Electronic Supplementary Material (ESI) for ChemComm.

A Porous Porphyrin Organic Polymer (PPOP) for Visible Light Triggered Hydrogen Production

Gargi Mukherjee,[a] Jayshri Thote,[a] Harshitha Barike Aiyappa,[ab] Sharath Kandambeth,[ab] Subhrashis Banerjee,[ab] Kumar Vanka[a] and Rahul Banerjee[a]*

[a]Physical/Materials Chemistry Division, CSIR- National Chemical Laboratory, Dr. HomiBhabha Road, Pune 411008, India.

[b]Academy of Scientific and Innovative Research (AcSIR), New Delhi, India.

Supporting Information

Section S-1: General Information

***General Remarks*:** Triformylphloroglucinol (**Tp**) was prepared from Phloroglucinol[1] and 5,10,15,20-Tetrakis(4-aminophenyl)-21H,23H-porphine (**Tph**) was synthesized by following the literature method[2]. All other reagents and solvents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalyticaldiffractometer for Cu K_α radiation (λ = 1.5406 Å), with a scan speed of 1° min^{-1} and a step size of 0.02° in 2θ. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm^{-1} region or using a Diamond ATR (Golden Gate). Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) or a SDT Q600 TG-DTA analyzer under N_2 atmosphere at a heating rate of 10 ºC min^{-1} within a temperature range of 30-900 °C. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope and FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. TEM images were recorded using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV.The TEM Samples were prepared by dropcasting the sample from isopropanol on copper grids TEM Window (TED PELLA, INC. 200 mesh).All gas adsorption experiments (up to 1 bar) were performed on a *Quantachrome Quadrasorb* automatic volumetric instrument. Solid state NMR (SSNMR) was taken in a Bruker 300 MHz NMR spectrometer. All measurements were carried out at room temperature on an (JobinYvon Horiba, France) using monochromatic radiation emitted by an AR-laser (514 nm) (NRS 1500 W) operating at 20 mW using 50x long distance objective. The experiment was repeated several times and at different positions to verify the consistency of the measurement.The samples were prepared simply by putting a drop of dispersion of the polymer materials in isopropanol on a clean piece of Silicon wafer.

Section S-2: Synthetic procedures

TpTph: A pyrex tube (o.d. × i.d. = 10 × 8 mm^2 and length 18 cm) is charged with Triformylphloroglucinol (**Tp**) (12.6 mg, 0.06 mmol) and tetra(*p*-amino-phenyl)porphyrin (**Tph**) (27.0 mg, 0.04 mmol) in presence of 6 M acetic acid (0.2 mL) using dichlorobenzene, tertiary butanol (1:1) as solvent combination (2 mL). This mixture was sonicated for few minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. After the reaction the material was filtered out, washed with ethanol and dried under vacuum at 150 °C for 12 hours to give purple colored powder in 85% (30 mg) isolated yield based on **Tph**. **FT-IR (powder):** 1617, 1591, 1572, 1454, 1287, 1180, 991, 964, 894, 796, 729 cm^{-1}.

Section S-3: Structure Modeling and Computational Details.

The calculation have been carried out with Turbomole 7.0 [3,4] using the SVP basis set[5] and the PBE[6] functional. Dispersion correction[7] have been included in all the geometry optimization calculations. The resolution of identity (RI)[8] along with the multipole accelerated RI (marij)[9] approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations.

The modelled geometry has been optimized computationally. The optimized geometry is provided below. Specifically, four aldehyde linkers connected to the central porphyrin ring have been considered, with further porphyrin linkages at the 2, 4 and 6 positions of the aldehyde linker are taken into account. Further, continuation of this linked structure would lead to the experimentally obtained polymer. The current model therefore provides a truncated, optimized model for the real polymeric system, thereby providing insight into the nature of the 3D structure of the linked aldehyde geometry.

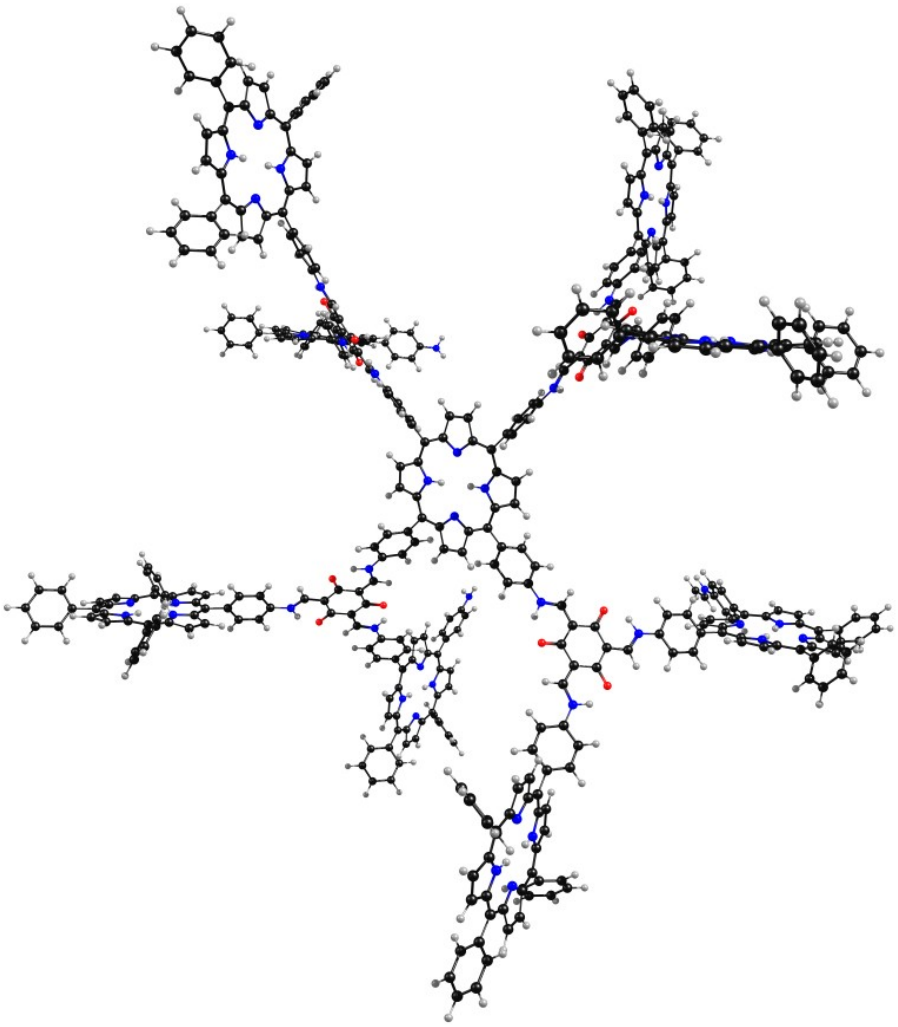

Figure S1: The optimized geometry having H-atom at the edge. The colour scheme is as follows: carbon: black, oxygen: red, nitrogen: blue, hydrogen: grey.

The optimized geometries of the structures reported in the manuscript (the atomic symbol followed by the three Cartesian coordinates, in Å).

C	23.570041	-10.029218	14.180546		C	3.701779	-17.040182	-8.378959	
C	23.536093	-8.625426	14.166991		C	3.722549	-17.059606	-9.745003	
C	22.788810	-7.947512	13.192646		C	4.899058	-17.845252	-10.123379	
C	22.062985	-8.660314	12.211705		N	5.560504	-18.310855	-9.015554	
C	22.106980	-10.072494	12.235969		C	5.264738	-18.073882	-11.477679	
C	22.853081	-10.749962	13.211639		C	6.319739	-18.912197	-11.907042	
H	24.101044	-8.051889	14.917888		C	6.777676	-19.099981	-13.260220	
H	22.770338	-6.847265	13.175154		C	7.817025	-20.008253	-13.234779	
H	21.537588	-10.636842	11.482061		C	8.025621	-20.404300	-11.865477	
H	22.870003	-11.850701	13.218180		N	7.111000	-19.706893	-11.105228	
C	-21.105764	8.002030	11.187292		C	8.980885	-21.329834	-11.385668	
C	-22.667602	10.845219	13.199821		C	9.204407	-21.638406	-10.016524	
C	-23.404847	10.139639	14.164695		N	8.612597	-21.025765	-8.942112	
C	-23.393730	8.735407	14.156370	14	C	9.153358	-21.630075	-7.836429	418
C	-22.649236	8.041668	13.190965		C	10.089550	-22.690617	-8.218007	
C	-21.903369	8.739210	12.214188		C	10.122644	-22.694661	-9.583936	
C	-21.924222	10.152019	12.233335		C	8.873015	-21.304847	-6.481723	
H	-23.974633	8.173965	14.904240		H	8.235190	-20.277677	-3.827644	
H	-22.649400	6.941175	13.177083		H	6.222692	-18.459229	-3.874482	
H	-21.339293	10.704095	11.482225		H	2.999615	-16.611254	-10.434837	
H	-22.666496	11.946153	13.202222		H	2.955543	-16.574642	-7.726227	
C	2.613212	16.529524	3.408603		H	7.062486	-19.737204	-10.078061	
C	2.741578	15.123252	3.352483		H	8.408417	-20.369228	-14.081892	
C	3.583725	14.478524	4.286966		H	6.365341	-18.582570	-14.131881	
C	4.274281	15.219126	5.250448		H	10.625585	-23.353539	-7.530358	
C	4.155399	16.626032	5.317003		H	10.691170	-23.361082	-10.241510	
C	3.312831	17.258767	4.373653		H	6.999322	-19.725038	-7.879350	
N	2.069276	14.334165	2.412450		C	-16.217553	3.274757	8.205413	
C	1.266435	14.735871	1.415779		C	-17.109193	4.350459	7.766891	
C	0.639546	13.849158	0.537937		N	-17.665821	4.999505	8.838474	
C	0.832192	12.401896	0.671562		C	-17.346695	4.639864	6.394332	
C	0.140725	11.529519	-0.288057		C	-18.296990	5.569662	5.910015	
C	-0.699676	12.062831	-1.364874		C	-18.500914	5.962684	4.538925	
C	-0.864878	13.520085	-1.447662		C	-19.538246	6.873255	4.507117	
C	-0.207424	14.434755	-0.509859		C	-19.999667	7.066115	5.857866	
C	0.316444	10.151247	-0.140921		N	-19.211226	6.273517	6.664952	
N	-0.247792	9.256477	-0.965624		C	-21.056097	7.904919	6.283024	
C	-0.178447	7.860353	-0.912070		C	-21.421238	8.134768	7.637478	
C	-0.691005	7.125767	-2.005275		N	-20.754972	7.674200	8.743854	
C	-0.644467	5.728804	-2.005777		C	-22.598350	8.919235	8.017536	
C	-0.088922	5.014218	-0.920958		H	-15.686320	2.571948	7.554656	
C	0.413645	5.759829	0.169773		H	-19.263304	6.254718	7.692250	
C	0.372384	7.157316	0.183078		H	-19.945739	7.389365	3.632396	
O	1.565770	11.917451	1.579188		H	-17.905960	5.603074	3.693736	
O	-0.357707	15.687201	-0.596550		H	-23.323772	9.364847	7.328330	
C	-1.679377	14.014360	-2.469912		C	-8.949658	-22.655557	8.005345	
N	-1.905157	15.324338	-2.647141		C	-8.180081	-21.470390	7.619308	
C	-2.688920	15.950876	-3.621529		N	-7.729961	-20.791738	8.722139	
C	-2.730253	17.363808	-3.631214		C	-7.951910	-21.110956	6.262973	

C	-3.491493	18.044998	-4.584546		C	-7.123161	-20.048906	5.832217	
C	-4.234679	17.347579	-5.564076		C	-6.928720	-19.598188	4.478100	
C	-4.187617	15.934107	-5.541347		C	-6.028347	-18.551840	4.503979	
C	-3.434208	15.240659	-4.589922		C	-5.643780	-18.330462	5.874767	
O	-1.267925	11.298559	-2.196627		N	-6.342184	-19.244609	6.635225	
H	0.955565	9.803237	0.687684		C	-4.726571	-17.365719	6.354493	
H	-2.144891	13.282184	-3.150340		C	-4.446602	-17.111666	7.726630	
H	1.082914	15.812427	1.264879		N	-5.092781	-17.667642	8.800118	
H	-0.804757	9.749253	-1.718872		C	-3.383942	-16.203166	8.162558	
H	2.149010	13.280752	2.424129		H	-9.384720	-23.390810	7.320006	
H	-1.383501	15.889446	-1.920312		H	-6.327320	-19.286248	7.663052	
H	-2.145721	17.925082	-2.885945	61	H	-5.670556	-17.962046	3.654364	465
H	-3.499625	19.145093	-4.587666		H	-7.436505	-20.019329	3.604955	
H	-4.769580	15.369610	-6.285000		H	-2.685577	-15.667372	7.510670	
H	-3.436468	14.141683	-4.599447		C	-23.293702	-11.452119	-14.324617	
H	-1.114475	7.665733	-2.866314		C	-22.439468	-12.051209	-13.384709	
H	-1.032766	5.173663	-2.872760		C	-21.781891	-11.265310	-12.426854	
H	0.833054	5.224125	1.034422		C	-21.965398	-9.864828	-12.392679	
H	0.753053	7.698732	1.060667		C	-22.826060	-9.274397	-13.344675	
H	3.697471	13.384365	4.243975		C	-23.485211	-10.061198	-14.300932	
H	4.932391	14.702108	5.964431		H	-22.279617	-13.140271	-13.399287	
H	3.191371	18.351533	4.415881		H	-21.106917	-11.732995	-11.694290	
H	1.955163	17.061130	2.707401		H	-22.985432	-8.185709	-13.318296	
C	3.680063	-2.371257	-0.911635		H	-24.158798	-9.583865	-15.029078	
C	2.976708	-1.113934	-0.906226		C	10.004186	-23.544047	-14.324628	
N	1.630157	-1.411716	-0.911311		C	11.394206	-23.347208	-14.356079	
C	1.434960	-2.776845	-0.911785		C	11.995423	-22.492003	-13.418437	
C	2.741782	-3.383425	-0.896493		C	11.212616	-21.838697	-12.455161	
C	3.554026	0.177857	-0.911107		C	9.812991	-22.027419	-12.413299	
C	2.829990	1.401444	-0.917086		C	9.220391	-22.889122	-13.363022	
C	3.489210	2.709977	-0.905983		H	13.083804	-22.327980	-13.439135	
C	2.489254	3.639954	-0.927096		H	11.682026	-21.162917	-11.724418	
C	1.232032	2.888128	-0.916578		H	8.132430	-23.052486	-13.330786	
N	1.465084	1.536415	-0.916996		H	9.525247	-24.218456	-15.050987	
C	-0.040832	3.521209	-0.921431		C	23.441561	11.512752	-14.337826	
C	-1.286321	2.849833	-0.922316		C	22.588328	12.112692	-13.397542	
C	-2.593225	3.456292	-0.910290		C	21.933105	11.327906	-12.437276	
C	-3.531337	2.444053	-0.922383		C	22.117877	9.927593	-12.400976	
C	-2.827780	1.186911	-0.912544		C	22.977625	9.336300	-13.353312	
N	-1.481236	1.484758	-0.917643		C	23.634442	10.122039	-14.311967	
C	-3.405158	-0.104802	-0.914747		H	22.427371	13.201596	-13.413798	
C	-2.681257	-1.328557	-0.917644		H	21.258848	11.796306	-11.704451	
N	-1.316143	-1.463337	-0.913774		H	23.138053	8.247765	-13.325382	
C	-1.083393	-2.815373	-0.910866		H	24.307270	9.644092	-15.040441	
C	-2.340631	-3.567051	-0.924073		C	-11.237812	23.425108	-14.369547	
C	-3.340598	-2.636848	-0.907093		C	-11.840485	22.570732	-13.432025	
C	0.189472	-3.448772	-0.911249		C	-11.058623	21.915236	-12.469470	
H	2.928377	-4.461378	-0.876131		C	-9.658592	22.100913	-12.428153	
H	4.769020	-2.476188	-0.925168		C	-9.064493	22.961760	-13.377748	
H	2.591137	4.729941	-0.949474		C	-9.847315	23.618859	-14.338692	

H	4.568986	2.890231	-0.883332	
H	-0.725292	0.786876	-0.917659	
H	-4.620506	2.548343	-0.937001	
H	-2.780202	4.534251	-0.894144	
H	-2.442234	-4.657162	-0.945329	
H	-4.420672	-2.816777	-0.887999	
H	0.874436	-0.713511	-0.914802	
C	20.094266	7.938086	-13.229090	
C	20.490922	8.141666	-11.859212	108
N	19.791956	7.226034	-11.101555	
C	18.995838	6.438624	-11.905753	
C	19.184105	6.900523	-13.257441	
C	21.418225	9.093642	-11.376328	
C	21.726330	9.312406	-10.006264	
C	22.784103	10.227174	-9.570193	
C	22.778676	10.190258	-8.204359	
C	21.715793	9.255250	-7.826366	
N	21.111500	8.718737	-8.934122	
C	21.388631	8.972095	-6.472699	
C	20.445171	8.008882	-6.045613	
C	20.012461	7.765787	-4.693329	
C	19.087897	6.740735	-4.721240	
C	18.930267	6.322897	-6.090834	
N	19.755667	7.125426	-6.849042	
C	18.091272	5.290611	-6.574214	
C	17.897109	4.971533	-7.946749	
N	18.393590	5.669619	-9.017067	
C	17.927834	5.012410	-10.127248	
C	17.142680	3.834169	-9.753352	
C	17.124161	3.807761	-8.387345	
C	18.156375	5.383028	-11.480095	
H	18.665762	6.491661	-14.130175	
H	20.456004	8.531392	-14.074597	
H	23.442157	10.722903	-7.514628	
H	23.452389	10.796140	-10.225561	
H	19.808564	7.103313	-7.876126	
H	18.539516	6.316585	-3.874548	
H	20.358194	8.328644	-3.820769	
H	16.694329	3.113976	-10.445987	
H	16.659597	3.058574	-7.737450	
H	19.822684	7.174658	-10.074537	
C	-16.435964	2.394777	3.440602	
C	-15.027690	2.508168	3.408791	
C	-14.388146	3.325693	4.368083	
C	-15.136418	4.009893	5.330155	
C	-16.545807	3.909731	5.369591	
C	-17.172860	3.088493	4.404079	
N	-14.232161	1.846005	2.466942	
C	-14.627924	1.058048	1.456651	
C	-13.736594	0.450295	0.569992	
H	-12.929210	22.409089	-13.452177	
H	-11.529129	21.240183	-11.738756	
H	-7.976196	23.122854	-13.345895	
C	3.015492	-16.051514	-14.571209	
C	3.014505	-17.454039	-14.501016	
C	3.744504	-18.110796	-13.499190	
C	4.487173	-17.376675	-12.547325	
C	4.479267	-15.966081	-12.628986	
C	3.750653	-15.310092	-13.632065	512
H	2.435117	-18.042964	-15.228542	
H	3.734055	-19.209606	-13.436768	
H	5.061445	-15.386187	-11.896937	
H	3.760890	-14.210430	-13.682780	
C	15.391356	3.877315	-13.638826	
C	16.132267	3.144669	-14.580360	
C	17.534817	3.142731	-14.510432	
C	18.192114	3.869392	-13.506527	
C	17.458531	4.609606	-12.552339	
C	16.047907	4.602590	-12.633676	
H	18.123332	2.565165	-15.239799	
H	19.290930	3.857950	-13.444152	
H	15.468362	5.182533	-11.899586	
H	14.291668	3.888178	-13.689228	
C	-2.861397	16.127910	-14.591289	
C	-2.858468	17.530124	-14.515649	
C	-3.590088	18.184021	-13.513099	
C	-4.336013	17.447197	-12.565868	
C	-4.330040	16.036977	-12.652957	
C	-3.599987	15.383851	-13.656933	
H	-2.276242	18.121066	-15.239314	
H	-3.578329	19.282568	-13.446345	
H	-4.914692	15.455042	-11.924492	
H	-3.611644	14.284403	-13.712002	
C	-15.977515	-3.090240	-14.590926	
C	-17.380030	-3.087067	-14.520721	
C	-18.037591	-3.810783	-13.514874	
C	-17.304229	-4.549080	-12.559127	
C	-15.893660	-4.543249	-12.640607	
C	-15.236850	-3.820952	-13.647711	
H	-17.968328	-2.510819	-15.251244	
H	-19.136361	-3.798667	-13.452134	
H	-15.314520	-5.121777	-11.905055	
H	-14.137201	-3.832501	-13.698187	
C	23.561749	9.836481	-3.453837	
C	23.382704	11.226452	-3.365178	
C	22.553300	11.879970	-4.291087	
C	21.907947	11.149254	-5.299513	
C	22.079088	9.750348	-5.399272	
C	22.914593	9.104782	-4.460581	
C	-23.291020	9.926240	3.178023	

C	-12.291076	0.651650	0.706418	
C	-11.414497	-0.012682	-0.268510	
C	-11.942118	-0.840448	-1.358128	
C	-13.397782	-1.019142	-1.439847	
C	-14.316408	-0.383312	-0.491204	
C	-10.038127	0.176198	-0.122975	155
N	-9.139065	-0.363232	-0.960115	
C	-7.743843	-0.278705	-0.907983	
C	-7.004279	-0.775099	-2.005649	
C	-5.607825	-0.716372	-2.006014	
C	-4.898159	-0.164993	-0.915736	
C	-5.648626	0.325547	0.177056	
C	-7.045825	0.271645	0.190399	
O	-11.811337	1.371123	1.627805	
O	-15.568106	-0.540861	-0.579334	
C	-13.887255	-1.826062	-2.470550	
N	-15.196000	-2.059457	-2.645961	
C	-15.820633	-2.843617	-3.620725	
C	-17.233459	-2.887404	-3.629871	
C	-17.913523	-3.651882	-4.581197	
C	-17.214815	-4.395819	-5.559307	
C	-15.801454	-4.344988	-5.538091	
C	-15.109088	-3.588415	-4.588494	
O	-11.174184	-1.386751	-2.200826	
H	-9.694847	0.804452	0.715728	
H	-13.153525	-2.278510	-3.158168	
H	-15.703304	0.871814	1.300797	
H	-9.627366	-0.914455	-1.720292	
H	-13.179138	1.929191	2.483615	
H	-15.762107	-1.547780	-1.911960	
H	-17.795300	-2.302621	-2.885199	
H	-19.013589	-3.662628	-4.583435	
H	-15.236216	-4.927823	-6.280500	
H	-14.010116	-3.589311	-4.597690	
H	-7.540127	-1.198434	-2.869267	
H	-5.048145	-1.096407	-2.873671	
H	-5.117503	0.741613	1.046486	
H	-7.590144	0.640765	1.071110	
H	-13.292104	3.426311	4.344998	
H	-14.624015	4.649599	6.063863	
H	-18.267590	2.980772	4.425711	
H	-16.963691	1.755491	2.719519	
C	-6.625592	19.171254	-13.276816	
C	-6.168970	18.981278	-11.923590	
N	-6.960281	19.775357	-11.121236	
C	-7.873526	20.474771	-11.881347	
C	-7.664236	20.080285	-13.251070	
C	-5.114445	18.141932	-11.495112	
C	-4.749038	17.911605	-10.141121	
C	-3.573130	17.124765	-9.763451	

C	-23.288692	8.523621	3.245620	
C	-22.564690	7.867017	4.251898	
C	-21.830976	8.601021	5.211044	
C	-21.842755	10.011858	5.131851	
C	-22.565448	10.667745	4.124534	
H	-23.860598	7.934572	2.512180	559
H	-22.572364	6.768044	4.311552	
H	-21.267058	10.592061	5.868819	
H	-22.557368	11.767527	4.075868	
H	22.403128	12.968542	-4.225423	
H	21.251602	11.659276	-6.020727	
H	23.063130	8.016897	-4.536901	
H	24.215721	9.316883	-2.736868	
C	-9.949590	-23.390154	3.174429	
C	-8.547131	-23.374774	3.243264	
C	-7.897862	-22.636114	4.243773	
C	-8.639147	-21.900403	5.195710	
C	-10.049792	-21.925505	5.115356	
C	-10.698432	-22.662985	4.113944	
C	-10.980882	23.369497	-3.395371	
C	-11.632917	22.540289	-4.322484	
C	-10.900456	21.893848	-5.328940	
C	-9.501085	22.063519	-5.425562	
C	-8.857077	22.898906	-4.485620	
C	-9.590520	23.547123	-3.480849	
H	-12.721747	22.390934	-4.259087	
H	-11.409580	21.237768	-6.051013	
H	-7.768891	23.046565	-4.559429	
H	-7.952372	-23.948242	2.515678	
H	-6.798945	-22.634002	4.304775	
H	-10.635678	-21.349007	5.847138	
H	-11.798203	-22.665651	4.064723	
C	23.512215	-9.848415	3.187038	
C	23.500318	-8.445804	3.253395	
C	22.764218	-7.792962	4.253445	
C	22.027638	-8.530788	5.207326	
C	22.049208	-9.941593	5.129504	
C	22.784142	-10.593793	4.128589	
C	-23.211735	-11.149194	-3.352081	
C	-22.382132	-11.802685	-4.277809	
C	-21.740073	-11.072550	-5.288736	
C	-21.914773	-9.674265	-5.391200	
C	-22.750383	-9.028699	-4.452574	
C	-23.394179	-9.759824	-3.443282	
H	-22.228891	-12.890708	-4.209836	
H	-21.083559	-11.582524	-6.009814	
H	-22.901631	-7.941308	-4.530877	
H	-24.047946	-9.240263	-2.726044	
H	24.074395	-7.853755	2.524123	
H	22.764548	-6.693943	4.312420	

C	-3.551554	17.105439	-8.397551	
C	-4.715712	17.879787	-7.960438	
N	-5.409673	18.377316	-9.032909	202
C	-5.038544	18.074587	-6.588750	
C	-6.071915	18.914004	-6.108331	
C	-6.493195	19.071874	-4.739824	
C	-7.518376	19.996411	-4.714593	
C	-7.758200	20.428922	-6.067492	
N	-6.872643	19.739317	-6.868666	
C	-8.720685	21.372142	-6.496926	
C	-9.000687	21.698573	-7.851460	
N	-8.460702	21.094132	-8.957516	
C	-9.051348	21.708603	-10.031591	
C	-9.967994	22.765991	-9.598372	
C	-9.935085	22.760879	-8.232432	
C	-8.827772	21.401073	-11.401008	
H	-8.254421	20.442792	-14.098350	
H	-6.212647	18.654784	-14.148767	
H	-2.805288	16.639280	-7.745207	
H	-2.851187	16.675563	-10.453902	
H	-6.847977	19.792433	-7.895705	
H	-8.083518	20.342206	-3.843541	
H	-6.071280	18.523483	-3.891988	
H	-10.535334	23.433907	-10.255454	
H	-10.470094	23.424310	-7.544471	
H	-6.912432	19.804596	-10.094008	
C	-0.223253	-7.084489	0.198085	
C	0.334155	-7.788758	-0.893043	
C	0.848298	-7.054746	-1.986044	
C	0.798716	-5.657851	-1.989307	
C	0.238064	-4.941978	-0.907758	
C	-0.267813	-5.687090	0.181907	
N	0.408440	-9.184448	-0.943088	
C	-0.152667	-10.079873	-0.116317	
C	0.026083	-11.457579	-0.262403	
C	0.865731	-11.989586	-1.340555	
C	1.030692	-13.446536	-1.425326	
C	0.373576	-14.362270	-0.488023	
C	-0.471097	-13.778078	0.561882	
C	-0.662213	-12.331271	0.699000	
C	1.843559	-13.940037	-2.449168	
N	2.066958	-15.250194	-2.627620	
C	2.848031	-15.878233	-3.602764	
C	2.886179	-17.291252	-3.611730	
C	3.644748	-17.974749	-4.565394	
C	4.388198	-17.279489	-5.546269	
C	4.343945	-15.865907	-5.524615	
C	3.593426	-15.170149	-4.572610	
O	1.433013	-11.224304	-2.172138	
O	-1.392188	-11.847613	1.609816	249

H	21.471738	-10.524722	5.862738	
H	22.784010	-11.693642	4.081243	
C	9.749205	-23.477850	-3.465872	606
C	11.139081	-23.296334	-3.380829	
C	11.788674	-22.465624	-4.308300	
C	11.054133	-21.821330	-5.314644	
C	9.655197	-21.994794	-5.410742	
C	9.013645	-22.831783	-4.470557	
C	10.093136	23.462298	3.191604	
C	8.691313	23.458638	3.273809	
C	8.045279	22.714676	4.272355	
C	8.789801	21.963172	5.209058	
C	10.199592	21.976207	5.115683	
C	10.844786	22.718221	4.115503	
H	8.094774	24.045106	2.558217	
H	6.946981	22.720529	4.343759	
H	10.787188	21.386727	5.835733	
H	11.943958	22.711505	4.055045	
H	12.877148	-22.313388	-4.245416	
H	11.561179	-21.163968	-6.037020	
H	7.925826	-22.982382	-4.543913	
H	9.232679	-24.132811	-2.747540	
C	19.740511	-7.027536	13.014959	
C	20.196610	-7.135810	11.653262	
N	19.389473	-6.313637	10.896588	
C	18.465440	-5.672302	11.694750	
C	18.684075	-6.138360	13.039530	
C	21.261868	-7.937235	11.177521	
C	21.611405	-8.107183	9.811098	
C	22.791633	-8.861909	9.383102	
C	17.247124	-4.380554	9.912975	
C	16.339953	-3.296578	9.532308	
C	17.494265	-4.733080	11.269418	
H	18.085064	-5.837787	13.904426	
H	20.161807	-7.585394	13.856905	
H	23.534333	-9.322880	10.043125	
H	15.807546	-2.632976	10.221999	
H	19.430165	-6.235176	9.871807	
C	3.617005	16.215141	9.522958	
C	4.678402	17.151267	9.899875	
C	5.026307	17.409125	11.253348	
C	5.950935	18.387524	11.685995	
C	6.386389	18.625116	13.038618	
C	7.276895	19.679854	13.018903	
C	7.412743	20.119597	11.653583	
N	6.607796	19.301561	10.889773	
C	8.216024	21.182983	11.179795	
C	8.389183	21.529246	9.812071	
C	9.145000	22.708607	9.383629	
H	2.977255	15.655939	10.214117	653

C	-1.098631	-14.666761	1.437735	
N	-1.899207	-14.267765	2.436781	
C	-2.575462	-15.059918	3.371866	
C	-3.404890	-14.416490	4.318282	
C	-4.098571	-15.160614	5.276917	
C	-3.995741	-16.569552	5.326528	
C	-3.165262	-17.200584	4.371341	
C	-2.462866	-16.468011	3.410728	
O	0.522623	-15.614796	-0.577421	
H	2.309345	-13.207719	-3.129371	
H	-0.917293	-15.743103	1.282885	
H	-0.791707	-9.732578	0.712609	
H	1.544533	-15.814450	-1.900112	
H	0.966432	-9.677356	-1.695654	
H	-1.976344	-13.214571	2.454039	
H	-3.505997	-13.320593	4.289088	
H	-4.746089	-14.644945	6.001419	
H	-3.055732	-18.294970	4.400399	
H	-1.815507	-16.998773	2.699059	
H	2.301040	-17.850495	-2.865441	
H	3.650300	-19.074862	-4.567748	
H	4.925847	-15.303232	-6.269696	
H	3.597954	-14.071212	-4.582854	
H	1.275888	-7.594834	-2.844886	
H	1.189131	-5.103544	-2.855895	
H	-0.692460	-5.151116	1.044007	
H	-0.606840	-7.624950	1.074988	
C	22.783651	-8.837241	8.016955	
C	21.599771	-8.066067	7.630214	
N	20.922321	-7.613121	8.732665	
C	21.240164	-7.839828	6.273581	
C	20.179097	-7.010659	5.841359	
C	19.727963	-6.818735	4.486982	
C	18.681893	-5.917914	4.511515	
C	18.461314	-5.530534	5.881645	
N	19.375741	-6.227450	6.643033	
C	17.496826	-4.612625	6.360195	
C	17.244601	-4.328742	7.731727	
N	17.802234	-4.971723	8.806287	
C	16.336783	-3.264787	8.165757	
H	23.517896	-9.274457	7.331889	
H	19.417673	-6.210469	7.670811	
H	18.091999	-5.561399	3.661530	
H	20.148544	-7.328457	3.614743	
H	15.799808	-2.568731	7.512397	
C	-19.854498	-7.682008	-4.691909	
C	-20.286723	-7.929692	-6.043483	296
N	-19.600091	-7.046096	-6.849200	
C	-18.776989	-6.239308	-6.092966	
C	-18.933204	-6.654123	-4.722292	

H	6.546007	19.337614	9.863511	
H	7.814278	20.114300	13.867395	
H	6.062679	18.041488	13.905941	
H	9.609022	23.449382	10.043787	
C	-18.566564	6.167994	13.068296	
C	-18.340256	5.704079	11.723956	
N	-19.249552	6.358053	10.919358	
C	-20.054539	7.187211	11.670944	
C	-19.612511	7.069158	13.036630	
C	-17.376089	4.756479	11.302631	
C	-17.124335	4.401546	9.947670	
C	-16.228024	3.306260	9.572054	
C	-21.444280	8.176116	9.818236	
C	-22.613279	8.944515	9.383394	
H	-20.036151	7.628043	13.876770	
H	-17.979666	5.857882	13.938278	
H	-15.708493	2.634489	10.263492	
H	-23.354113	9.414604	10.039030	
H	-19.281112	6.282700	9.894031	
C	-7.154642	-19.606664	13.005308	
C	-7.258953	-20.063460	11.643479	
N	-6.437021	-19.254611	10.888464	
C	-5.799493	-18.328958	11.687762	
C	-6.268086	-18.548113	13.031589	
C	-8.056933	-21.130804	11.166637	
C	-8.224065	-21.481327	9.800163	
C	-8.975928	-22.663227	9.371505	
C	-4.505169	-17.110828	9.907788	
C	-3.420244	-16.203905	9.529053	
C	-4.860892	-17.356579	11.263745	
H	-5.970879	-17.948112	13.897019	
H	-7.713199	-20.029220	13.846126	
H	-9.436206	-23.406617	10.031092	
H	-2.759031	-15.670179	10.219943	
H	-6.355675	-19.294939	9.863929	
C	10.293627	23.514169	14.174866	
C	8.889918	23.483483	14.152966	
C	8.215990	22.728029	13.181892	
C	8.933428	21.990541	12.213245	
C	10.345474	22.031285	12.245612	
C	11.018721	22.785787	13.217811	
H	8.313145	24.057757	14.894166	
H	7.115824	22.713459	13.157203	
H	10.913351	21.453930	11.500492	
H	12.119410	22.800827	13.230360	
C	-10.869046	-22.727484	13.197188	
C	-10.148171	-23.442216	14.167643	700
C	-8.744432	-23.404911	14.156330	
C	-8.066736	-22.656646	13.182595	
C	-8.779701	-21.933133	12.200077	

C	-21.227688	-8.896779	-6.467312	
C	-21.555771	-9.184135	-7.819829	
C	-22.617686	-10.121754	-8.193919	
C	-22.625843	-10.160997	-9.559773	
C	-21.570087	-9.245678	-9.999588	
N	-20.954187	-8.648976	-8.929683	
C	-21.263977	-9.029489	-11.370430	
C	-20.337001	-8.078725	-11.856271	
C	-19.941127	-7.878319	-13.226819	
C	-19.030377	-6.841372	-13.258103	
C	-18.841333	-6.376291	-11.907524	
N	-19.637244	-7.161695	-11.101161	
C	-18.002356	-5.319179	-11.484758	
C	-17.774826	-4.943106	-10.133239	
N	-18.240695	-5.595978	-9.020597	
C	-17.745530	-4.892857	-7.952948	
C	-16.973220	-3.730366	-8.397805	
C	-16.990818	-3.762613	-9.763739	
C	-17.940183	-5.206665	-6.579281	
H	-18.385948	-6.226596	-3.876535	
H	-20.198227	-8.243945	-3.817995	
H	-23.294563	-10.731956	-10.212724	
H	-23.278742	-10.654361	-7.501893	
H	-19.667897	-7.108245	-10.074269	
H	-18.512464	-6.434794	-14.132219	
H	-20.303959	-8.473214	-14.070671	
H	-16.509464	-2.978124	-7.750800	
H	-16.542497	-3.044980	-10.458982	
H	-19.652576	-7.026276	-7.876441	
C	16.589497	-2.361431	3.409714	
C	15.181784	-2.479360	3.372390	
C	14.541909	-3.306870	4.322830	
C	15.289027	-3.994061	5.283739	
C	16.697661	-3.886440	5.331349	
C	17.325142	-3.057439	4.372709	
N	14.385978	-1.810802	2.434817	
C	14.779819	-1.010448	1.433482	
C	13.887168	-0.393450	0.554153	
C	12.441822	-0.596212	0.689194	
C	11.564334	0.080963	-0.276635	
C	12.091149	0.919961	-1.358008	
C	13.546915	1.097922	-1.439635	
C	14.466111	0.452520	-0.497659	
C	10.188078	-0.107890	-0.131035	343
N	9.287817	0.440892	-0.960891	
C	7.892607	0.355579	-0.907372	
C	7.151433	0.852045	-2.003849	
C	5.755077	0.791631	-2.003017	
C	5.046980	0.238644	-0.912525	
C	5.798841	-0.251443	0.179365	
C	-10.191798	-21.980348	12.222177	
H	-8.170854	-23.967942	14.908627	
H	-6.966503	-22.635444	13.167001	
H	-10.756288	-21.412567	11.467199	
H	-11.969733	-22.746920	13.202090	
N	-2.405994	-14.218569	15.393163	
C	-2.965308	-14.972264	14.376543	
C	-3.723668	-14.362676	13.345292	
C	-4.325607	-15.132985	12.347284	
C	-4.210827	-16.542498	12.328490	
C	-3.454998	-17.145093	13.360695	
C	-2.841544	-16.384556	14.359348	
H	-1.654882	-14.647455	15.933433	
H	-3.846928	-13.267879	13.339222	
H	-4.915703	-14.635519	11.562685	
H	-3.330357	-18.238687	13.362928	
H	-2.248886	-16.885450	15.141429	
N	14.364665	-2.266304	15.398272	
C	15.116348	-2.828261	14.381544	
C	14.504415	-3.587469	13.352322	
C	15.272600	-4.192208	12.354342	
C	16.682237	-4.079462	12.333562	
C	17.287150	-3.322602	13.363632	
C	16.528777	-2.706441	14.362284	
H	13.369037	-2.131127	15.223282	
H	13.409453	-3.709127	13.347778	
H	14.773240	-4.782753	11.571336	
H	18.380883	-3.199387	13.364196	
H	17.031569	-2.113217	15.142685	
C	3.130069	15.032365	14.331021	
C	3.969170	14.423661	13.383678	
C	4.583078	15.194864	12.385797	
C	4.371147	16.590094	12.318888	
C	3.526569	17.190579	13.279038	
C	2.910355	16.418205	14.274926	
H	4.151628	13.338790	13.423907	
H	5.245513	14.719837	11.646475	
H	3.345183	18.274969	13.227967	
H	2.248492	16.902477	15.009270	
C	-16.442749	2.685488	14.381368	
C	-15.030336	2.793624	14.401782	
C	-14.409141	3.564894	13.387044	
C	-15.164046	4.192133	12.395003	
C	-16.574664	4.090888	12.367781	747
C	-17.187303	3.326535	13.386161	
N	-14.230342	2.182260	15.360894	
C	-14.619551	1.390851	16.426689	
C	-13.782724	0.807801	17.316451	
H	-15.707184	1.252336	16.519912	
H	-13.224838	2.331085	15.253644	

C	7.196094	-0.195921	0.191495	
O	11.962555	-1.326776	1.601940	
O	15.717548	0.612143	-0.584544	
C	14.035872	1.912246	-2.464631	
N	15.344606	2.146714	-2.639889	
C	15.969385	2.932638	-3.613122	
C	17.382279	2.977035	-3.621228	
C	18.062756	3.740937	-4.572730	
C	17.364642	4.483760	-5.551966	
C	15.951268	4.433541	-5.531068	
C	15.258387	3.677459	-4.581274	
O	11.322559	1.475791	-2.193824	
H	9.845981	-0.745282	0.701232	
H	13.301149	2.369315	-3.148136	
H	15.854719	-0.820405	1.279206	
H	9.774911	0.998836	-1.716782	
H	13.333576	-1.896242	2.451310	
H	15.911169	1.630568	-1.909510	
H	17.943831	2.392512	-2.876206	
H	19.162823	3.751421	-4.574757	
H	15.386473	5.015406	-6.274519	
H	14.159454	3.677574	-4.591161	
H	7.685852	1.276407	-2.867793	
H	5.194479	1.171853	-2.869810	
H	5.269000	-0.667623	1.049497	
H	7.741905	-0.563842	1.071750	
H	13.446344	-3.411727	4.294751	
H	14.776279	-4.640315	6.011403	
H	18.419238	-2.944483	4.400566	
H	17.117431	-1.715616	2.694546	
C	6.175074	18.624412	4.502942	
C	5.793702	18.393941	5.872884	
N	6.491426	19.303805	6.638243	
C	7.272261	20.112381	5.839478	
C	7.075324	19.671068	4.482524	
C	4.883099	17.420296	6.348662	
C	4.611646	17.156974	7.719871	
C	3.572798	16.221053	8.157236	
N	5.249154	17.724711	8.792502	
N	7.892043	20.841560	8.734664	
C	8.341175	21.521298	7.631554	390
C	9.116208	22.702829	8.017899	
C	8.105497	21.169009	6.274902	
H	7.582196	20.097684	3.611505	
H	5.815481	18.039518	3.650759	
H	2.886653	15.668855	7.506271	
H	9.552284	23.437728	7.332594	
H	6.471787	19.339666	7.666124	
C	6.644611	-19.006903	-4.722755	
C	6.223233	-18.848220	-6.091195	
H	-13.312339	3.672966	13.387080	
H	-14.654819	4.788917	11.623540	
H	-18.282048	3.214145	13.382406	
H	-16.970962	2.088393	15.137103	
H	-23.810754	-12.069236	-15.075299	
H	-15.461526	-2.522322	-15.380099	
H	12.008943	-23.860817	-15.111071	
H	2.442633	-15.536159	-15.357197	
H	-11.851781	23.940545	-15.123856	
H	-9.367181	24.292545	-15.064907	
H	-2.287357	15.614760	-15.377904	
H	23.956672	12.128999	-15.090466	
H	15.616468	2.574505	-15.368050	
H	-10.680249	-24.028401	14.932351	
H	-2.272335	-13.222847	15.217771	
H	-10.459038	-23.969404	2.389201	
H	-23.716251	-11.722611	-2.559580	
H	24.155399	-10.561427	14.945810	
H	14.795169	-1.514272	15.936010	
H	24.089356	-10.360668	2.402125	
H	11.715940	-23.802591	-2.591880	
H	-23.988426	10.684137	14.922638	
H	-12.688758	0.923141	17.255490	
H	-14.188390	0.195795	18.131739	
H	-23.858722	10.441475	2.388200	
H	-11.556158	23.877612	-2.606526	
H	-9.072023	24.200682	-2.762696	
H	10.822532	24.106382	14.937136	
H	2.646777	14.426705	15.112859	
H	23.889996	11.800318	-2.574766	
H	10.600009	24.045769	2.408013	784

N	7.023761	-19.673139	-6.852174	
C	7.909643	-20.362864	-6.051575	
C	7.669873	-19.931377	-4.698356	
C	5.190149	-18.008307	-6.571100	
C	4.866695	-17.813763	-7.942648	404

Section S-4: Powder X-Ray Diffraction Analysis (PXRD)

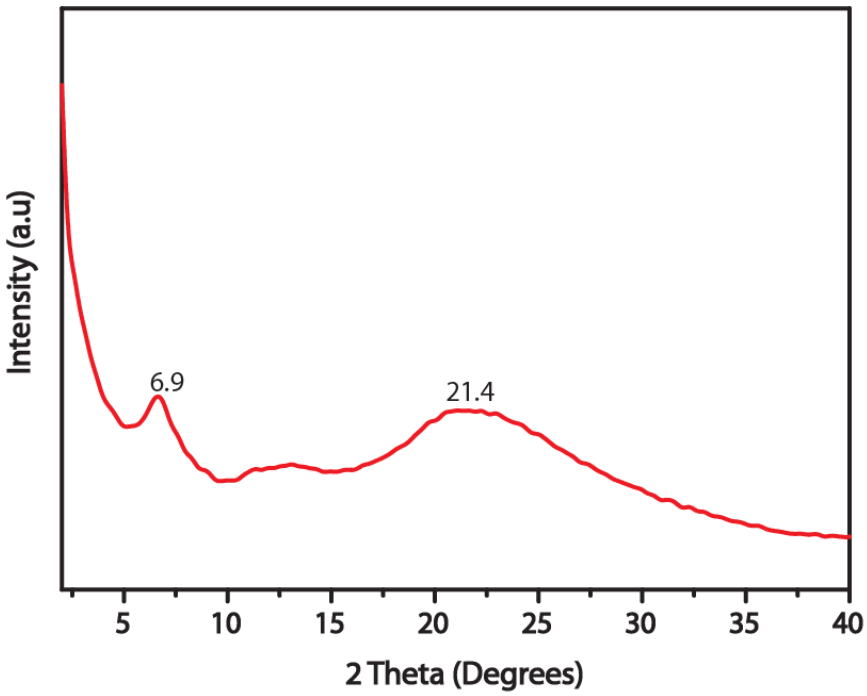

Figure S2: PXRD pattern of As-synthesized **TpTph** shows amorphous character.

Section S-5: FT-IR Spectra

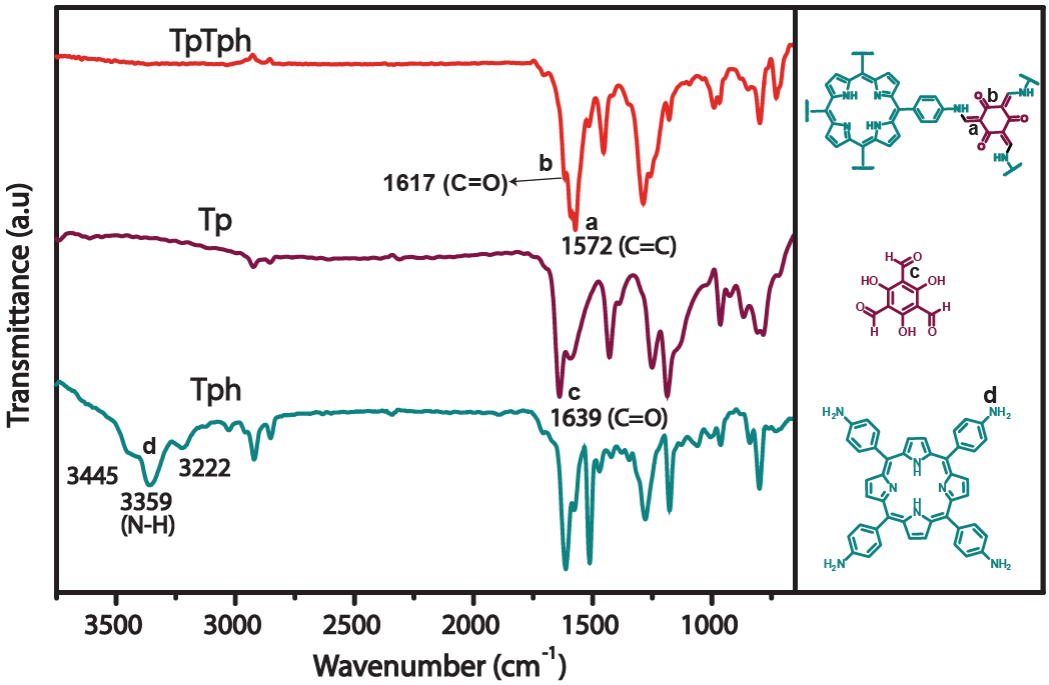

Figure S3: FT-IR spectra of **TpTph** (red), 1,3,5-triformylphloroglucinol (**Tp**) (red accent), and 5,10,15,20-Tetrakis(4-aminophenyl)-21H,23H-porphine (**Tph**) (green).

Section S-6: ^{13}C CP/MAS NMR Spectra

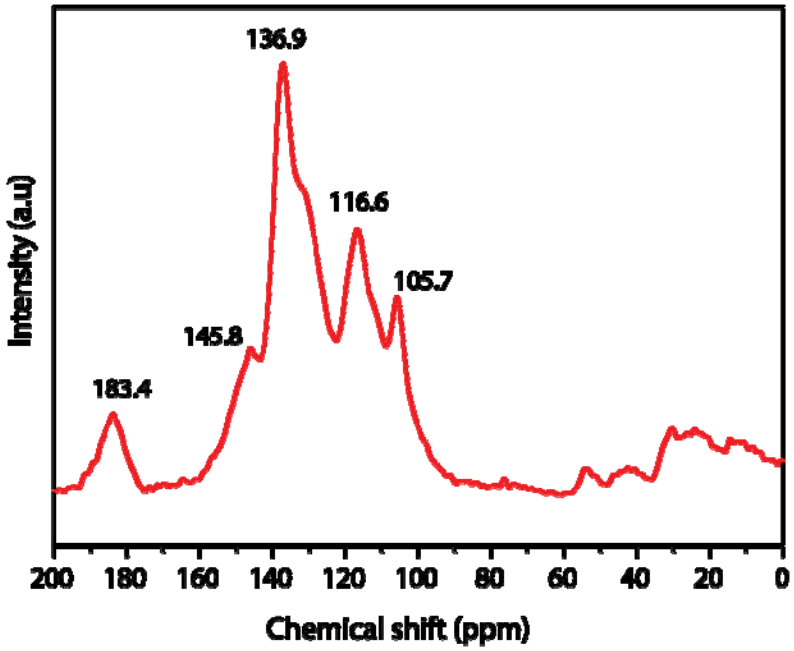

Figure S4: ^{13}C CP-MAS spectrum of **TpTph**.

Section S-7: Gas Adsorption Studies of TpTph

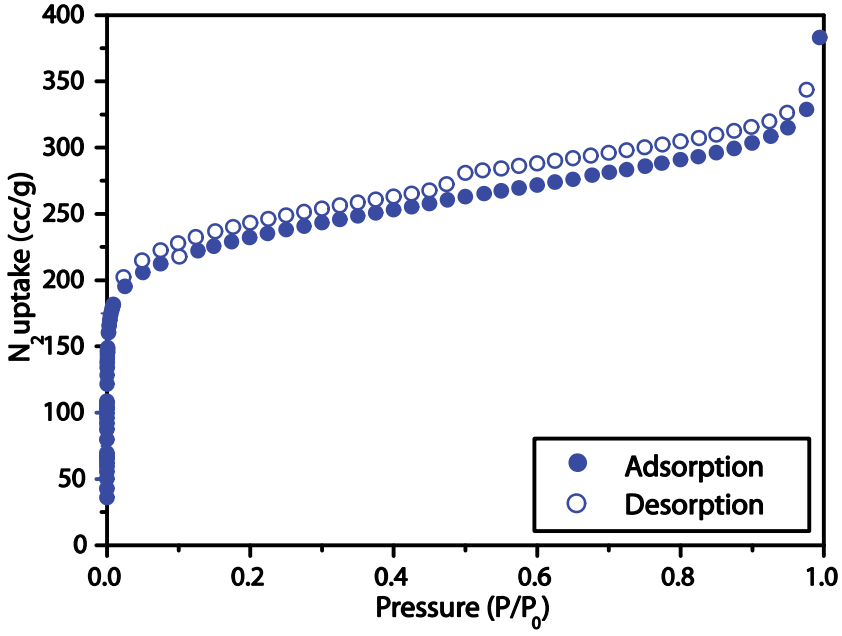

Figure S5: N_2 adsorption isotherm of **TpTph.**

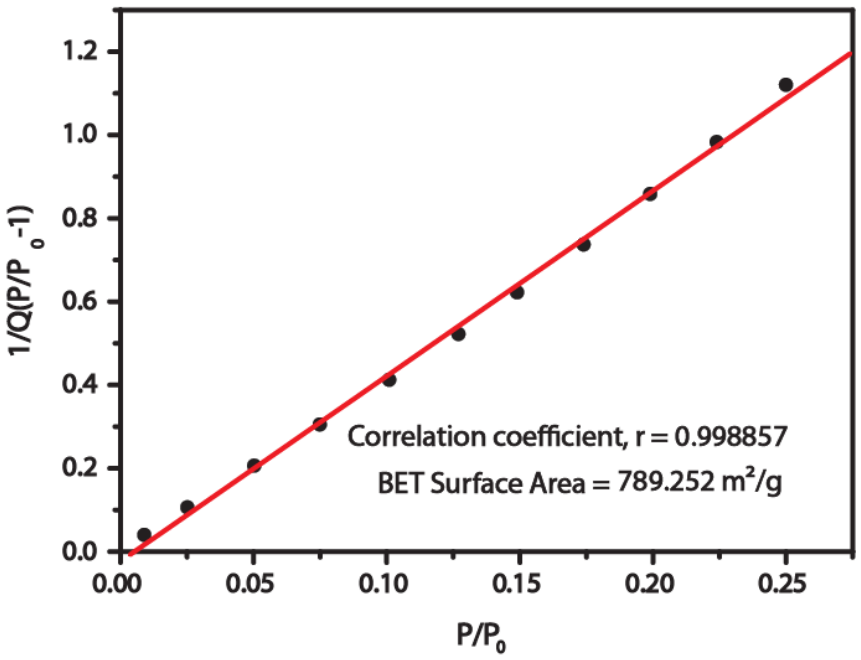

Figure S6: Langmuir surface area plot for **TpTph** calculated from the isotherm.

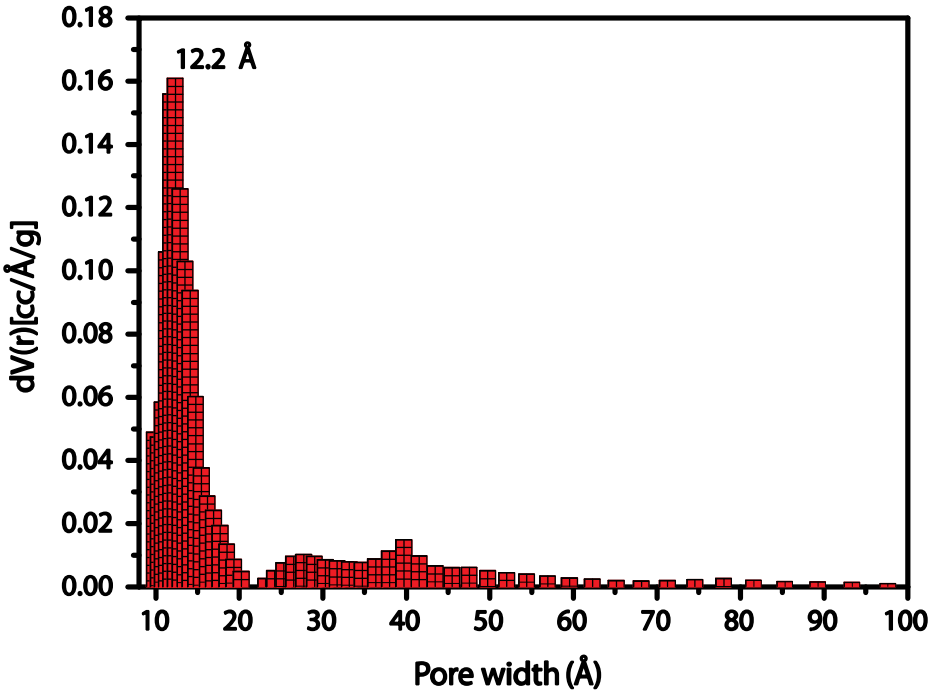

Figure S7: Pore size distribution of **TpTph.**

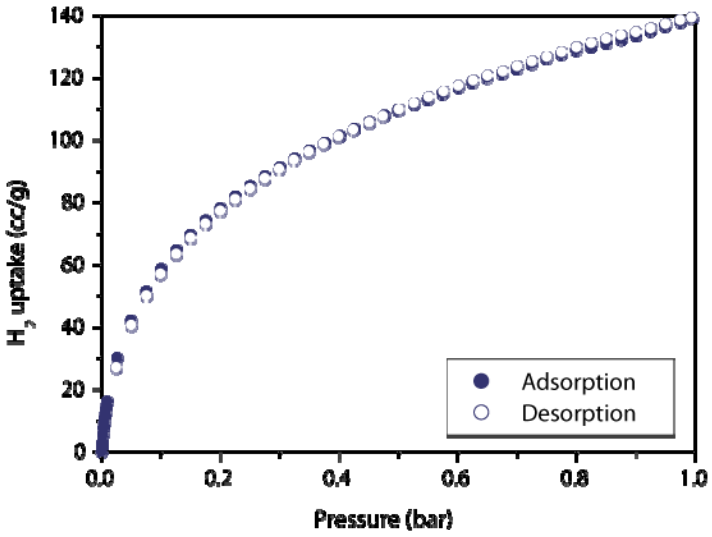

Figure S8: Hydrogen adsorption isotherm of **TpTph** at 77K.

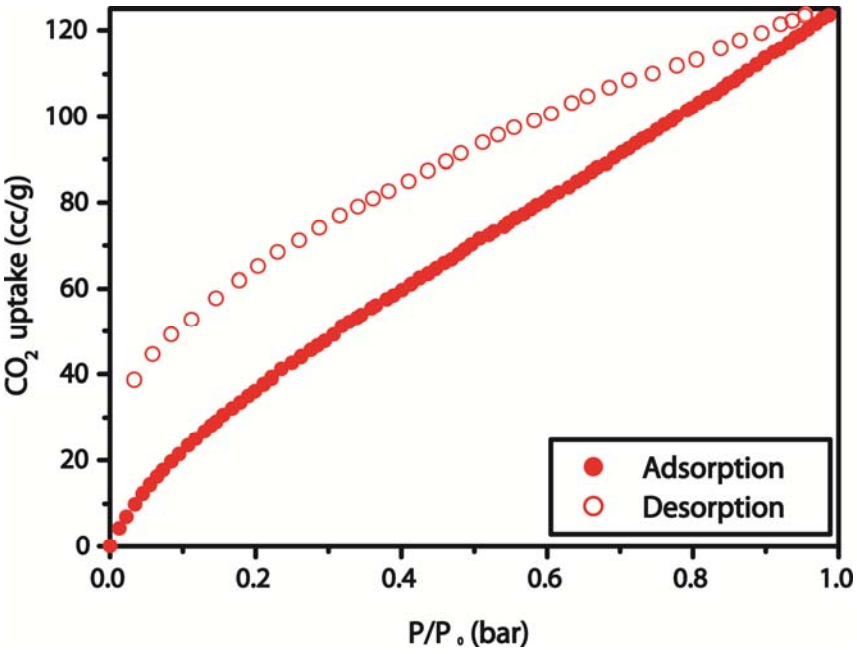

Figure S9: Carbon dioxide adsorption isotherms of **TpTph (Red)** at 273 K.

Section S-8: Vapor Adsorption Studies of TpTph

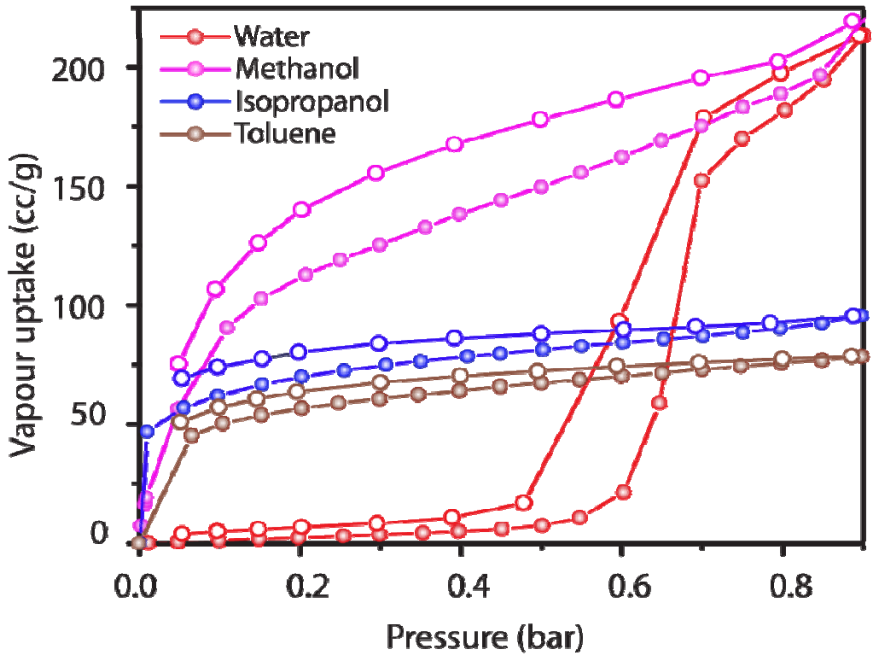

Figure S10: Water and vapor adsorption isotherms of **TpTph (Red)**.

Section S-9:Thermogravimetric Analysis (TGA)

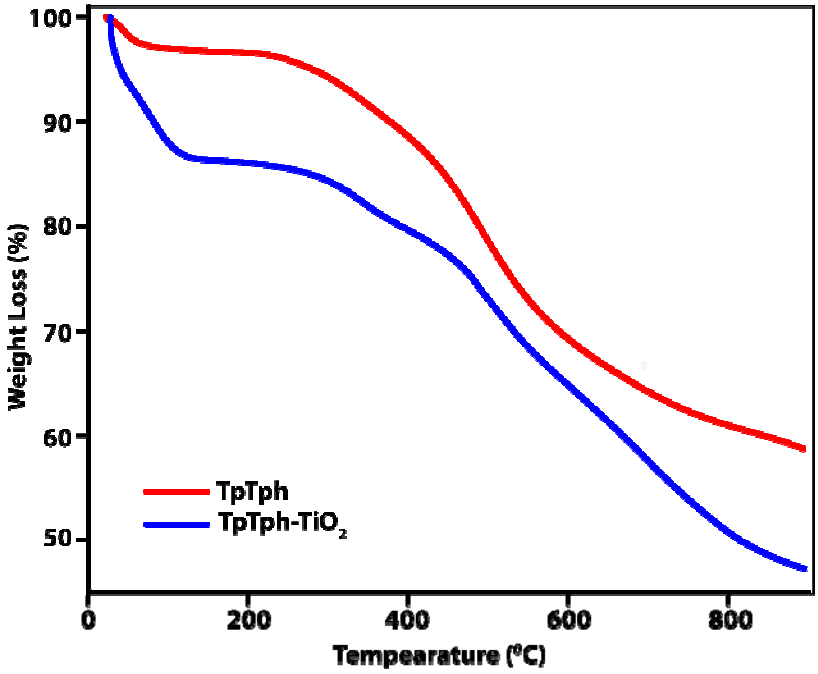

Figure S11: TGA data of activated **TpTph** under N_2 atmosphere.

Section S-10:Scanning Electron Micrographs (SEM)

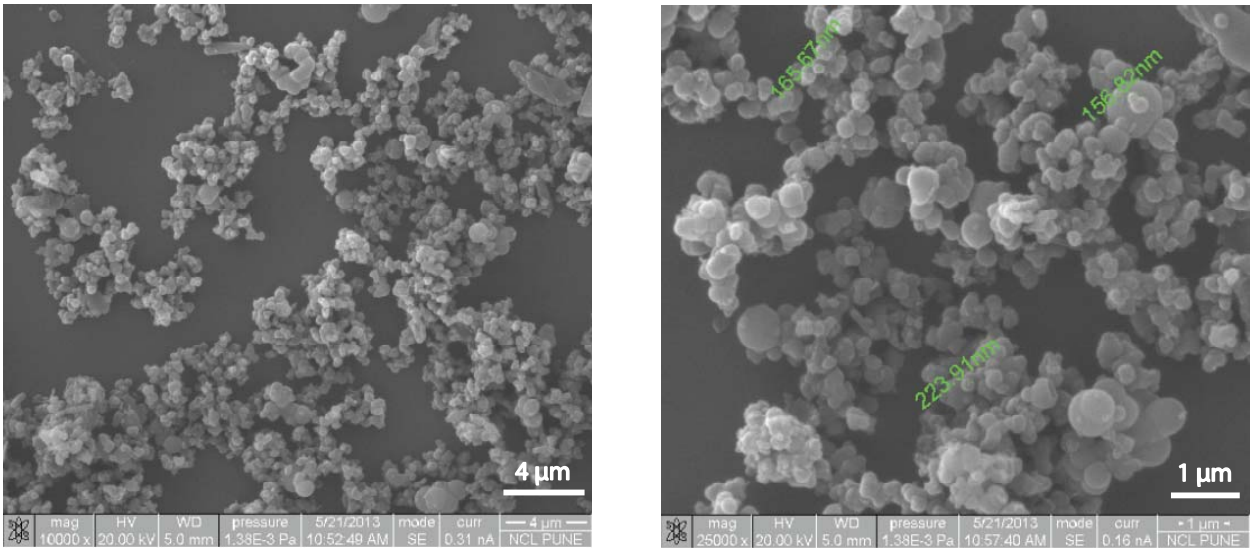

Figure S12: SEM images of **TpTph**.

Section S-11:Transmission Electron Micrographs (TEM)

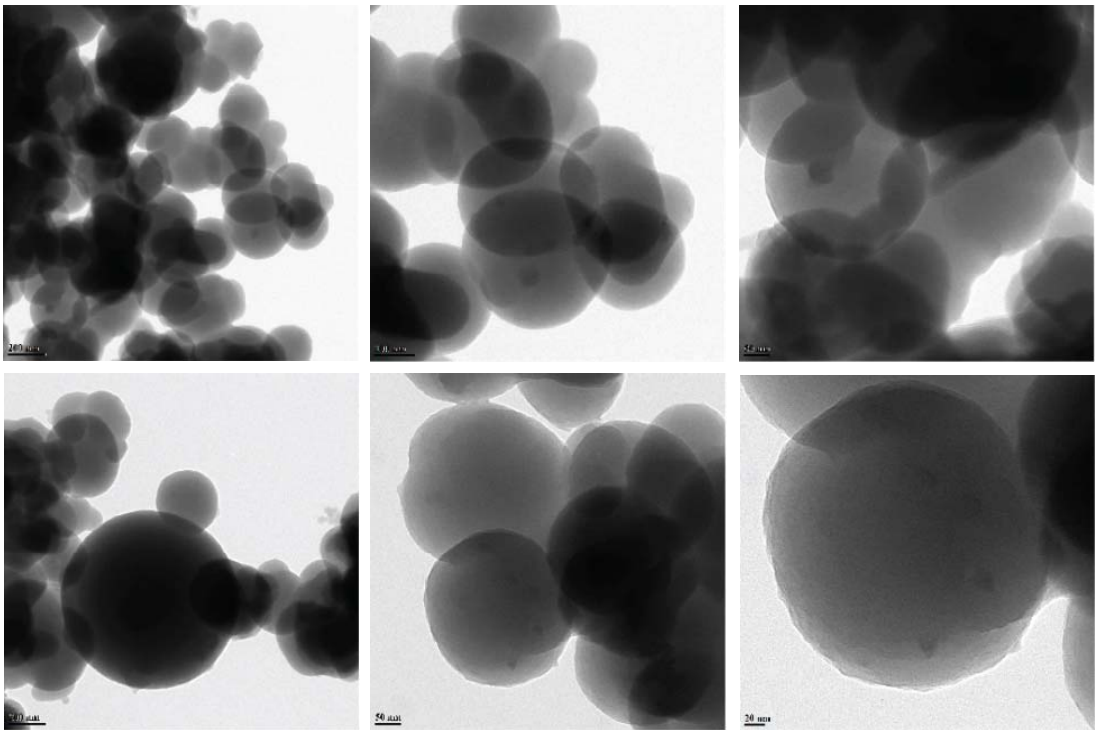

Figure S13: TEM images of **TpTph**.

Section S-12:UV-VIS Spectra

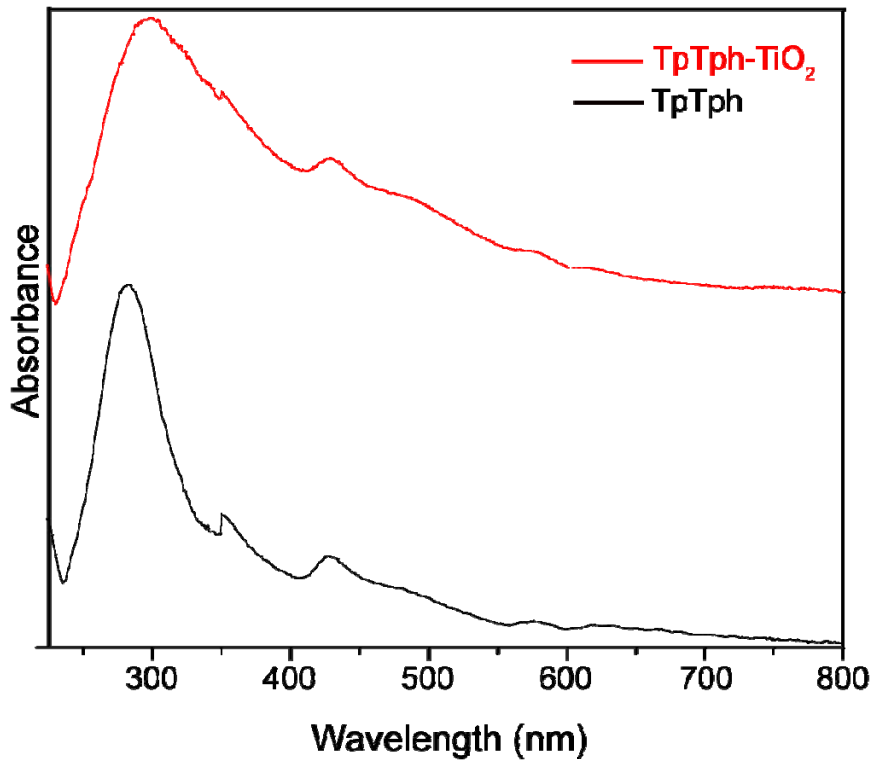

Figure S14: UV spectra of **TpTph** and **TpTph-TiO_2(2:1)** composite.

Section S-13: Stability test for TpTph in water, acid and base

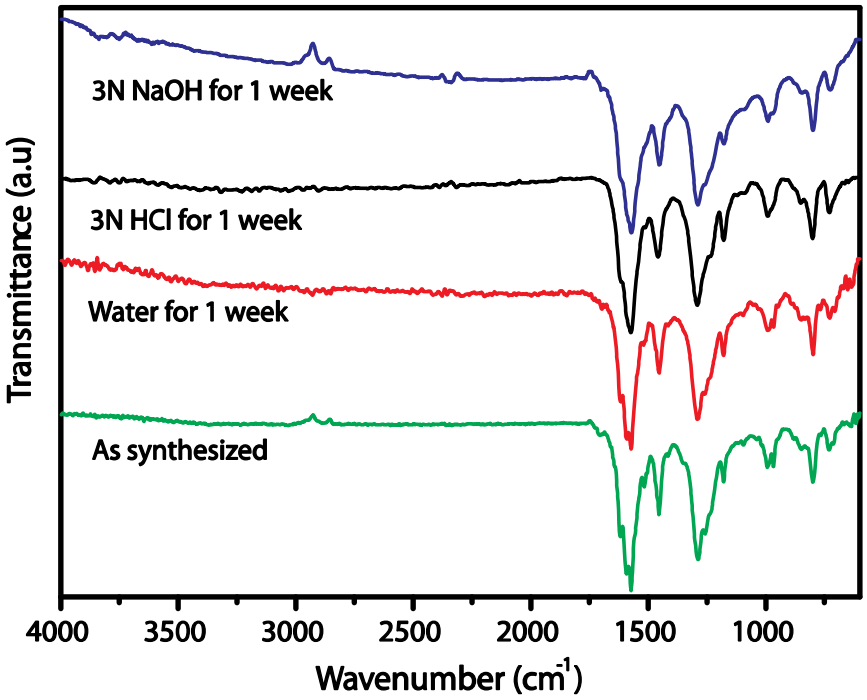

Figure S15: FT-IR spectrum of **TpTph** after treatment with water, 3(N) HCl, 3(N) NaOH for 1 week.

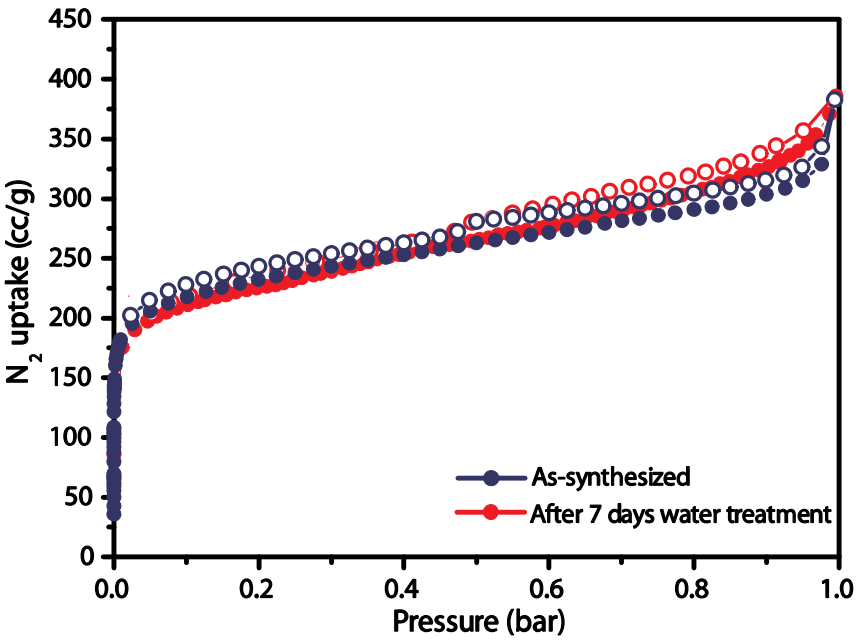

Figure S16: N_2 adsorption properties of **TpTph** before and after water treatment.

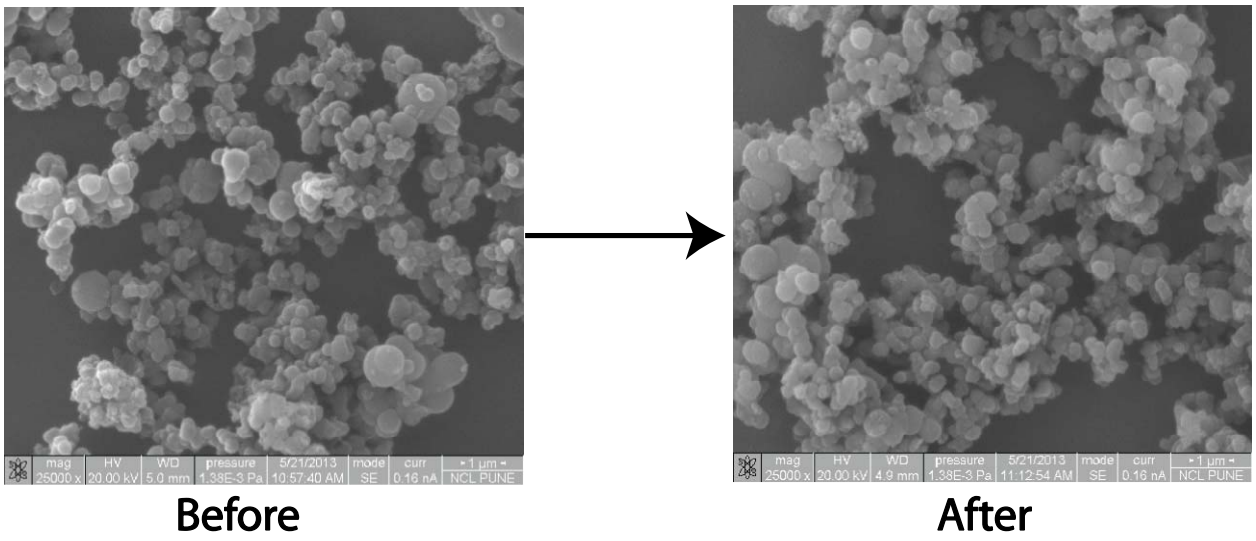

Figure S17: SEM of **TpTph** after treatment with 3(N) HCl for 1 week.

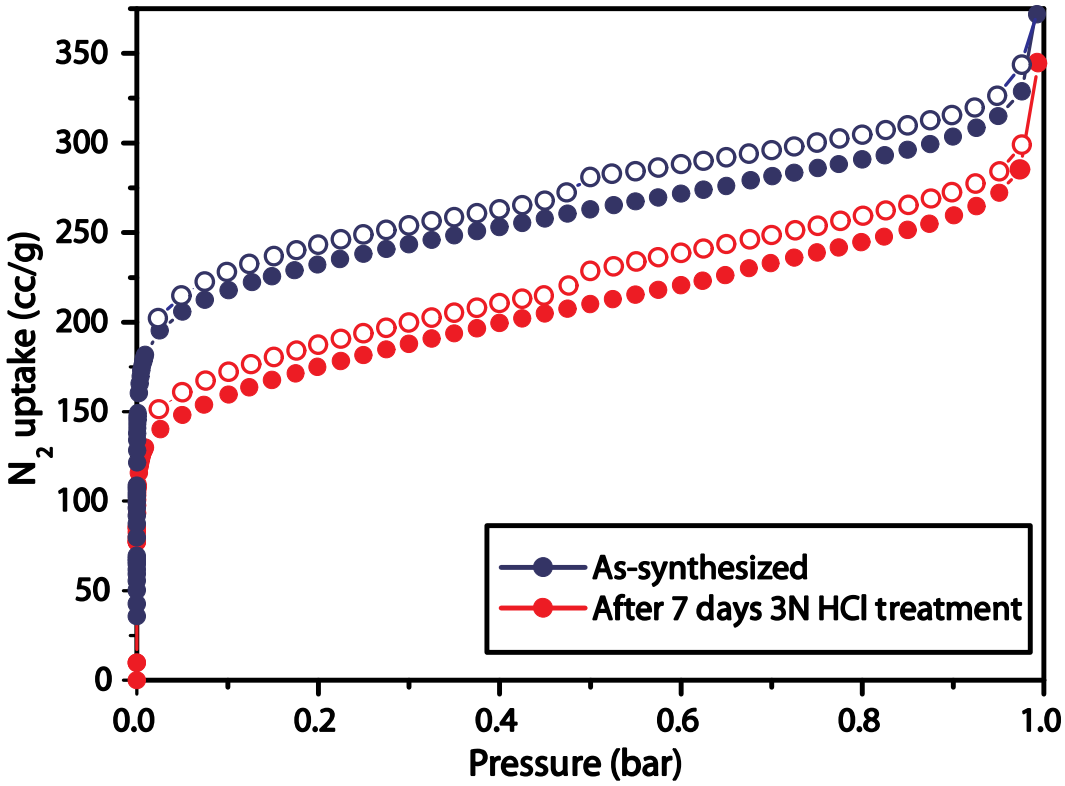

Figure S18: N_2 adsorption properties of **TpTph** before and after acid for 1 week.

Section S-14: References

1. J. H. Chong, M. Sauer, B. O. Patrick, M. J. MacLachlan, *Org. Lett*. 2003, **5**, 3823.

2. M. Yuasa, K. Oyaizu, A. Yamaguchi, and M. Kuwakado, *J. Am. Chem. Soc*., 2004, **126**, 11128.

3. R. Ahlrichs, Bär, Michael, M. Häser, H . Horn, C. Kölmel, *Chem. Phys. Lett*., 1989, **162** , 165.

4. TURBOMOLE V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

5. F. Weigend, R. Ahlrichs, Phys. *Chem.Chem.Phys*., 2005, **7**, 3297.

6. J. P. Perd ew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865.

7. S. Grimm e, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.

8. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett*., 1995, **240**, 283.

9. M . Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys*., 2003, **118**, 9136.