study of Pb(II) sorption. A 50 mL solution containing 10 ppm Pb [in form of $Pb(NO_3)_2$] was prepared with deionized water and loaded into a round bottom flask with a magnetic stirrer. HOTT-HATN (20 mg) was added and the solution was stirred vigorously at room temperature. Samples were removed from the suspension with a dropper at intervals and quickly filtered over 0.45-µm membrane filter. The concentration of Pb remaining in the sample was determined by ICP-AES.

Time (min)	Concentration of Pb (ppm)		
0	<mark>10.0</mark>		
<mark>0.67</mark>	<mark>1.74</mark>		
<mark>1.67</mark>	<mark>0.585</mark>		
3	<mark>0.029</mark>		
5	<mark>0.007*</mark>		
7	<mark>-0.002*</mark>		
10	<mark>-0.006*</mark>		
15	<mark>-0.004*</mark>		
20	<mark>-0.004*</mark>		
30	<mark>-0.006*</mark>		
60	<mark>-0.005*</mark>		
90	<mark>-0.007*</mark>		
120	<mark>-0.004*</mark>		
180	<mark>-0.006*</mark>		
240	<mark>-0.004*</mark>		
300	<mark>-0.004*</mark>		
510	<mark>-0.004*</mark>		

Table S2. Pb concentrations at various times observed in a kinetic study of Pb uptake by the HOTT-HATN absorbent.

* Lead concentration below the detection limit of ICP-AES (15-20 ppb).



Fig. S12. A kinetic study plot (concentration vs. time) of Pb uptake by the HOTT-HATN polymer. The neighboring data points are manually connected for easier visualization. The black and empty boxes represent instrument readouts above and below the detection limits of the instrument.



Fig. S13. A pseudo-second-order kinetic plot for Pb(II) adsorption. Starting from the 5th point (t = 7.0 min), C_t drops below ICP detection limit, the q_t value of 25 mg·g⁻¹ is used here for the point at (t = 7.0 min).

Isotherm study of Pb(II) sorption. A series of 5.0 mL aqueous $Pb(NO_3)_2$ solutions (as listed in Table S3) were loaded into glass vials where 5.0 mg HOTT-HATN polymer was added. The vials were shaken at 200 rpm for 4.5 h at room temperature, then separated over a filter membrane separately. The filtrates were tested *via* ICP-AES.

Entry	Initial concentration (C _i)	Equilibrium concentration (C_e)		
	(mg·L ⁻¹)	(mg·L ⁻¹)		
1	10	<mark>0.005*</mark>		
2	20	<mark>0.001*</mark>		
3	30	<mark>0.003*</mark>		
4	40	<mark>0.001*</mark>		
5	50	<mark>0.149</mark>		
6	60	<mark>0.644</mark>		
7	80	<mark>20.82</mark>		
8	100	<mark>34.82</mark>		
9	120	<mark>53.63</mark>		
10	150	<mark>82.85</mark>		

Table S3. Tabulated isotherm data of Pb sorption by the HOTT-HATN polymer.

* Lead concentration below the detection limit of ICP-AES.



Fig. S14 A Pb(II) Langmuir sorption isotherm of an acetic acid-treated HOTT-HATN sample for illustrating the key role of the alkaline N donors: after treating HOTT-HATN with acetic acid, the Langmuir sorption isotherm as shown here indicates that Pb sorption capacity q_{max} was reduced to be 30 mg·g⁻¹, which is less than half of the pristine sample (66.8 mg·g⁻¹). Inset: linear expression fitted with the Langmuir model.

Stripping of Pb from Pb-loaded HOTT-HATN. HOTT-HATN polymer (10 mg) with Pb previously loaded (67.6 mg·g⁻¹) was loaded in a glass vial. A 10% w/w HCl aqueous solution (3.0 mL) was added. The glass vial was covered and shaken at 200 rpm at room temperature for 4 h and then filtered. The powder was washed with deionized water until the pH was neutral. This was followed by an acetone wash and the polymer was dried *in vacuo*. The extracted sample was characterized *via* EDX analysis (Fig. S10). The EDX spectrum indicates that most of Pb is successfully stripped from the polymer matrix with only a trace amount (0.03 atom%) of Pb left. The Pb-stripped polymer thus obtained, after activated by stirring in a 5 wt% ammonia solution, and washing by water, continues to feature strong heavy metal uptake capabilities (e.g., removing over 95% of Hg(II) within 1.5 hours from a water sample originally containing Hg(II) at about 5.0 ppm).



Fig. S15. An EDX spectrum of a Pb-loaded HOTT-HATN polymer sample after being stripped of Pb by HCl washing.

Selectivity Study

100 mL of a mixed solution of Hg²⁺, Pb²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Ca²⁺, Na⁺ nitrate or chloride was loaded into a 250-mL round bottom flask with a magnetic stirrer. The solution was under vigorous stirring while 100 mg of HOTT-HATN polymer was added. Samples were taken out at intervals and quickly filtered over syringe filter membrane and tested by ICP-AES.

the HOTT-HATN polymer as absorbent. t Zn Hg Cu Na Pb Cd Ca min mg/L mg/L <mark>mg/L</mark> <mark>mg/L</mark> <mark>mg/L</mark> mg/L <mark>mg/L</mark> 0 <u>6.358</u> **5.650** 5.900 <mark>4.880</mark> **5.952 53.336** 20.1412 <mark>4.254</mark> 1.753 **3.478** 55.217 2.605 <mark>4.522</mark> 20.000 6 <mark>4.169</mark> 0.937 2.582 54.300 2.008 <mark>4.398</mark> 20.326 10 **1.886** <mark>4.108</mark> 0.602 54.591 1.548 4.103 20.127 <mark>30</mark> <mark>4.238</mark> 0.351 1.049 **53.090** 1.084 **3.920** 19.995 <mark>60</mark> **4.200** 0.236 0.658 <u>52.237</u> 0.841 **3.901** 19.782 <mark>210</mark> <mark>4.284</mark> 0.141 0.295 **51.985** 0.611 3.890 19.333 <mark>450</mark> <mark>4.284</mark> 0.109 0.209 **50.996** 0.575 3.870 18.998

Table S4. Tabulated metal concentrations at various times observed in a selectivity study of

study of the HOTT-HATN polymer as absorbent.								
t	<mark>Zn</mark>	Hg	<mark>Cu</mark>	Na	<mark>Pb</mark>	Cd	Ca	
<mark>min</mark>	<mark>%</mark>							
<mark>0</mark>	<mark>100.0</mark>							
<mark>2</mark>	<mark>75.3</mark>	<mark>29.7</mark>	<mark>54.7</mark>	103.5	<mark>53.4</mark>	<mark>76.0</mark>	<mark>99.3</mark>	
<mark>6</mark>	<mark>73.8</mark>	<mark>15.9</mark>	<mark>40.6</mark>	<mark>101.8</mark>	<mark>41.1</mark>	<mark>73.9</mark>	<mark>100.9</mark>	
<mark>10</mark>	<mark>72.7</mark>	<mark>10.2</mark>	<mark>29.7</mark>	<mark>102.4</mark>	<mark>31.7</mark>	<mark>68.9</mark>	<mark>99.9</mark>	
<mark>30</mark>	<mark>75.0</mark>	<mark>6.0</mark>	<mark>16.5</mark>	<mark>99.5</mark>	<mark>22.2</mark>	<mark>65.9</mark>	<mark>99.3</mark>	
<mark>60</mark>	<mark>74.3</mark>	<mark>4.0</mark>	<mark>10.3</mark>	<mark>97.9</mark>	<mark>17.2</mark>	<mark>65.5</mark>	<mark>98.2</mark>	
<mark>210</mark>	<mark>75.8</mark>	<mark>2.4</mark>	<mark>4.6</mark>	<mark>97.5</mark>	12.5	<mark>65.4</mark>	<mark>96.0</mark>	
<mark>450</mark>	<mark>75.8</mark>	<mark>1.8</mark>	<mark>3.3</mark>	<mark>95.6</mark>	<mark>11.8</mark>	<mark>65.0</mark>	<mark>94.3</mark>	

Table S5. Tabulated remaining metal percentage at various times observed in a selectivity



Fig. S16. A kinetic study plot (remained percentage vs. time) of selectivity test by the HOTT-HATN polymer adsorbent.

t (min)

Typical conditions for heterogeneous catalytic Knoevenagel condensation. An aldehyde substrate (0.25 mmol), malononitrile (25 mg, 0.375 mmol), deionized water (1.0 mL) and HOTT-HATN polymer (5.0 mg) were loaded in a glass vial. Note that a small amount of chloroform (0.2 mL) was also added for solid aldehyde substrates or aldehyde substrates with poor solubility in water, e.g., entries 8, 9 and 10 of Table 1. The vial was then sealed and shaken at 250 rpm at 40 °C for several hours (as specified in Table 1). The polymer was separated *via* filtration and washed with dichloromethane (3 mL x 3). The filtrated was extracted with dichloromethane three times, and the combined organic layer were washed with deionized water three times and dried over anhydrous MgSO₄. The mixture was then filtered and solvent was removed under vacuum to give the crude product. Conversion of the condensation reaction was determined by ¹H NMR analysis.

General procedure for recycling HOTT-HATN. After finishing the catalytic reaction, HOTT-HATN polymer was recovered by washing with acetone, then filtered, washed with acetone again and dried under vacuum. A new batch of starting materials were loaded into a glass vial for the next catalytic cycle. The recyclability of HOTT-HATN heterogeneous catalyst was tested at least five times *via* this method without any significant decreases in catalytic activity.

Aerobic photooxidation of benzylamine and derivatives. A benzyl amine (0.5 mmol), HOTT-HATN (5.0 mg) and acetonitrile (MeCN, 10 mL) were added to a flask equipped with a magnetic stir bar. The mixture was sonicated for 3 minutes to ensure even dispersion of the polymer. The dispersion was pumped using a peristaltic pump through the commercial photochemical reactor (Vapourtec Ltd.) equipped with a white light LED lamp ($\lambda > 400$ nm, Fig. S15) at a flow rate of 1 mL·min⁻¹. Concurrently, oxygen was pumped through a second pump at the same flow rate. The dispersion and the oxygen then mixed *via* a T-junction prior entering the photochemical reactor. The reaction mixture was cycled through the system until consumption of the benzyl amine was determined *via* TLC (EtOAc:Hexane v/v 1:1). When starting material was no longer present the reaction was stopped. The reaction mixture was filtered *via* syringe filter and evaporated and the residue diluted with CDCl₃ for ¹H NMR analysis. Continuous flow chemistry equipment (Vapourtec, Ltd.)



Fig. S17. Easy-Photochem flow system from Vapourtec Ltd. equipped with cool white light LED module emitting light at >400 nm.

¹H NMR spectra of Knoevenagel condensation products



Fig. S18. ¹H NMR spectrum of 2-benzylidenemalononitrile (300 MHz, 30 °C, CDCl₃): δ = 7.91 (d, *J* = 7.4 Hz, 2H), 7.78 (s, 1H), 7.68 – 7.60 (m, 1H), 7.52 – 7.57 (m, 2H).



Fig. S19. ¹H NMR spectrum of 2-(4-fluorobenzylidene)malononitrile (400 MHz, 30 °C, CDCl₃): δ = 7.96 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.75 (s, 1H), 7.24 (t, *J* = 8.5 Hz, 2H).



Fig. S20. ¹H NMR spectrum 2-(4-hydroxybenzylidene)malononitrile (400 MHz, 30 °C, acetone-D₆): $\delta = \delta$ 7.96 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H).



Fig. S21. ¹H NMR spectrum of 2-(2-bromobenzylidene)malononitrile (300 MHz, 30 °C, CDCl₃): $\delta = 8.22$ (s, 1H), 8.12 (dd, J = 2.09, 7.36 Hz, 1H), 7.74 (dd, J = 1.66, 7.59 Hz, 1H), 7.43-7.53 (m, 2H).



Fig. S22. ¹H NMR spectrum of 2-(2-bromo-4,5-dimethoxybenzylidene)malononitrile (300 MHz, 30 °C, CDCl₃): δ = 8.13 (s, 1H), 7.86 (s, 1H), 7.15 (s, 1H), 3.97 (s, 3H), 3.93 (s, 3H).



Fig. S23. ¹H NMR spectrum of 2-(3,5-bis(benzyloxy)benzylidene)malononitrile (300 MHz, 30 °C, CDCl₃): $\delta_{ppm} = 7.64$ (s, 1H), 7.46 – 7.39 (m, 8H), 7.38 (t, J = 2.2 Hz, 2H), 7.11 (s, 2H), 7.10 (s, 2H), 6.85 (t, 1H), 5.09 (s, 1H), 5.08 (s, 4H).

¹ H NMR analysis of aerobic Photooxidation of benzylamine and derivatives.



Fig. S24. ¹H NMR spectrum of benzyl amine (300 MHz, 30 °C, CDCl₃): δ = 1.42 (s, 2H), 3.86 (s, 2H), 7.27-7.39 (m, 5H).



Fig. S25. ¹H NMR spectrum of N-benzyl-1-phenylmethanimine (300 MHz, 30 °C, CDCl₃): δ = 4.86 (s, 2H), 7.37-7.46 (m, 8H), 7.81 (dd, 2H), 8.43 (s, 1H).



Fig. S26. ¹H NMR spectrum of 4-methoxybenzylamine (300 MHz, 30 °C, CDCl₃): δ = 1.50 (s, 2H), 3.80 (s, 2H+3H), 6.90 (d, 2H), 7.22 (d, 2H).



Fig. S27. The ¹H NMR spectrum of (*E*)-N-(4-methoxybenzyl)-1-(4-methoxyphenyl) methanimine (300 MHz, 30 °C, CDCl₃): δ = 3.82 (s, 3H), 3.87 (s, 3H), 4.75 (s, 2H), 6.91 (d, 2H), 6.93 (d, 2H), 7.26 (d, 2H), 7.75 (d, 2H), 8.32 (s, 1H).



Fig. S28. ¹H NMR spectrum of 4-methylbenzylamine (300 MHz, 30 °C, CDCl₃): δ = 1.49 (s, 2H), 2.38 (s, 3H), 3.85 (s, 2H), 7.20 (d, 2H), 7.24 (d, 2H).



Fig. S29. ¹H NMR spectrum of (*E*)-N-(4-methylbenzyl)-1-(4-methylphenyl)methanimine (300 MHz, 30 °C, CDCl₃): δ = 2.37 (s, 3H), 2.47 (s, 3H), 4.80 (s, 2H), 7.19 (d, 2H), 7.22 (d, 2H), 7.26 (d, 2H), 7.68 (d, 2H), 8.37 (s, 1H).



Fig. S30. ¹H NMR spectrum of 4-fluorobenzylamine (300 MHz, 30 °C, CDCl₃): δ = 1.42 (s, 2H), 3.84 (s, 2H), 7.01 (distorted doublet, 2H), 7.28 (distorted doublet, 2H).



Fig. S31. ¹H NMR spectrum of (*E*)-N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (300 MHz, 30 °C, CDCl₃): δ = 4.80 (s, 2H), 7.06 (distorted doublet, 2H), 7.13 (distorted doublet, 2H), 7.32 (distorted doublet, 2H), 7.80 (distorted doublet, 2H), 8.38 (s, 1H).



Fig. S32. ¹H NMR spectrum of 4-chlorobenzylamine (300 MHz, 30 °C, CDCl₃): δ = 1.44 (s, 2H), 3.81 (s, 2H), 7.24 (d, 2H), 7.28 (d, 2H).



Fig. S33. ¹H NMR spectrum of (*E*)-N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (300 MHz, 30 °C, CDCl₃): δ = 4.79 (s, 2H), 7.31 (d, 2H), 7.33 (d, 2H), 7.42 (d, 2H), 7.74 (d, 2H), 8.37 (s, 1H).



Fig. S34. ¹H NMR spectrum of 4-(trifluoromethyl)benzylamine (300 MHz, 30 °C, CDCl₃): δ = 1.45 (s, 2H), 3.94 (s, 2H), 7.45 (d, 2H), 7.58 (d, 2H).



Fig. S35. ¹H NMR spectrum of (*E*)-N-(4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)methanimine (300 MHz, 30 °C, CDCl₃): δ = 4.93 (s, 2H), 7.52 (d, 2H), 7.63 (d, 2H), 7.73 (d, 2H), 7.92 (d, 2H), 8.50 (s, 1H).



Fig. S36 ¹H NMR spectrum of the model reaction after prolonged irradiation of HOTT-HATN (300 MHz, 30 °C, CDCl₃): $\delta_{ppm} = 4.87$ (s, 2H), 7.37-7.47 (m, 8H), 7.82 (dd, 2H), 8.44 (s, 1H).



Fig. S37 FTIR anaylsis of HOTT-HATN before and after photocatalytic experiment with a total irradiation time of 36 h.

References

- 1. S. Barlow, Q. Zhang, B. R. Kaafarani, C. Risko, F. Amy, C. K. Chan, B. Domercq, Z. A. Starikova, M. Y. Antipin and T. V. Timofeeva, *Chem. Eur. J.*, 2007, **13**, 3537-3547.
- 2. S. Skujins and G. Webb, *Tetrahedron*, 1969, **25**, 3935-3945.
- 3. P. M. Budd, B. Ghanem, K. Msayib, N. B. McKeown and C. Tattershall, *J. Mater. Chem.*, 2003, **13**, 2721-2726.