

Porphyrin Hetero-Trimer Involving a Hydrophilic and a Hydrophobic Structure with Application in the Fluorescent Detection of Toluidine Blue

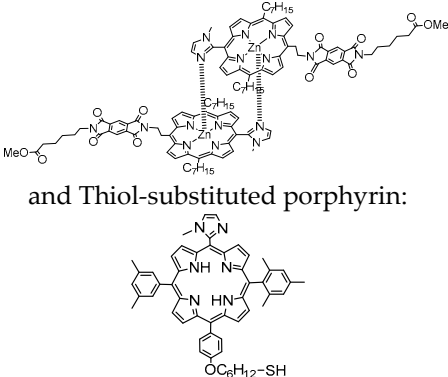
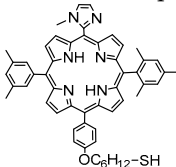
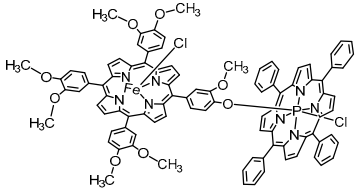
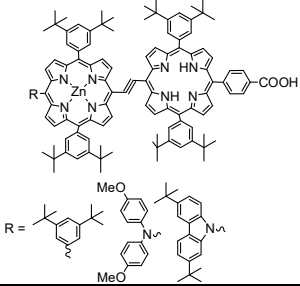
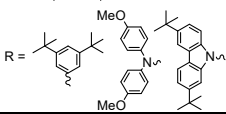
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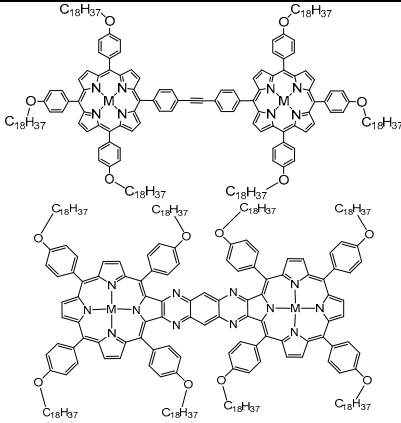
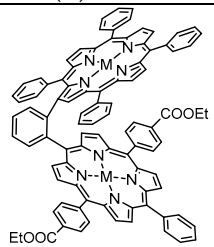
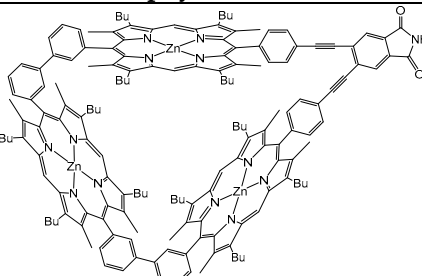
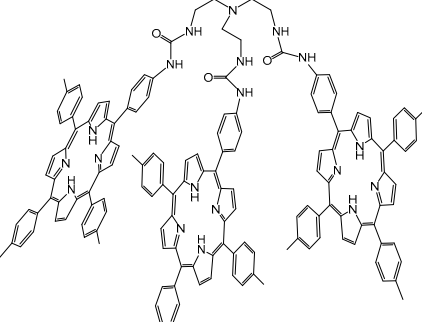
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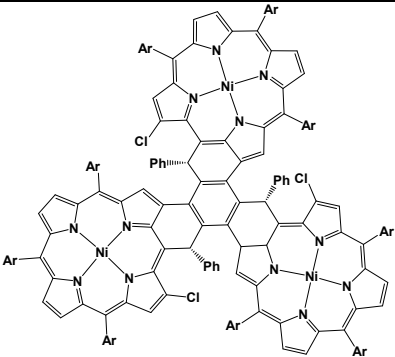
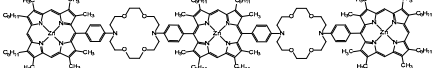
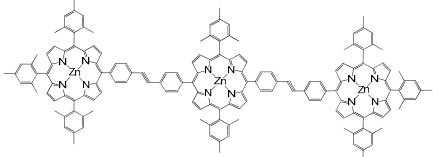
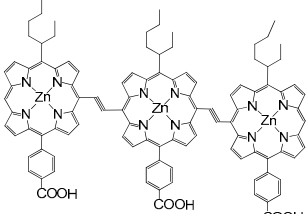
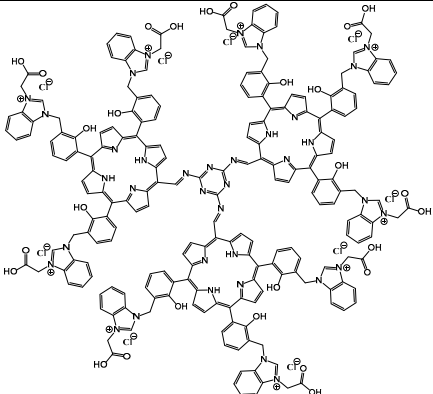
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Table S1. Porphyrins used for the formation of homo- and hetero-dimers and trimers with or without linkers and their applications.

Porphyrin dimers	Linker	Application	Results	Ref.
 <p>and Thiol-substituted porphyrin:</p> 	No; self-assembling on a substrate	Photocurrent generation	Self-assembling provides larger photocurrent values than pre-organized structures	[1]
	No	Fluorescent detection of hydrogen peroxide from water	Accurate in concentration range 40–90 μM	[4]
 <p>R = </p>	Ethynyl bridge	Investigation regarding photovoltaic performances	Stronger electron-donating abilities do not improve the short-circuit photocurrent densities	[2]

	<p>-Single bond -Ethyne, or - Di-ethyne bridges</p>	<p>Photosensitizers for PDT</p>	<p>Porphyrin dimer connected by diethyne link is more efficient singlet oxygen generator</p>	<p>[3]</p>
	<p>Diethynyl bridge</p>	<p>-PDT treatment -In MRI as contrast agent</p>	<p>-Induce medium-size contrast; -Is easily internalized in cancer cells</p>	<p>[5]</p>
<p>R=Gd-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate</p>				
	<p>Diethynyl bridge</p>	<p>Improving perovskite solar cells</p>	<p>-Power conversion efficiency of 19.44%</p>	<p>[6]</p>
	<p>Diethine bridge</p>	<p>Measurement of viscosity</p>	<p>Viscosity range of 0 – 10³ cP, even at elevated temperatures of 90 °C</p>	<p>[7]</p>
<p>R = CH₃</p>	<p><i>meta</i>-dimethyl-aryl bridges</p>	<p>Formation of inclusion complexes with Lindqvist-type polyoxometalate (POM) anions</p>	<p>Fluorescence quenching due to the formation of inclusion complexes</p>	<p>[8]</p>

 <p>M = Mn(II)- and/or Cu(II)</p>	<p>-Flexible alkyne linker; -Rigid conjugated spacer</p>	<p>Investigation of the self-assembling properties at a solid-liquid interface</p>	<p>The Cu-containing porphyrin dimer self-assembled into more stable monolayers, regardless of the type of linker</p>	[9]
 <p>Where M = Mn(III), Fe(III), Ni(II), Cu(II), Zn(II), and Pd(II)</p>	<p>Benzene ring spacer</p>	<p>Investigation of the relationships between crystalline structure and UV-Vis allure</p>	<p>Straightforward new synthesis route for both homo- and heterobimetallic porphyrin dimers; Metal-metal distances differ with the type of ligand and are correlated with Soret band shifts and splitting</p>	[10]
Porphyrin trimers	Linker	Application	Results	Ref.
	<p>Biphenyl bridges</p>	<p>Receptor for fullerene</p>	<p>Cyclic porphyrin able to chelate fullerene guest</p>	[11]
	<p>Tripodal tris-urea backbone</p>	<p>Receptor for fullerene</p>	<p>Stable inclusion complexes with fullerene in solution</p>	[12]

	Fused by 1,3,5- tribenzylben- zene	molecule- based chiroptical materials	Amplified circular dichroism response	[13]
	Piperazine	Chelating agents for metal ions	New synthesis route, optimized geometry calculations	[14]
	Diarylethynyl bridges	-	“Click” synthesis route, complete characterization	[15]
	Ethynyl bridges	Dye-sensitized Solar Cells	Successful anchoring to TiO ₂ surface	[16]
	Triazole linker	Dye-sensitized solar cells	Simple, stable, additive-free, energy generating device	[17]

UV-Vis, fluorescence and FT-IR spectra for TSPP:

The UV-Vis spectrum of bare TSPP, realized in ethanol (EtOH) in order to limit the possibility of protonation and aggregation of TSPP is presented in Figure S1. The *ethio* shape and the location of all bands are perfectly fitted with those reported in literature data [18].

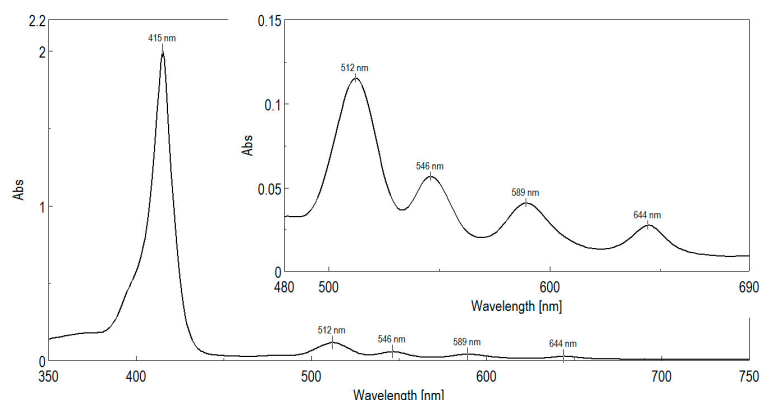


Figure S1. UV-Vis spectrum of 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin (TSPP) in ethanol ($c = 6.4377 \times 10^{-6}$ M).

In case of using water as solvent, the protonation of the sulfonated groups is evident; it produces the splitting of the Soret band into two bands, one located at 413 nm and the other one at 433 nm, even at a pH level of 4.9 due to starting of self-association phenomena when both H- and J-type aggregates are formed (Figure S2-black spectrum). When the pH is lowered to 1.4, the complete inner protonation of the porphyrin is observed: only the Soret band at 433 nm is present, along with the appearance of a supplementary band at 488 nm caused by enhanced J-type aggregation [19,20]. The hyperchromic effect of both the Soret and the QI band, located at 645.5 nm is also noticed (Figure S2-red spectrum).

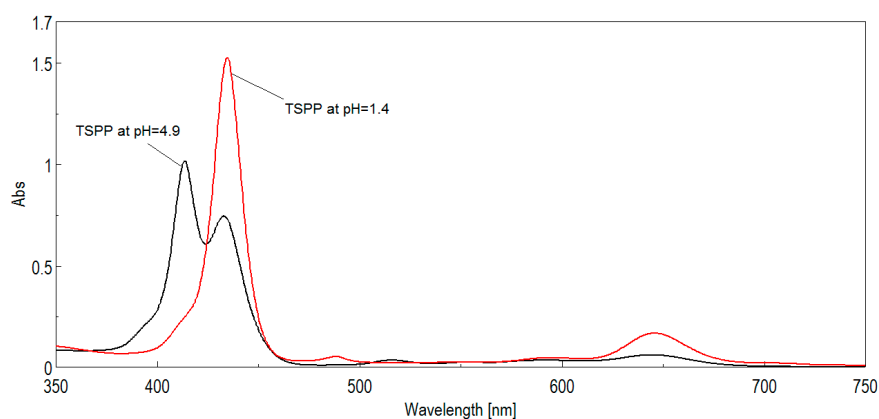


Figure S2. UV-Vis spectra for TSPP ($c = 8 \times 10^{-6}$ M) at initial pH=4.9 and at acid pH=1.4, for the same concentration.

Fluorescence spectra for TSPP were performed at $\lambda_{\text{exc}} = 435$ nm, slit width = 10 nm for excitation and 5 nm for emission without additional filter at a scan rate of 100 nm/min. The two emission spectra of TSPP were registered at different pH values, 4.9 and 2.7 respectively (Figure S3). The shape of the two spectra is similar, emphasizing higher differences in intensity of emission. Our results are in agreement with the reported data [21].

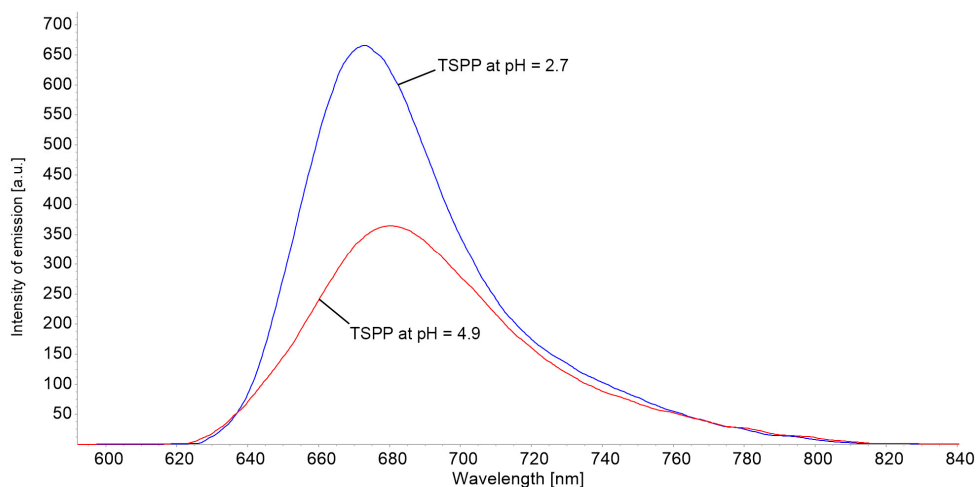


Figure S3. The emission spectra of TSPP at different pH values.

All the characteristic FT-IR bands of the protonated TSPP porphyrin (Figure S4) are in accordance to literature data [18,22,24,25].

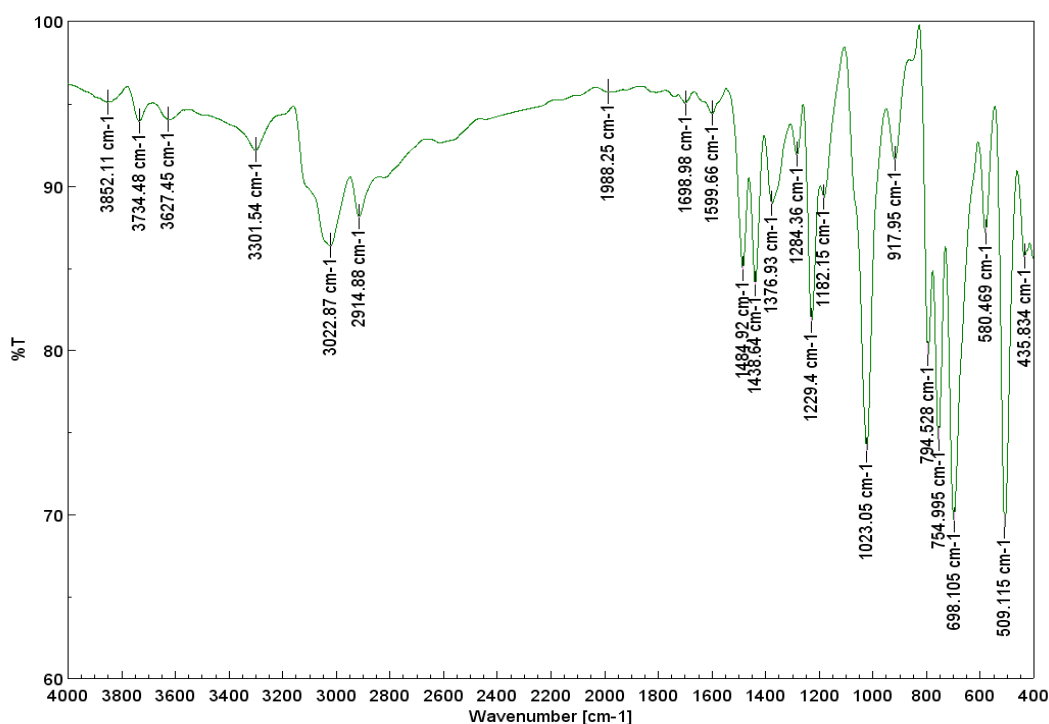


Figure S4. FT-IR spectrum of 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin (TSPP).

The bending vibrations of the C-C bonds of the aromatic ring 698 cm^{-1} [23]. The symmetric and asymmetric stretching vibrations of SO_2 are identified in the ranges $1182\text{--}1229\text{ cm}^{-1}$ and $1438\text{--}1484\text{ cm}^{-1}$ respectively [24]. The band at 1023 cm^{-1} is assigned as S-O stretching vibration [22]. The bands observed at 3022 cm^{-1} in the IR spectrum are assigned as the $\nu\text{C-H}$ modes of the phenyl ring [25].

Regarding the formation of the hetero-trimer, isosbestic points are clearly illustrated (Figure S5), at 414 nm and 416 nm on the Soret band and at 498 nm and 516 nm on the Q bands. These prove that

multiple absorbing species are generated during the process of obtaining the hetero-trimer. In addition a new Q band appears at 547 nm that can be associated with the generation of Pt-allyloxyPP-TSPP- hetero-trimer and the new location of Q(0-1) band absorption.

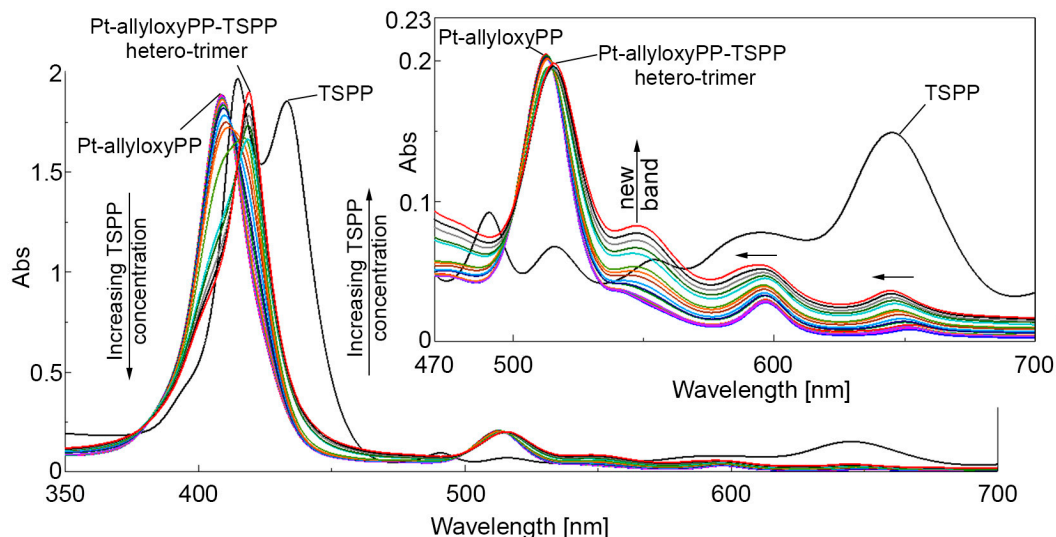


Figure S5. Overlapped UV-Vis spectra during the formation of the hetero-trimer. In detail the Q bands.

Regarding the ^1H -NMR spectrum of the Pt-allyloxyPP-TSPP hetero-trimer, the integrals for the equivalent protons are in fair correspondence with the proposed Pt-allyloxyPP-TSPP hetero-trimer structure that is in detail described in the main text (Figure S6).

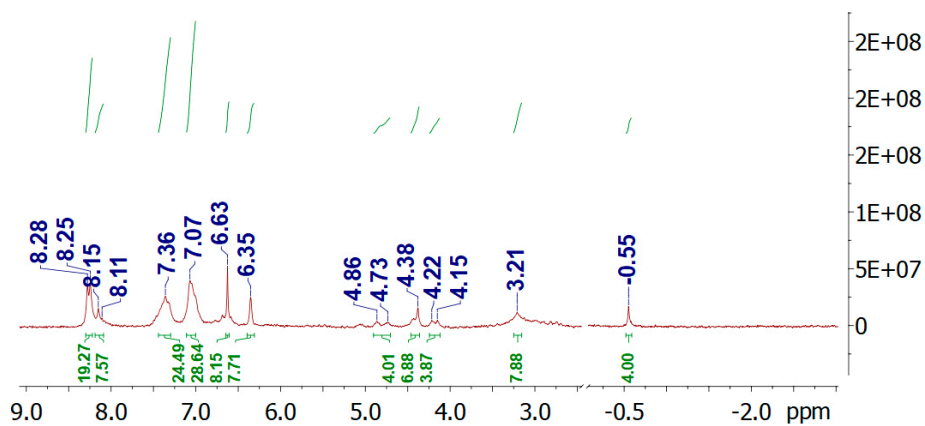


Figure S6. ^1H -NMR spectrum of the Pt-allyloxyPP-TSPP hetero-trimer.

The emission spectra illustrating the effect of the main interference species toward the TB detection are presented in Figure S7.

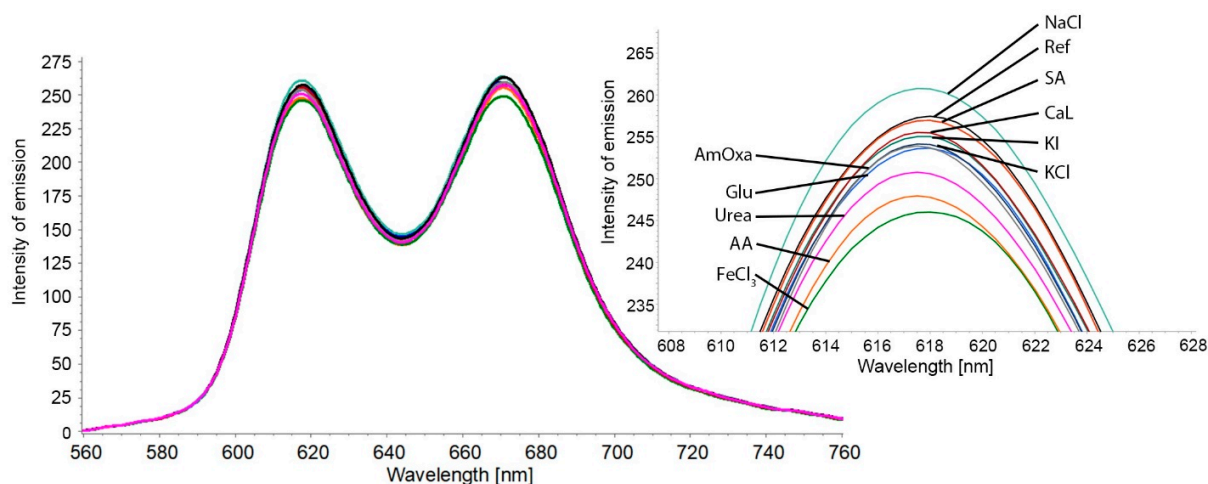


Figure S7. Overlapped emission spectra for interfering species that are exceeding 100 times the concentration of the main analyte (toluidine blue, represented as Ref curve).

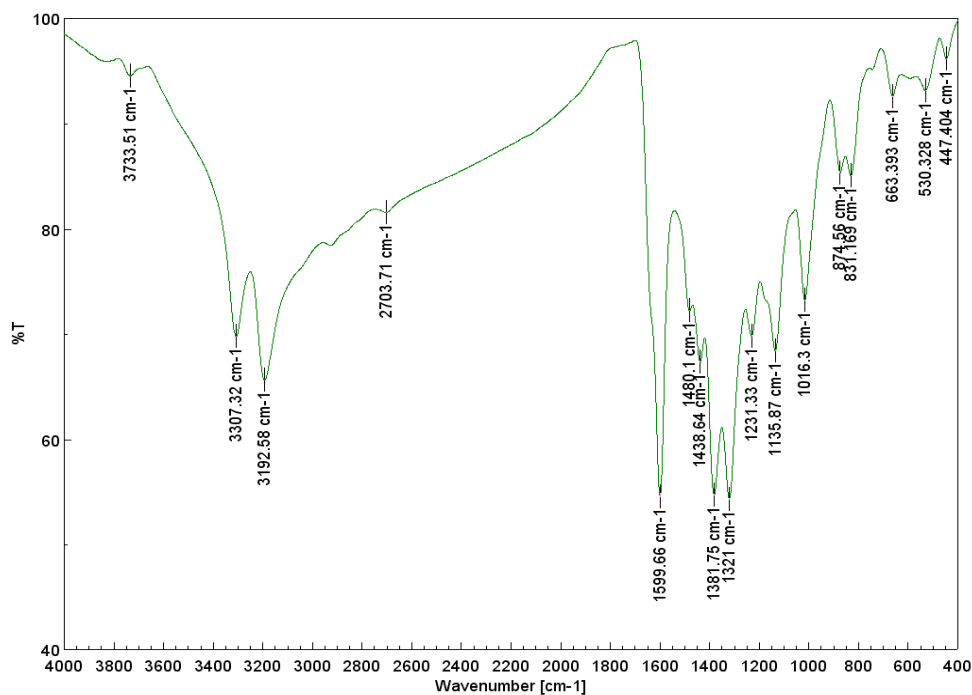


Figure S8. FT-IR spectrum of toluidine blue.

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