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Spectroscopic markers of phenothiazine drug adsorption on mesoporous anatase TiO_2

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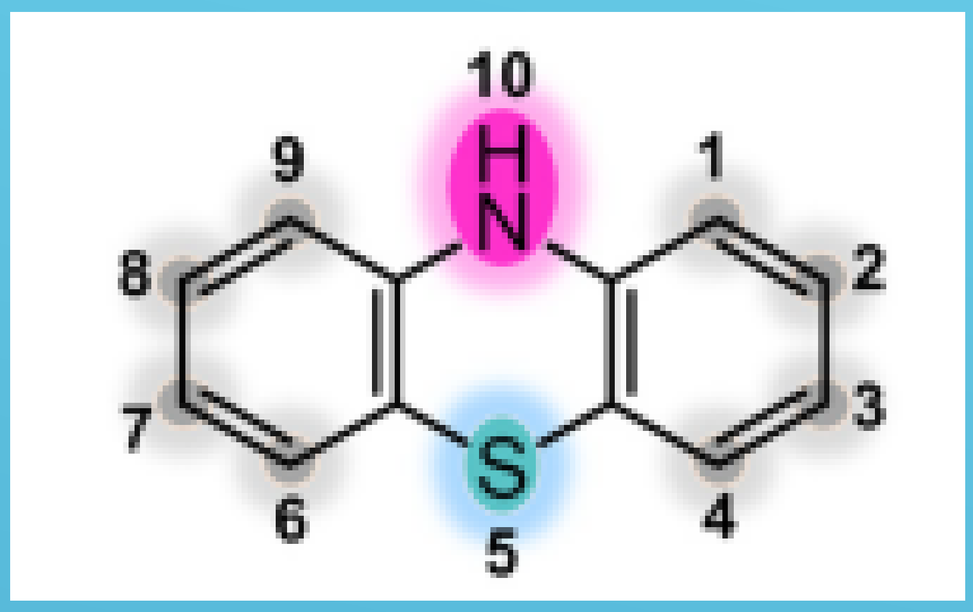
Our interest

- PTZ is nitrogen and sulfur-containing heterocyclic compound with unique non-planar butterfly molecular structure;
- PTZ is an efficient therapeutic agent used to treat a variety of psychiatric conditions;
- PTZ play a very important part in chemotherapy;

but

PTZ is water-insoluble so to improve its formulations and applicability one has to use other means of drug delivery.

- One of the ways for targeted delivery and controlled release of therapeutic agents is to use nanomaterials.
- TiO_2 nanoparticles are recognized as multifunctional platform for biomedical applications due to their potent antibacterial activity, biocompatibility, and low cost.



$S(C_6H_4)_2NH$

Our objective

To identify spectroscopic markers of PTZ interaction with TiO2 surface for the understanding of nature of their interaction.

PTZ adsorption on mesoporous anatase TiO_2

- Synthesis of mesoporous anatase TiO_2 particles (thermal hydrolysis of titanium tetrachloride ($TiCl_4$) hydrochloric acid solution followed by annealing in air at 200 °C for 5 h).
- Mechanical milling of dry anatase TiO_2 with PTZ (5 wt%) in an agate mortar; storage in dark for 48 hours.
- Or: soaking of dry TiO_2 powder with PTZ solution in acetone (1mg/1ml) at room temperature;
- different concentrations.

Spectroscopy methods

- FTIR spectroscopy (380-4000cm^{-1}, Bruker IFS-88, 64 scans, 2cm^{-1} resolution);
- FT-Raman spectroscopy (80-4000 cm-1, Bruker IFS-88, FRA attachment, 520 scans, 2 cm^{-1} resolution)
- Photoluminescence (PL) (400–700 nm, Edinburgh Instruments FLS1000 grating spectrometer, λ_{ex}=266 nm of diode-pumped laser).

PL spectra of pure PTZ and TiO_2

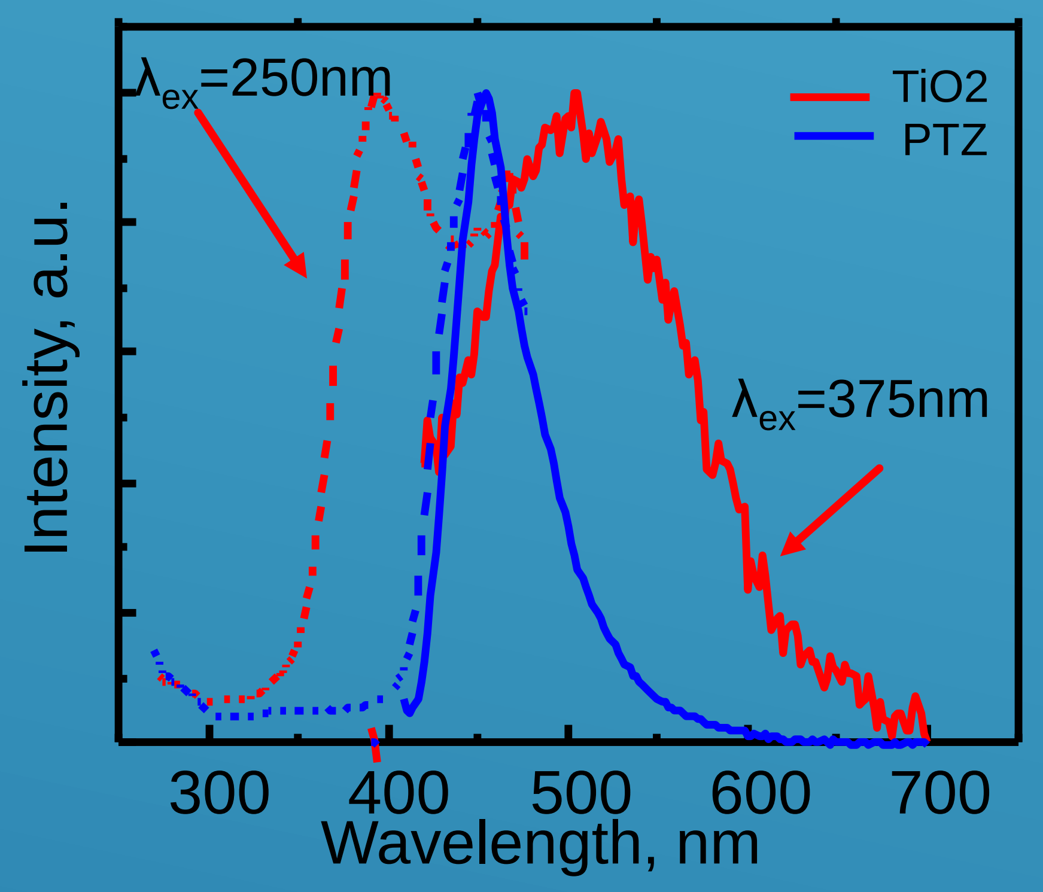


Fig. 1. PL emission from anatase TiO2 and PTZ at excitation with λex=250 and 375 nm (both above the band gap ~3.2 eV). The observed TiO_2 emission bands are due to annihilation of self-trapped excitons (387 nm) and emission from oxygen dafacts present on the surface (Scheme 1) [1].

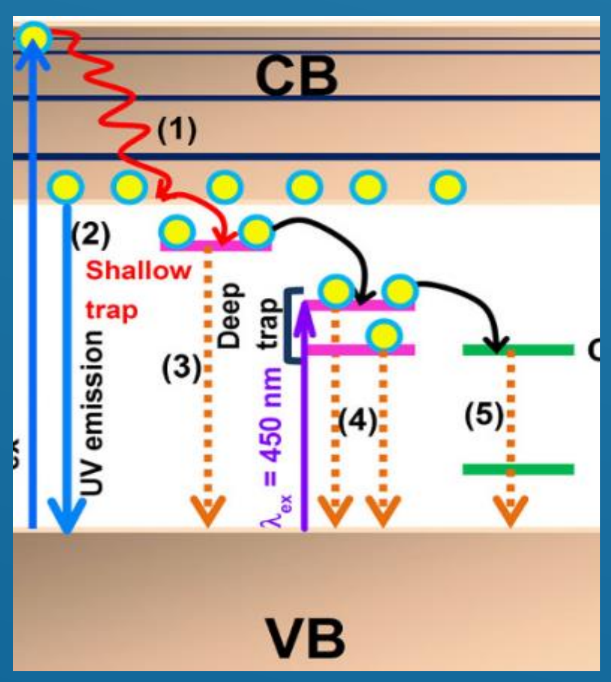
PL emission in anatase TiO_2

- ✓ Two bands are observed with maxima at λ=395 nm (green emission, G-PL) and λ=508 nm (red emission, R-PL);
- ✓ G-PL is observed at the excitation with λ = 250 nm;
- ✓ R-PL band is better seen at the excitation with λ = 375 nm;

Both PTZ and TiO_2 emissions are quenched after PTZ is bonded to the surface of TiO_2 particles evidencing effective energy transfer from excited PTZ molecules to TiO_2

PL of PTZ-TiO_2 composite

- ✓ No PTZ fluoreescence is observed in the PL spectra of PTZ-TiO_2 composite;
- ✓ Both G-PL and R-PL bands of TiO_2 are present;
- ✓ G-PL emission faded with PTZ addition;
- ✓ The intensity of R-PL increased with an increase of PTZ concentration.



Scheme 1. Energy transfer and light emission in TiO_2 [2].

FTIR spectroscopy

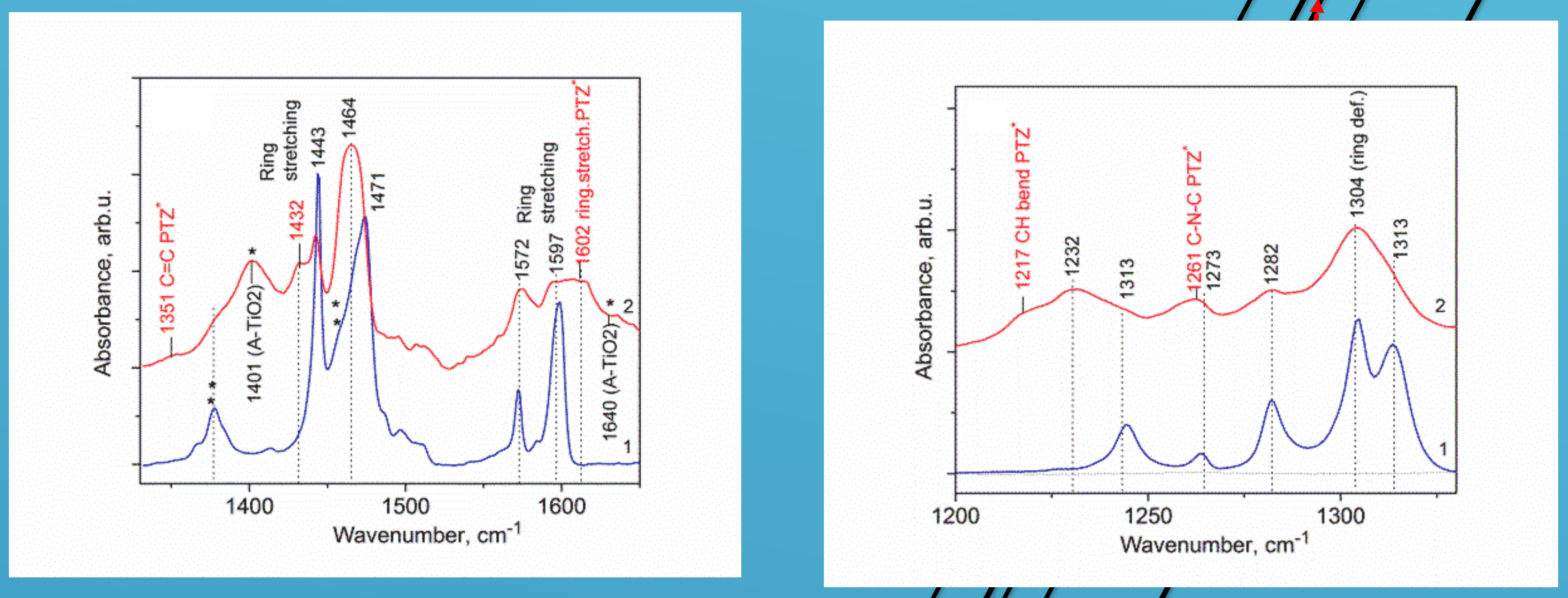


Fig. 2. Fragments of FTIR absorption spectra of PTZ (1) and dry-milled PTZ-TiO_2 (2) in PTZ fingerprint regions. Evidence of non-covalent molecular interactions.

FT-Raman spectroscopy

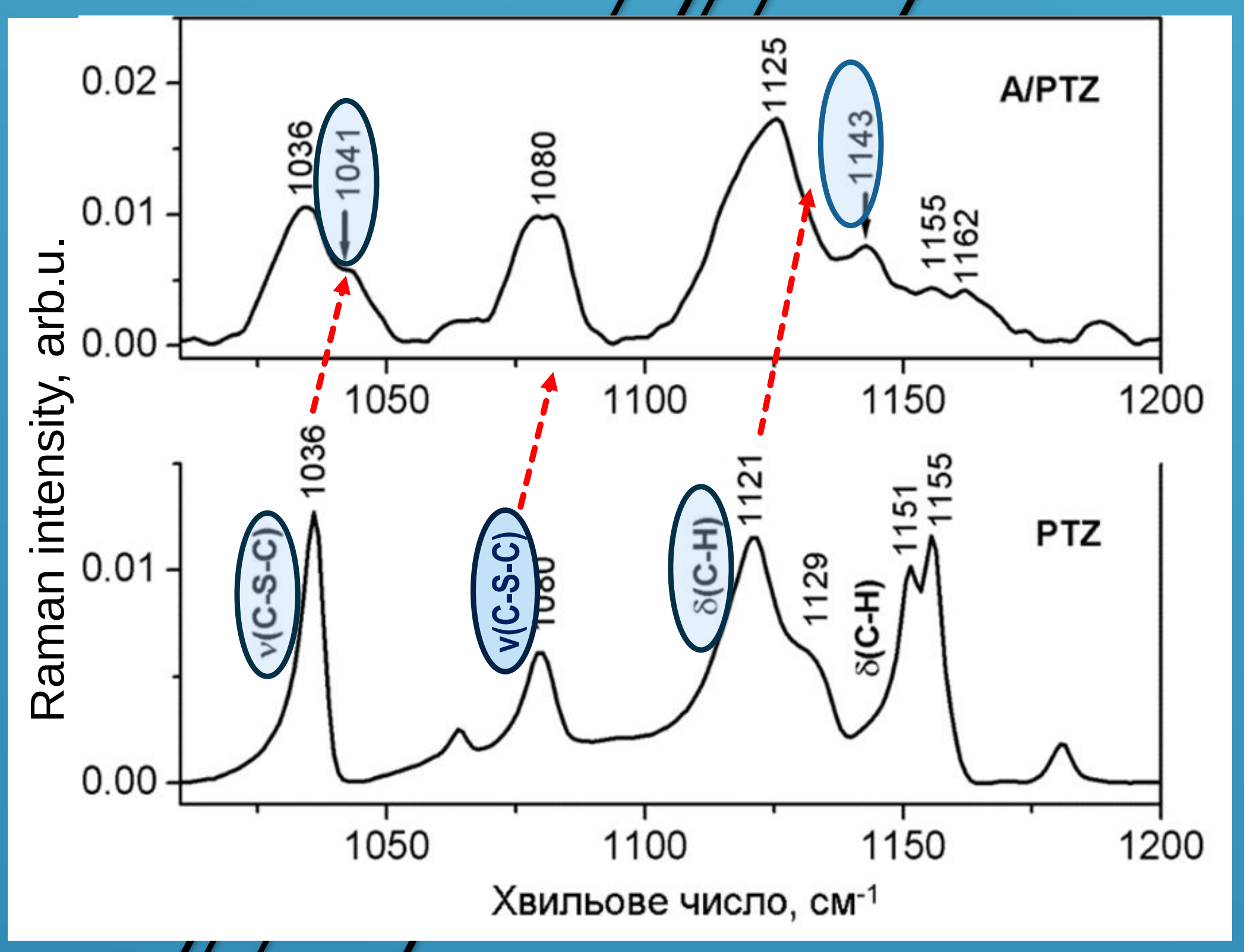
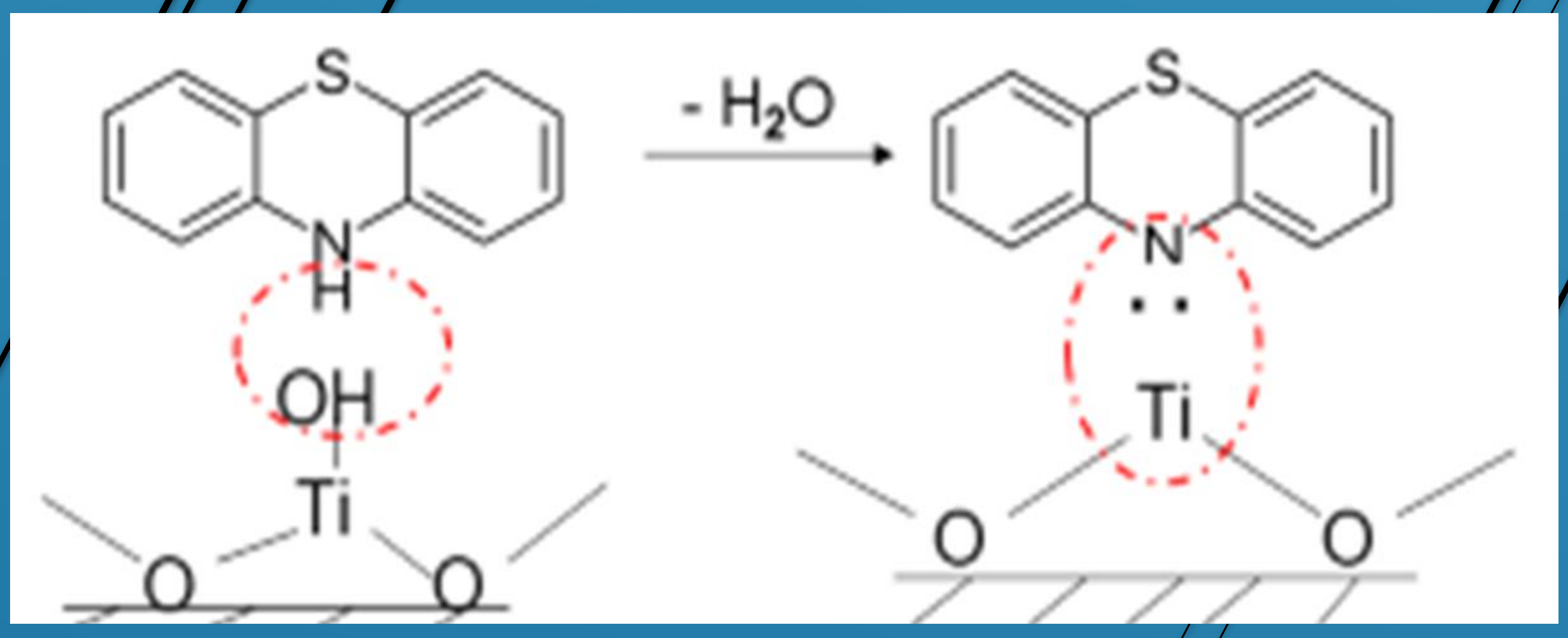


Fig. 3. FT-Raman spectra of PTZ and PTZ-TiO_2 composite (dry-milled) in the region of characteristic PTZ vibrations bands



Scheme 2. Possible mechanism of PTZ molecule interaction with TiO2 surface via covalent nitrogen (or sulfur) coordination, forming a direct bond to the titanium.

Conclusions

- ✓ Fluorescence quenching upon PTZ bonding to TiO_2 surface evidences resonance energy transfer from excited PTZ molecules to TiO_2.
- ✓ FT-IR and FT-Raman spectroscopic markers (shift of characteristic CNC and CSC vibration bands) indicate coordination bonding of PTZ molecules to Ti atoms.
- ✓ Loading PTZ on mesoporous TiO_2 from acetone solution requires less drug.

References

[1] O.F. Isaieva, V.V. Naumov, V.V. Shymanovska, E.G. Gule, G.Yu. Rudko, Book of Abstracts of XXIV Galyna Puchkovska International School-Seminar “Spectroscopy of Molecules and Crystals”, August 25-30, 2019, Odesa, Ukraine p. 147.

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