Supporting Information

Thiophene based-Covalent Triazine Frameworks as Visible-light Driven Heterogeneous Photocatalysts for the Oxidative Coupling of Amines

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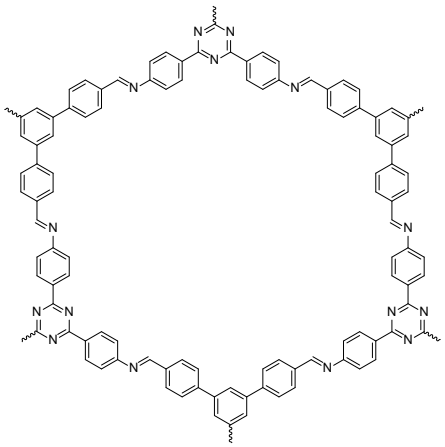
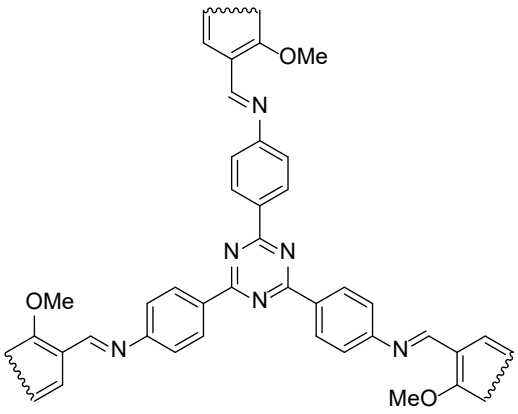
CTF's synthesis

To a Schlenk flask tube with vacuum valve, 1,3,5-tris(4-formylphenyl)benzene (0.57 mmol, 1 eq) and 4´,4´´-(1,3,5-triazine-2,4,6-triyl)trianiline (0.57 mmol, 1 eq) were added, followed by o-dichlorobenzene:ethanol:DMSO (2:1.8:0.2, 10.0 mL) along the walls of the flask (to push down any remaining solids atop of the flask), and 6 M acetic acid (1 mL). The flask was sealed and sonicated at room temperature for 10 min. The reaction mixture was then degassed through three freeze-pump-thaw cycles, after which the flask was charged with N_2 through the vacuum valve. The flask was then allowed to stand in a 120°C pre-heated oil bath for three days without stirring. The flask was removed from the oil bath, cooled to room temperature and filtered through a Buchner funnel equipped with a filter paper. The solid was washed with THF (50 mL x 3) and acetone (50 mL x 3) to ensure all of the material is filtered from the flask to the Buchner funnel. The solid was washed in a Soxhlet extractor with THF for 24 h and then was collected and dried at 120°C for 24 h under vacuum.



Me-CTF's synthesis

To a Schlenk flask tube with vacuum valve, 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (0.86 mmol, 1.5 eq) and 4´,4´´-(1,3,5-triazine-2,4,6-triyl)trianiline (0.57 mmol, 1 eq) were added, followed by o-dichlorobenzene:n-buthanol (1:1, 10.0 mL) along the walls of the flask (to push down any remaining solids atop of the flask), and 6 M acetic acid (1 mL). The flask was sealed and sonicated at room temperature for 10 min. The reaction mixture was then degassed through three freeze-pump-thaw cycles, after which the flask was charged with N_2 through the vacuum valve. The flask was then allowed to stand in a 120°C pre-heated oil bath for three days without stirring. The flask was removed from the oil bath, cooled to room temperature and filtered through a Buchner funnel equipped with a filter paper. The solid was washed with THF (50 mL x 3) and acetone (50 mL x 3) to ensure all of the material is filtered from the flask to the Buchner funnel. The solid was washed in a Soxhlet extractor with THF for 24 h and then was collected and dried at 120°C for 24 h under vacuum.



Elemental analysis of TP-CTF-type materials

Table S1. Elemental analysis of TP-CTF

Catalyst	N(%)	C(%)	H(%)	S(%)	C:S exp.	C:S calc.	C:N exp.	C:N calc.
Fresh TP-CTF	12.5	65.8	3.4	14.6	12.0	12.0	6.1	6.0
Recovered TP-CTF	13.0	69.1	4.3	15.0	12.0	12.3	6.1	6.2

XRD patterns of CTF-type materials

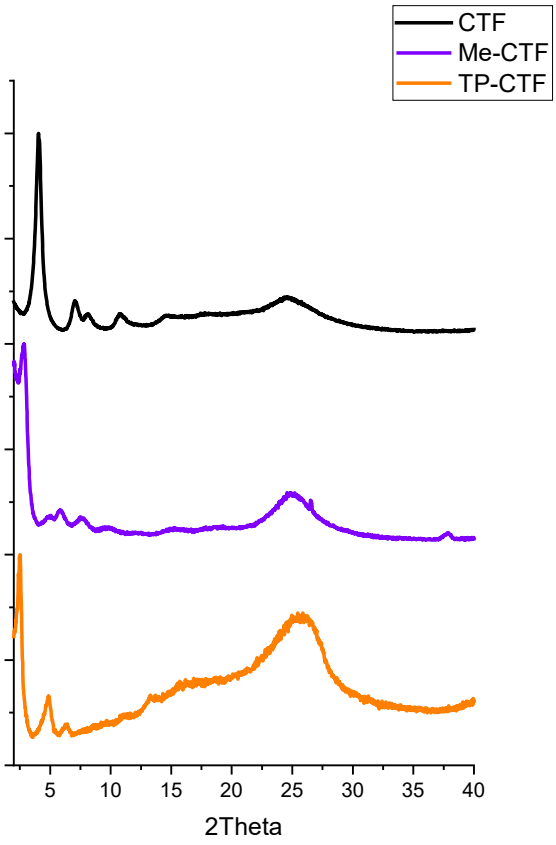


Figure S1. XRD patterns of CTF (a), Me-CTF (b) and TP-CTF (c) materials.

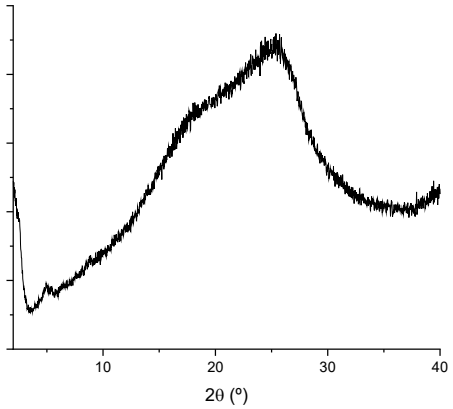


Figure S2. XRD pattern of recovered TP-CTF after 1st catalytic cycle.

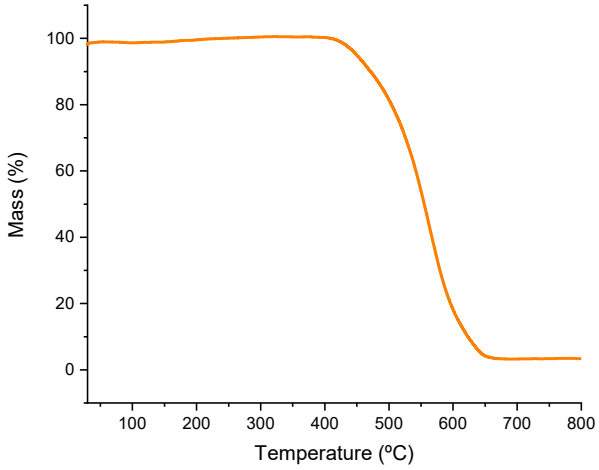


Figure S3. TG analysis of TP-CTF material.

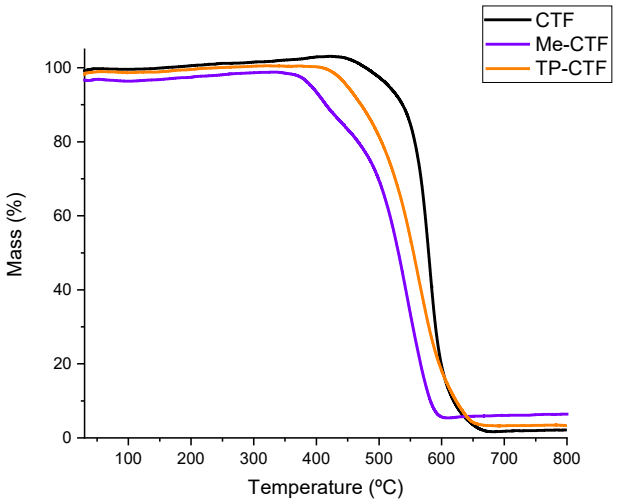


Figure S4. Comparative TG analysis of CTF (a), Me-CTF (b) and TP-CTF (c) materials.

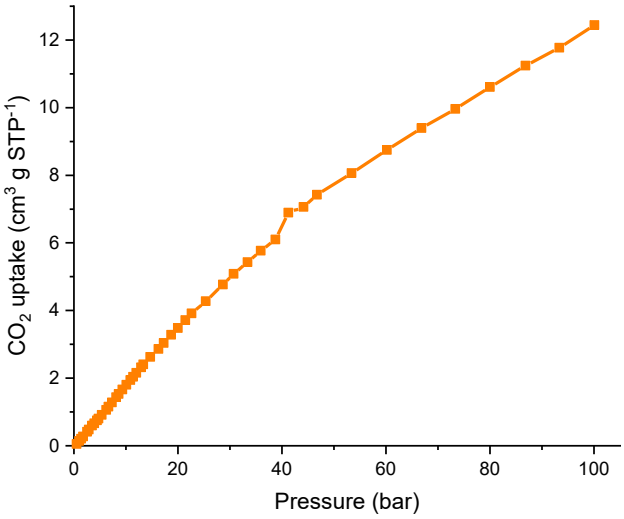


Figure S5. CO_2 adsorption isotherm of TP-CTF material.