sewan

ITMO UNIVERSITY

TOMSK
POLYTECHNIC
UNIVERSITY

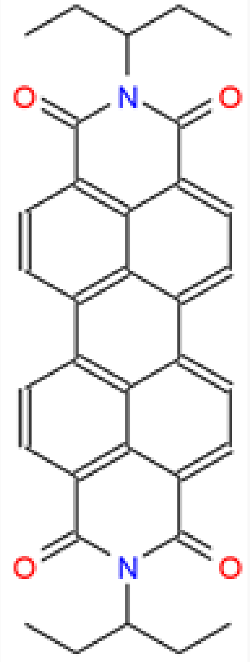
22 April
2021

Surgut State University

MOLECULAR-IMPRINTED COMPOSITE MATERIALS WITH IMPROVED OPTICAL PROPERTIES FOR PHOTOVOLTAIC CELLS

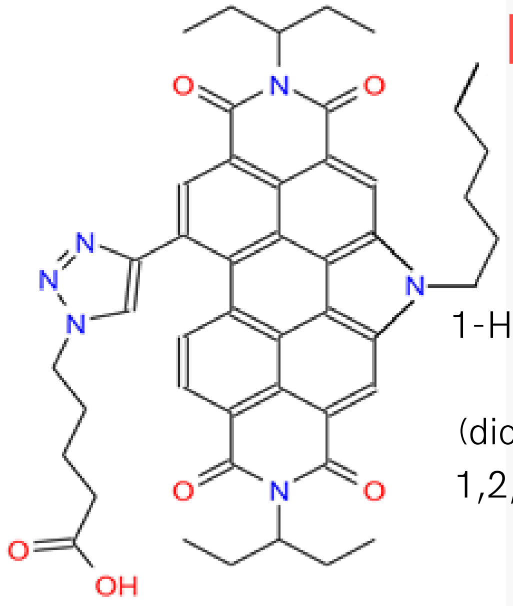
YU.YU. PETROVA, E.V. BULATOVA

Perylenediimide (PDI) dyes - acceptors of organic semiconductor systems



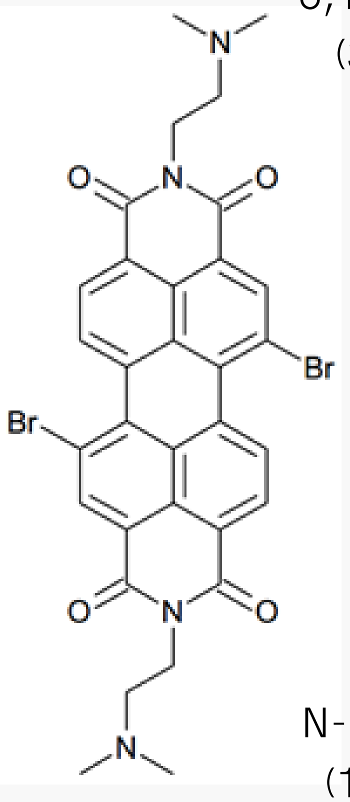
EP-PDI

N,N′-bis (3-pentyl) perylene-3,4,9,10-bis(dicarboximide

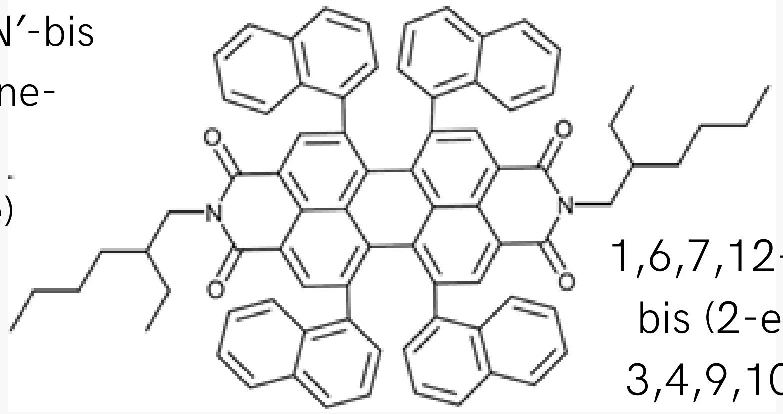


PDI-Taz-C5OOH

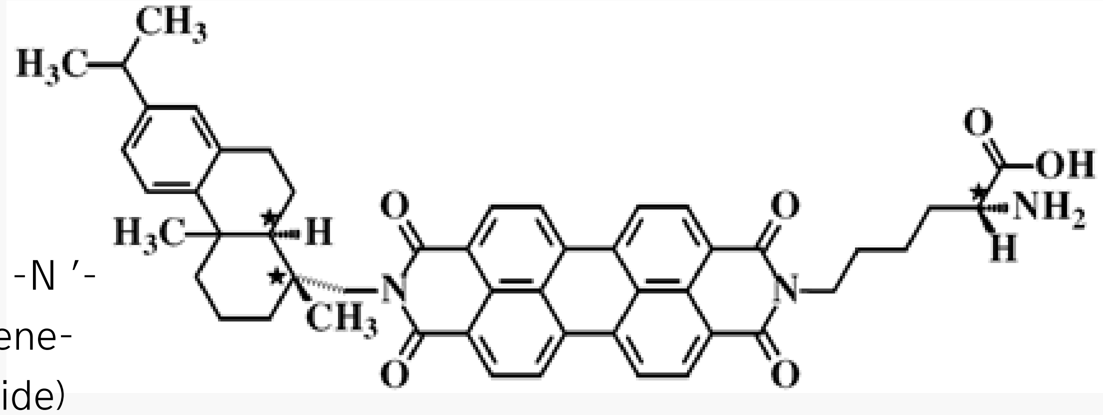
1-H- pyrrole- N,N′- bis (3-pentyl) perylene-3,4,9,10-bis (dicarboximide) -5-hexyl-11 1H-1,2,3-triazol-1-yl-pentanoic acid



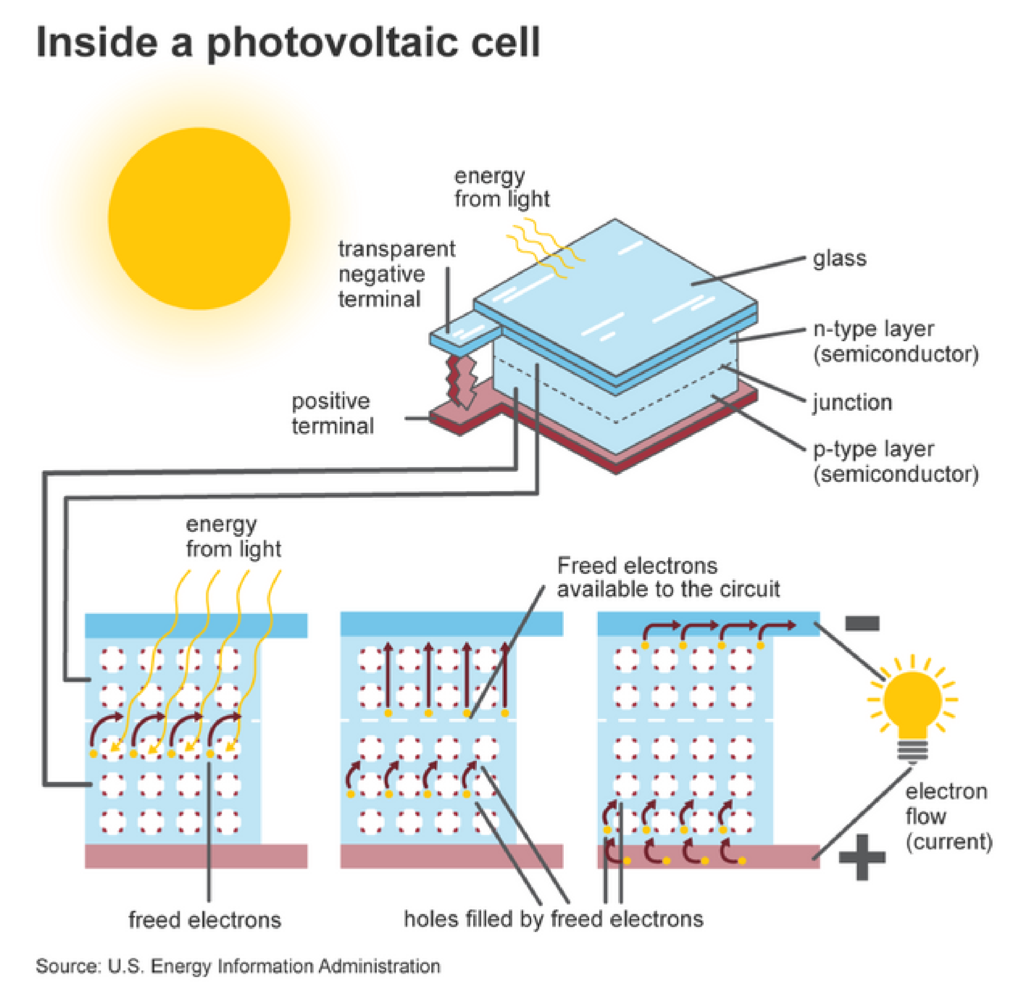
6,12-dibromo-N, N′-bis (3-pentyl) perylene-3,4,9,10-bis (dicarboximide)



1,6,7,12-tetranaphthyl-N, N'-bis (2-ethylhexyl) perylene-3,4,9,10-bis (dicarboximide)



N- (2-aminohexanoic acid) -N ′-(1-dihydroabiethyl) perylene-3,4,9,10-bis (dicarboximide)



Inside a photovoltaic cell

Source: U.S. Energy Information Administration

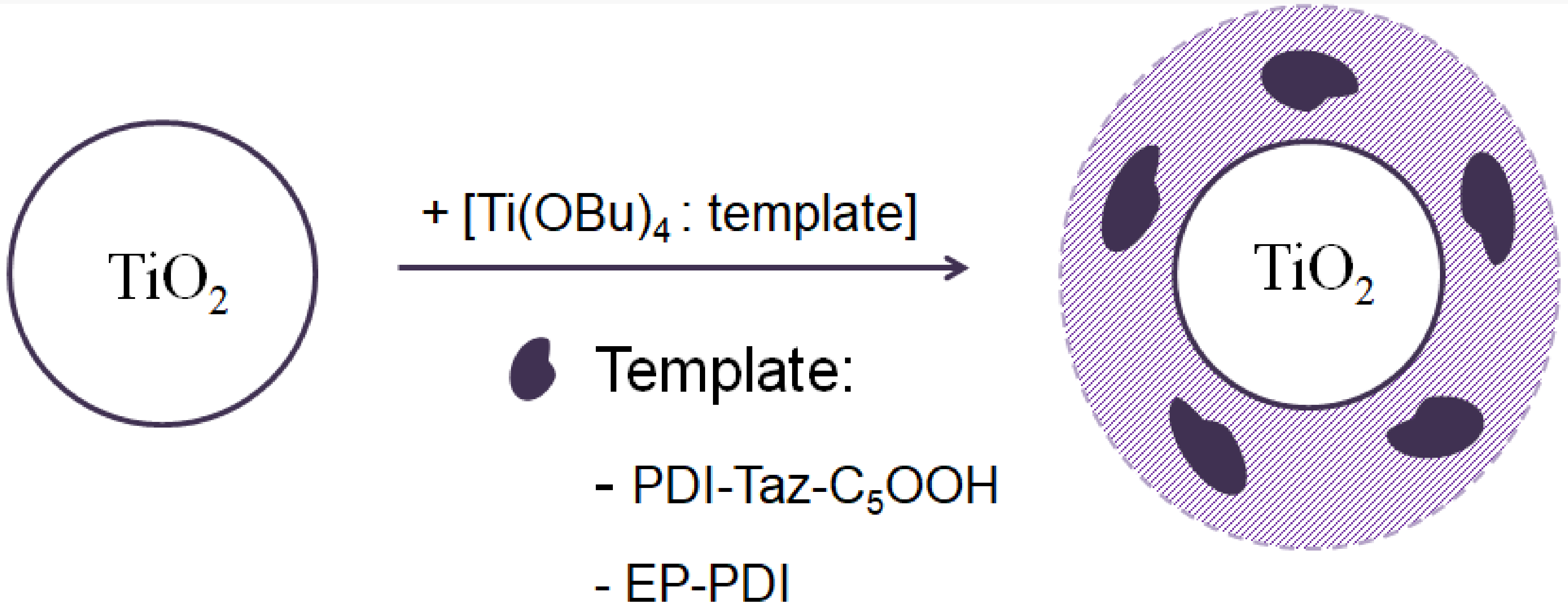
Dye Sensitized Solar Cell (DSSC)
Materials:
PDI-TiO2 nanoPts

The purpose of this work is to create an organo-mineral composite based on TiO2 nanoparticles with semiconductor properties using molecular imprinting technology.

Tasks:

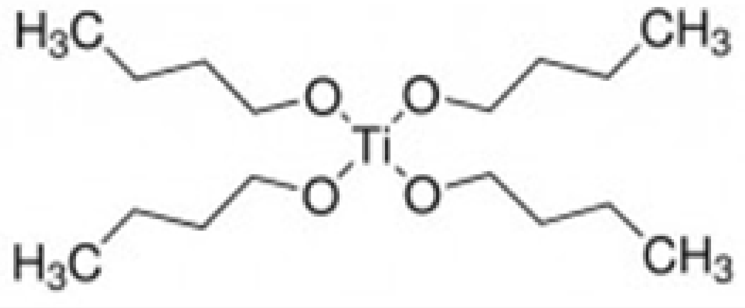
1. Production of polymer films by molecular imprinting on the surface of TiO2 nanoparticles; using an organic semiconductor as a template;
2. Characterization of the composite by a complex of physical methods;
3. Study of optical and sorption properties of molecular-imprinted composites.

Sol-gel method in surface molecular imprinting using nanoparticles TiO2



Hydrolysis scheme of titanium *t*-butoxide in sol-gel process

$$Ti–(OBu)_4 + 2H_2O \rightarrow TiO_2 + 4Bu–OH$$



Surface Molecular Imprinting Technique

Preparation of TiO_2 nanoparticle suspension in toluene → Precomplex Template: Titanium Butoxide → Sol-gel synthesis → TiO_2 separation and drying

Conditions	Sol-gel synthesis				
	PDI-Taz-C_5OOH			EP- PDI	
	I	II	III	I	II
Activated TiO_2, mg	**500**	250	273	**273**	250
PDI, mg	9.3	9.3	**11.5**	7.3	6.2
Titanium butoxide, mcl (mmol)	79 (0.23)	400 (1.17)	400 (1.17)	400 (1.17)	400 (1.17)
The ratio of template: titanium butoxide	**1:20**	**1:100**	**1:81**	**1:85**	**1:100**
Temperature (drying), ° C	80	80	**110**	110	80
The output of the sol-gel,%	NIP - 92 MIP - 96	NIP - 94 MIP - 97	NIP - 92 MIP - 96	NIP - 86 MIP - 83	NIP - 87 MIP -92

Titanium(IV) oxide, anatase
nanopowder, <25 nm particle size, 99.7% trace metals basis

PDI-TiO2 composite characterization

Laser diffraction

SALD-2300, Shimadzu

FTIR spectroscopy

Spectrum 100 Series, Perkin Elmer

TGA & DSC

Mettler Toledo TGA/DSC 3+ Star System

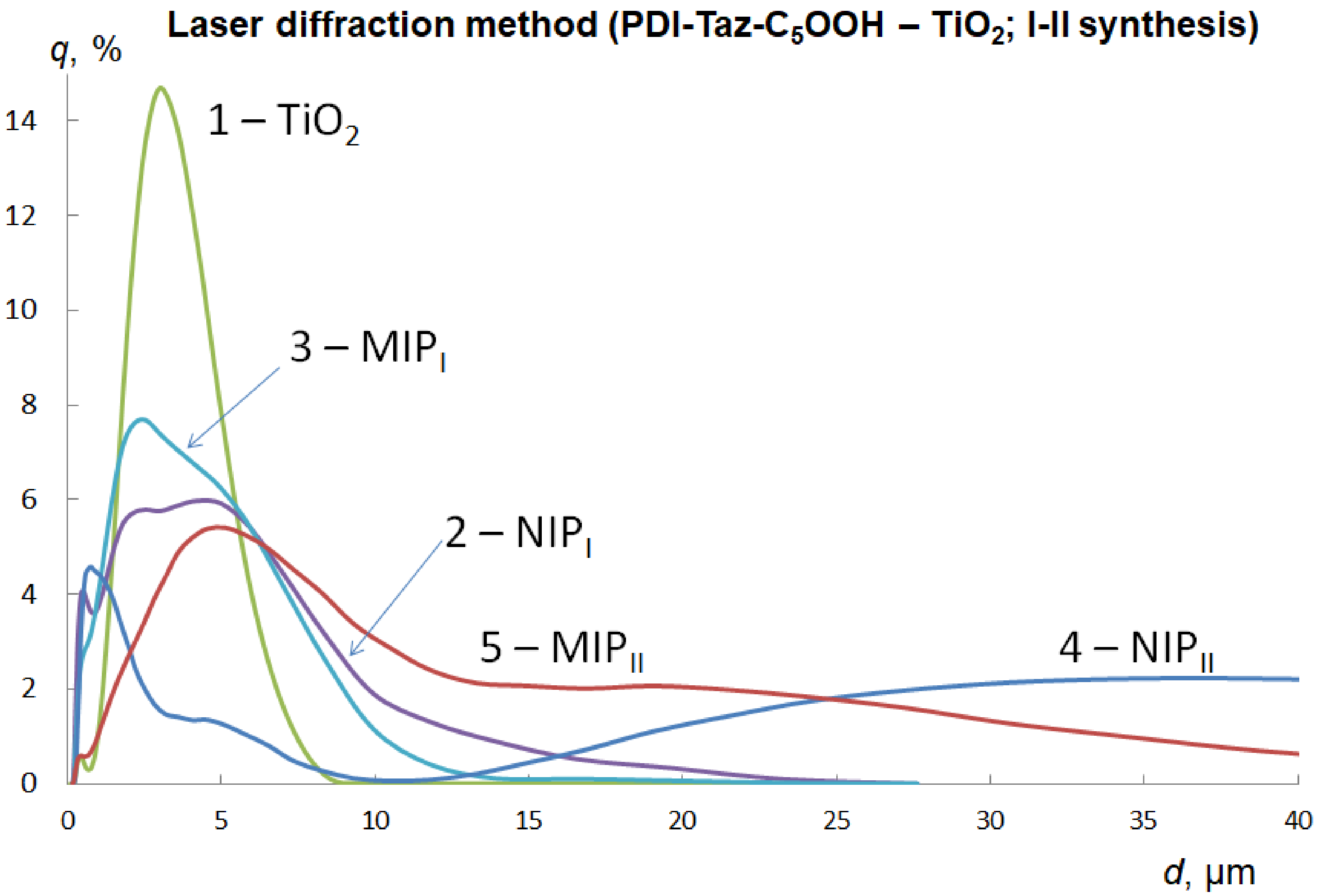
Diffuse reflectance spectroscopy

UV-Vis spectroscopy

Shimadzu UV-2600

Laser diffraction method

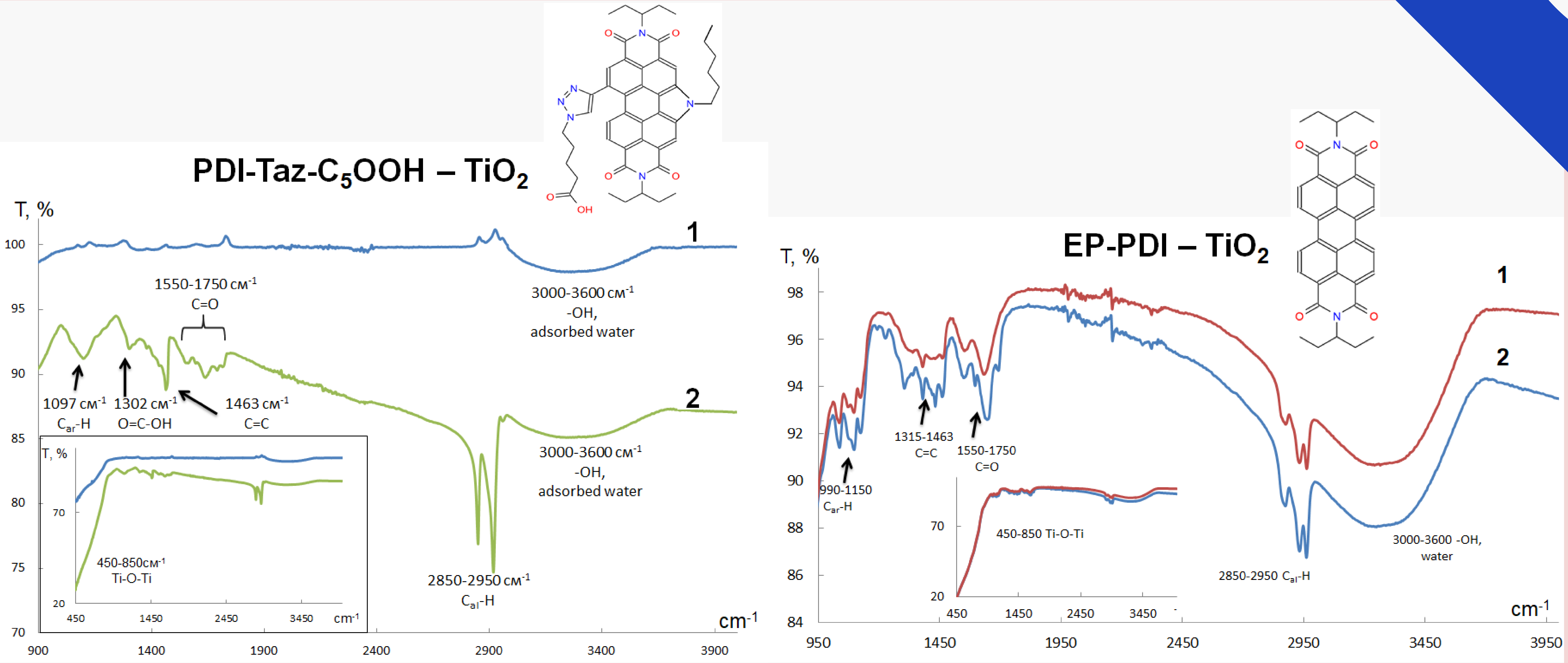
Sample	Median diameter, µm	Modal diameter, µm	Average diameter, µm
TiO$_2$	2.65	2.83	2.50
I (PDI-Taz-C$_5$OOH)			
MIP	2.10	2.23	1.93
NIP	1.98	3.56	1.81
II (PDI-Taz-C$_5$OOH)			
MIP	**4.65**	**4.56**	**4.59**
NIP	1.41	0.68	2.57
III (PDI-Taz-C$_5$OOH)			
MIP	**1.14**	**1.39**	**1.16**
NIP	**0.79**	**0.54**	**0.87**
I (EP- PDI)			
MIP	3.79	5.79	3.22
NIP	3.51	5.79	3.63
II (EP- PDI)			
MIP	**13.00**	**19.02**	**8.89**
NIP	6.50	19.02	6.01



Graphs of volume distribution (q,%) on particle diameter:

1 -TiO2; 2 - NIP (I synthesis); 3 - MIP (I synthesis); 4 - NIP (II synthesis); 5 - MIP (II synthesis)

FTIR spectroscopy (ATR)

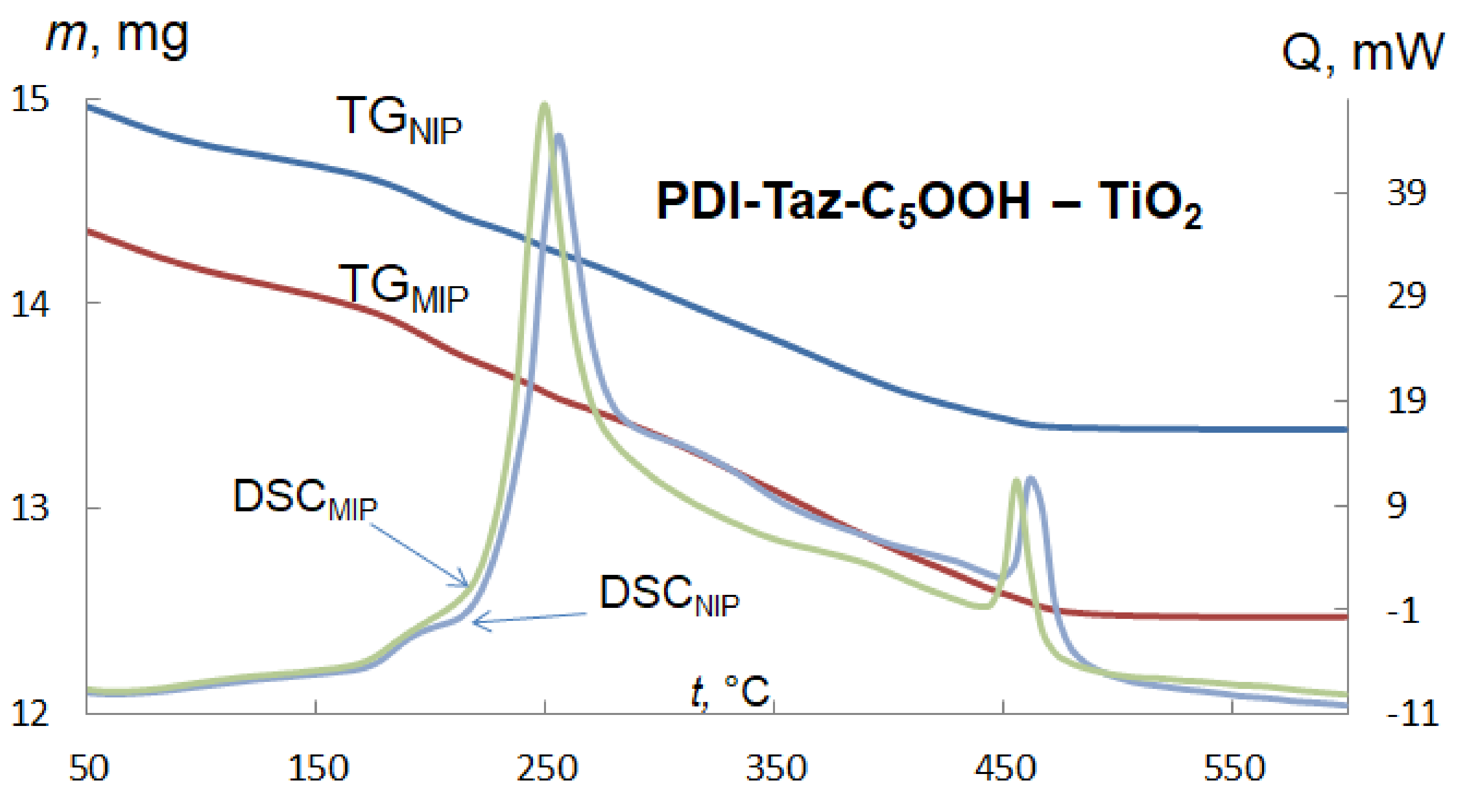


PDI-Taz-C$_5$OOH – TiO$_2$

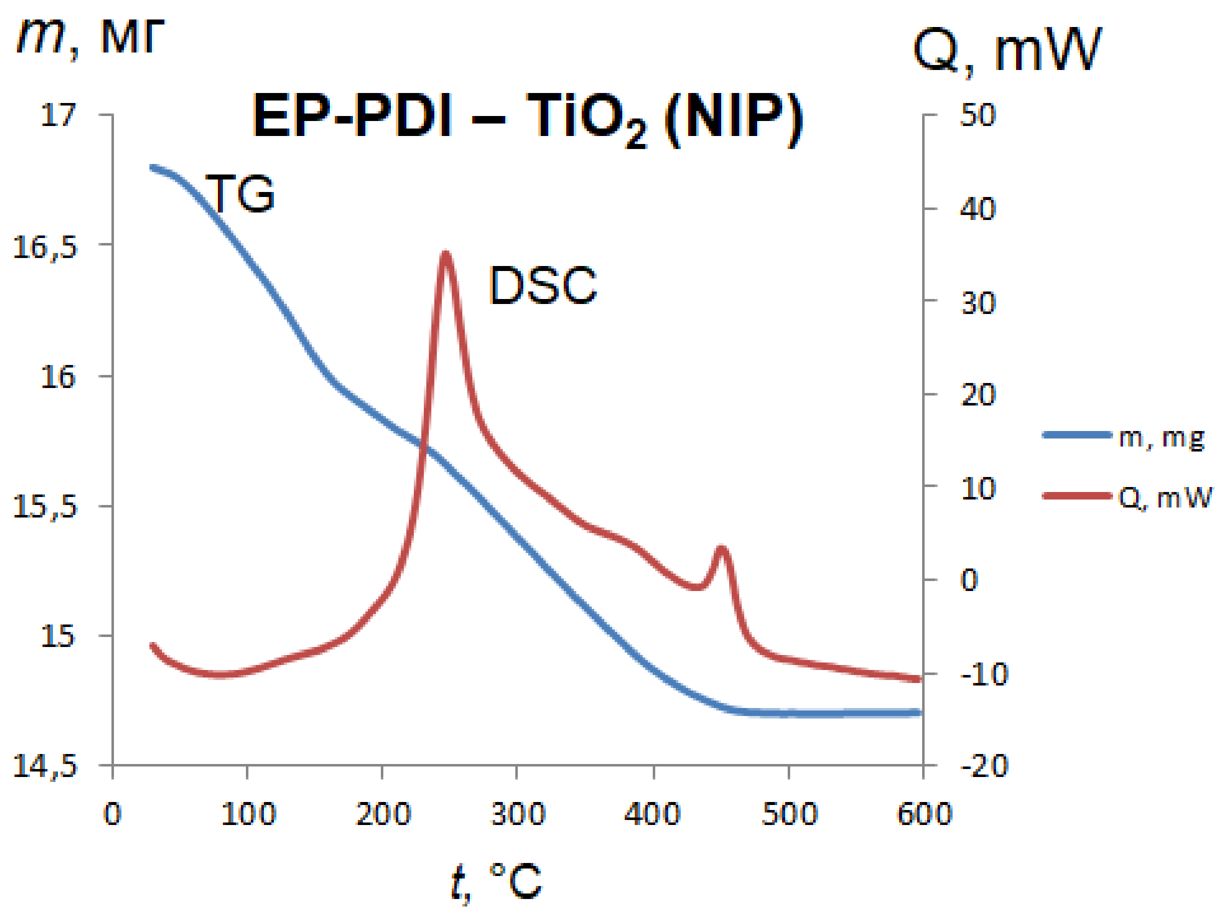
EP-PDI – TiO$_2$

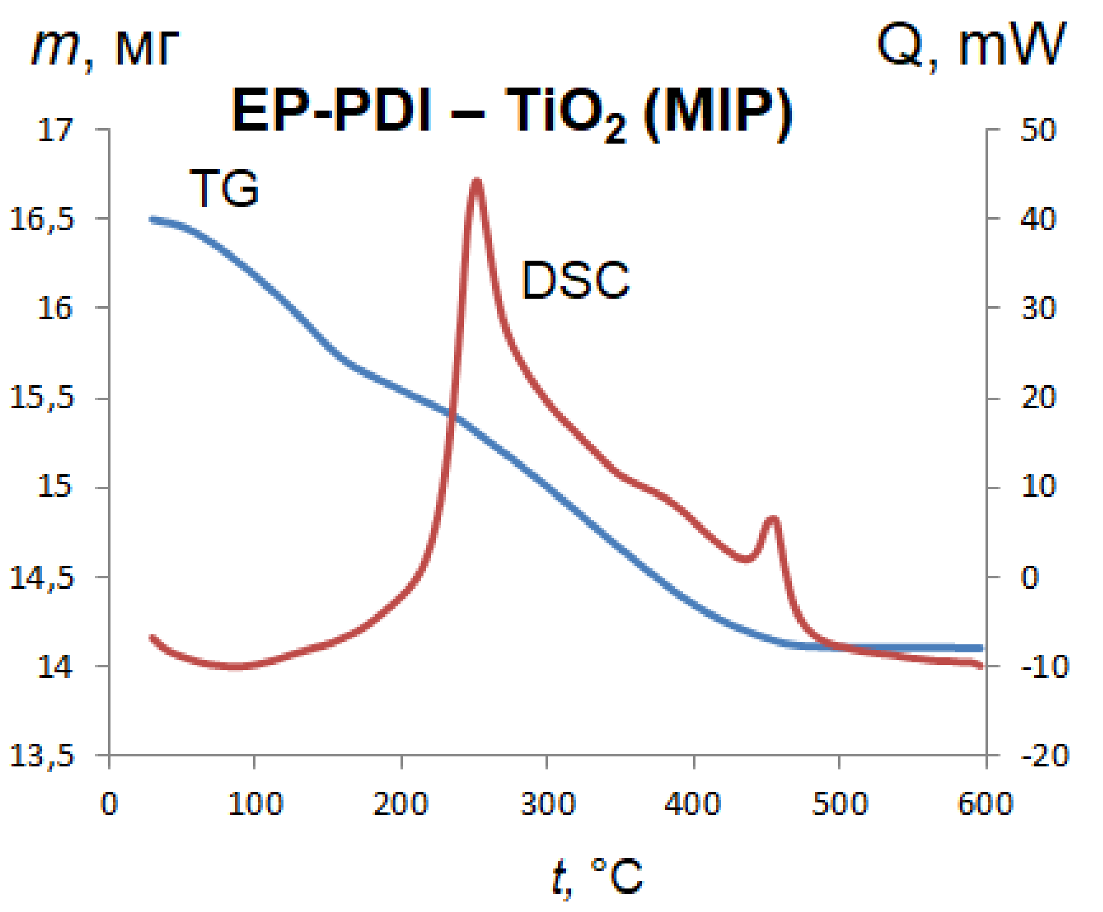
FTIR spectra of MIP (2) and NIP (1) samples after PDI – TiO$_2$ (I synthesis)

TGA & DSC method (oxidizing environment, 10° C/min)



PDI-Taz-C_5OOH – TiO_2						
Synthesis	I		II		III	
Sample	MIP	NIP	MIP	NIP	MIP	NIP
Mass loss, wt.%	**22.39**	**3.77**	**13.36**	**10.75**	13.10	11.91





Synthesis	EP-PDI – TiO_2 (I)	
Sample	MIP	NIP
Mass loss, wt. %	**14.53**	**12.47**

Diffuse reflectance spectroscopy for determining the band gap energy (*E*g, eV)

$$\alpha h\nu = K \cdot (h\nu - E_g)^{n/2} \qquad (1)$$

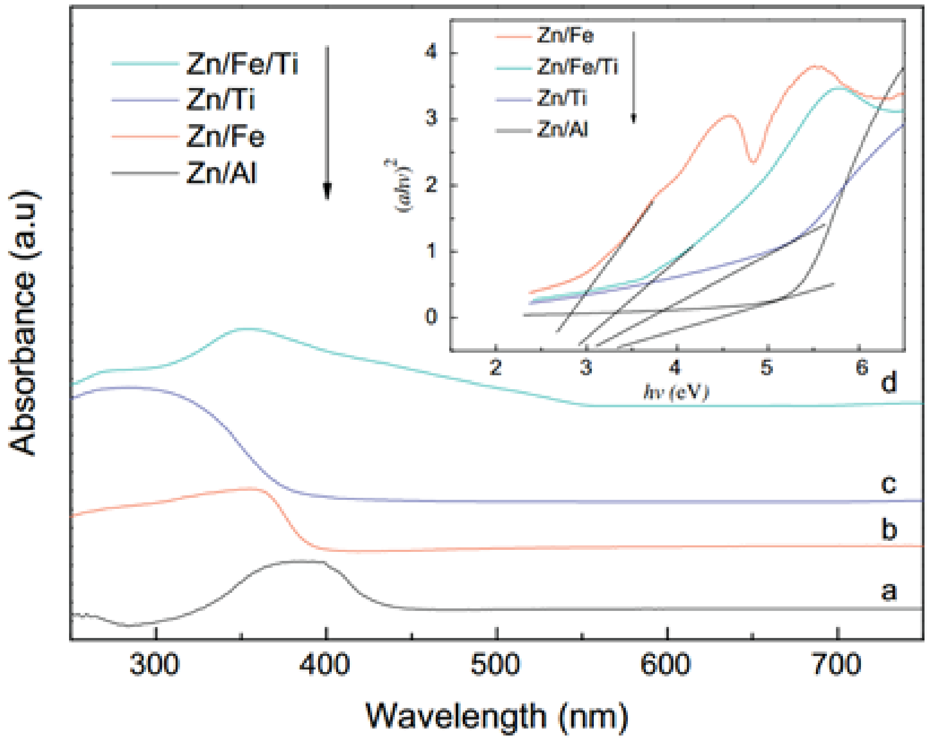
$$(\alpha h\nu)^2 = K^2 \cdot (h\nu - E_g) \qquad (2)$$

$$K^2 \cdot E_g = K^2 \cdot h\nu \text{, } (\alpha h\nu)^2 = 0 \qquad (3)$$

$$E_g = h\nu \qquad (4)$$

where α, h, ν and K are the absorption coefficient, Planck constant, light frequency, proportionality constant, respectively.

n = 1 (is for a directly allowed transition).



* Xia S.-J., Liu F.-X., Ni Z.-M.. Xue J.-L., Qian P.-P. Layered double hydroxides as efficient photocatalysts for visible-light degradation of Rhodamine B / S.-J. Xia. F.-X. Liu. Z.-M. Ni. J.-L. Xue. P.-P. Qian // J. Colloid Interface Sci. – 2013. –V. 405. – P. 195–200.

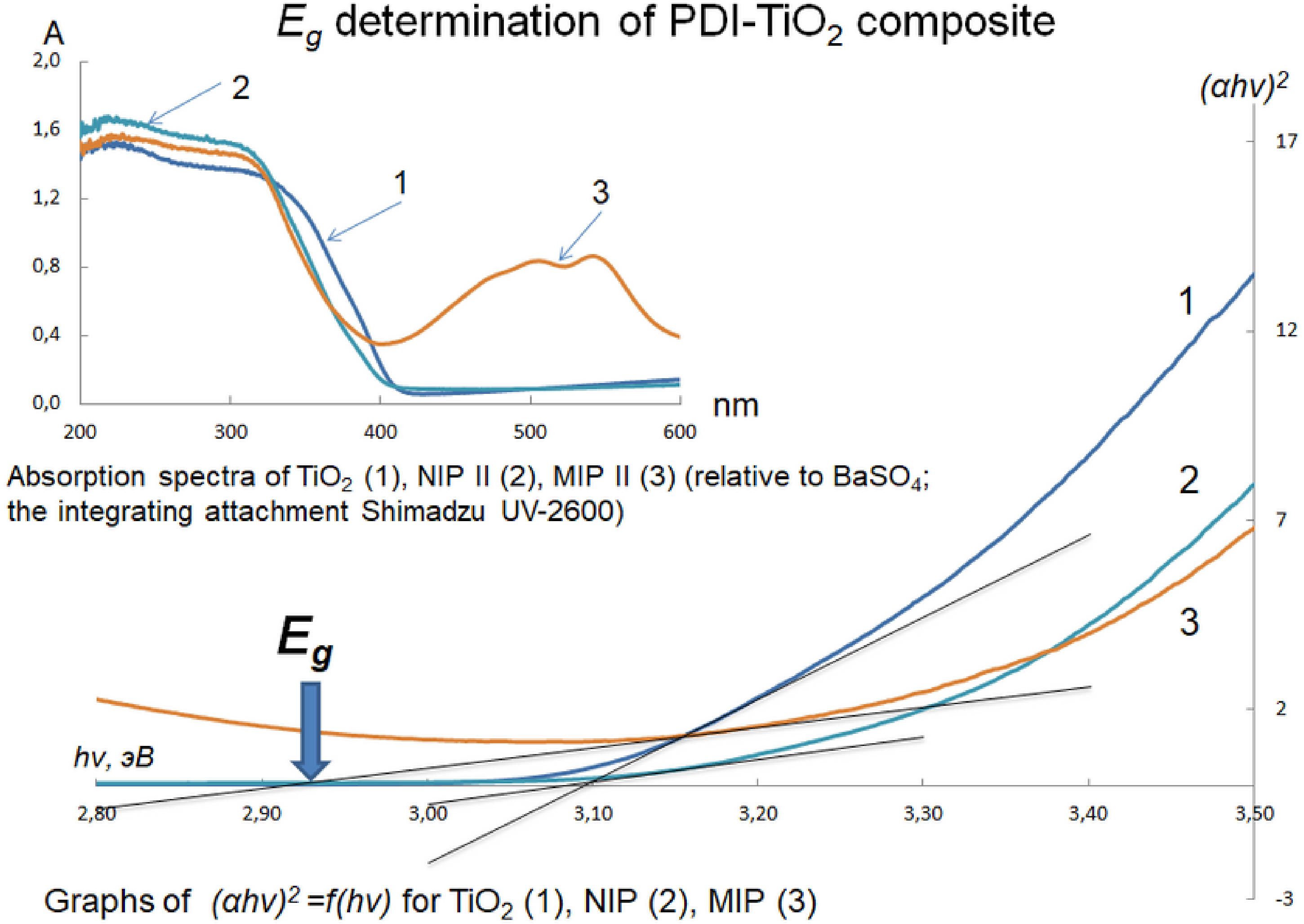
Method: → 50 mg sample → 300 µl ethanol → 10 min utrasound → Putting suspension on glass

NIP

MIP

* – washed with 5 ml of ethanol
** – after rebinding

E_g determination of PDI-TiO$_2$ composite



Absorption spectra of TiO$_2$ (1), NIP II (2), MIP II (3) (relative to BaSO$_4$; the integrating attachment Shimadzu UV-2600)

Graphs of $(\alpha h\nu)^2 = f(h\nu)$ for TiO$_2$ (1), NIP (2), MIP (3)

Sample	Precursor: template	E_g, eV	±δ, eV (n=3, P = 0.95)	Δλ, nm
TiO$_2$		3.110	0.006	
EP- PDI (I)				
NIP	1:85	3.109	0.007	0.64
MIP		3.076	0.011	4.39
EP- PDI (II)				
NIP	1:100	3.155	0.008	-
MIP		3.109	0.005	5.82
PDI-Taz-C$_5$OOH (III)				
NIP	1:81	2.976	0.049	15.8
MIP		2.886	0.104	**28.9**
MIP*		2.624	0.157	**71.7**
MIP**		2.847	0.016	**34.6**

Adsorption properties of NIP and MIP PDI-TiO2 nanoparticles

Sample	*Rebinding 1*		*Rebinding 2*		*Rebinding 3*		IF_1 (max)	IF_2 (max)	IF_3 (max)
	$q_{max} \cdot 10^7$, mol/g	Time, t	$q_{max} \cdot 10^7$, mol/g	Time, t	$q_{max} \cdot 10^7$, mol/g	Time, t			
PDI-Taz-C_5OOH (I)									
MIP	5.7	24 h	6.2	48 h	4.19	3 h	1.15	0.92	**7.94**
NIP	5.0	2 h	6.7	48 h	4.57	4 h			
PDI-Taz-C_5OOH (II)									
MIP	7.0	48 h	**7.5**	48 h	**18.6**	24 h	0.40	**2.24**	4.2
NIP	21.7	5 min	**4.1**	48 h	**10.2**	8 h			
PDI-Taz-C_5OOH (III)									
MIP	1.6	10 min	5.7	24 h	0.437	3.5 h	0.09	**1.15**	0.08
NIP	22	5 min	4.9	24 h	14	4 h			
EPI-PDI (I)									
MIP*			**17.8**	24 h				**1.13**	
NIP*			**15.7**	24 h					

*-after calcination at 400°C

Templat removing conditions:

1) acetic acid: ethanol (96.5%) 1: 9, 1 day in a dark place, centrifugation and drying until 40 °C.

2) calcination at 400°C for 1 h

Statical sorption conditions:

1) 100 mg of MIP and NIP samples into 50 mL 2.0 µmol/L PDI.

2) 3 ml aliquote through 5-10 min was centrifuged and measured at 522 nm (for 6-24 h).

Pseudo-first order kinetics:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2,303} t$$

Pseudo-second order kinetics:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

$$IF = \frac{q_{МИП}}{q_{НИП}} \qquad q_t = \frac{(c_0 - c_t) * V}{m}$$

q_t – sorption capacity, mol / g;

c_0 – initial concentration PDI-Taz-C_5OOH, M ($2 \cdot 10^{-6}$);

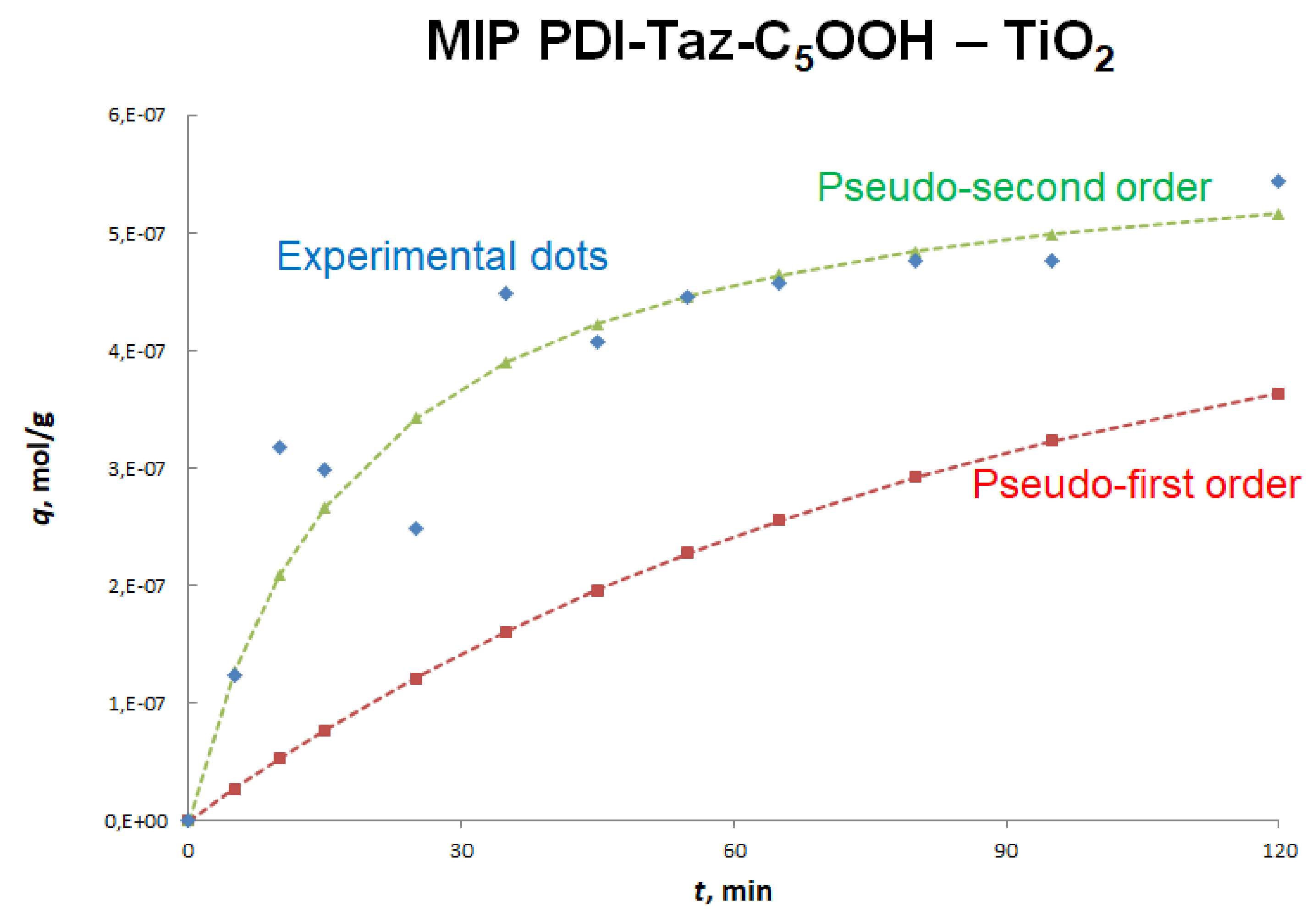
c_t – concentration PDI-Taz-C_5OOH in the moment of time t, M;

V – volume of solution PDI-Taz-C_5OOH, l;

m – sample weight, g; IF – imprinting factor

Rebinding kinetics of PDI-Taz-C5OOH – TiO2 samples

Sample	**3^{rd} Rebinding**					
	Pseudo-first order			Pseudo-second order		
	k_1, min^{-1}	$q_e \cdot 10^7$, mol/g	R^2	k_2, g·mol^{-1}·min^{-1}	$q_e \cdot 10^7$, mol/g	R^2
Synthesis I						
MIP	$1{,}3 \cdot 10^{-3}$	2.2	0.715	**$2{,}9 \cdot 10^{5}$**	**3.0**	**0.828**
NIP	**$3{,}6 \cdot 10^{-3}$**	**8.5**	**0.881**	$2{,}4 \cdot 10^{3}$	11.2	0.822
Synthesis II						
MIP	$2{,}2 \cdot 10^{-3}$	17.7	0.916	$2{,}8 \cdot 10^{3}$	16.9	0.901
NIP	$3{,}1 \cdot 10^{-3}$	11.5	0.797	$4{,}0 \cdot 10^{3}$	9.3	0.840
Synthesis III						
MIP	$7{,}1 \cdot 10^{-4}$	0.3	0,542	**$5{,}0 \cdot 10^{5}$**	**0,4**	**0,877**
NIP	**$4{,}7 \cdot 10^{-3}$**	**2.5**	**0.931**	**$1{,}6 \cdot 10^{3}$**	**28.3**	**0.929**



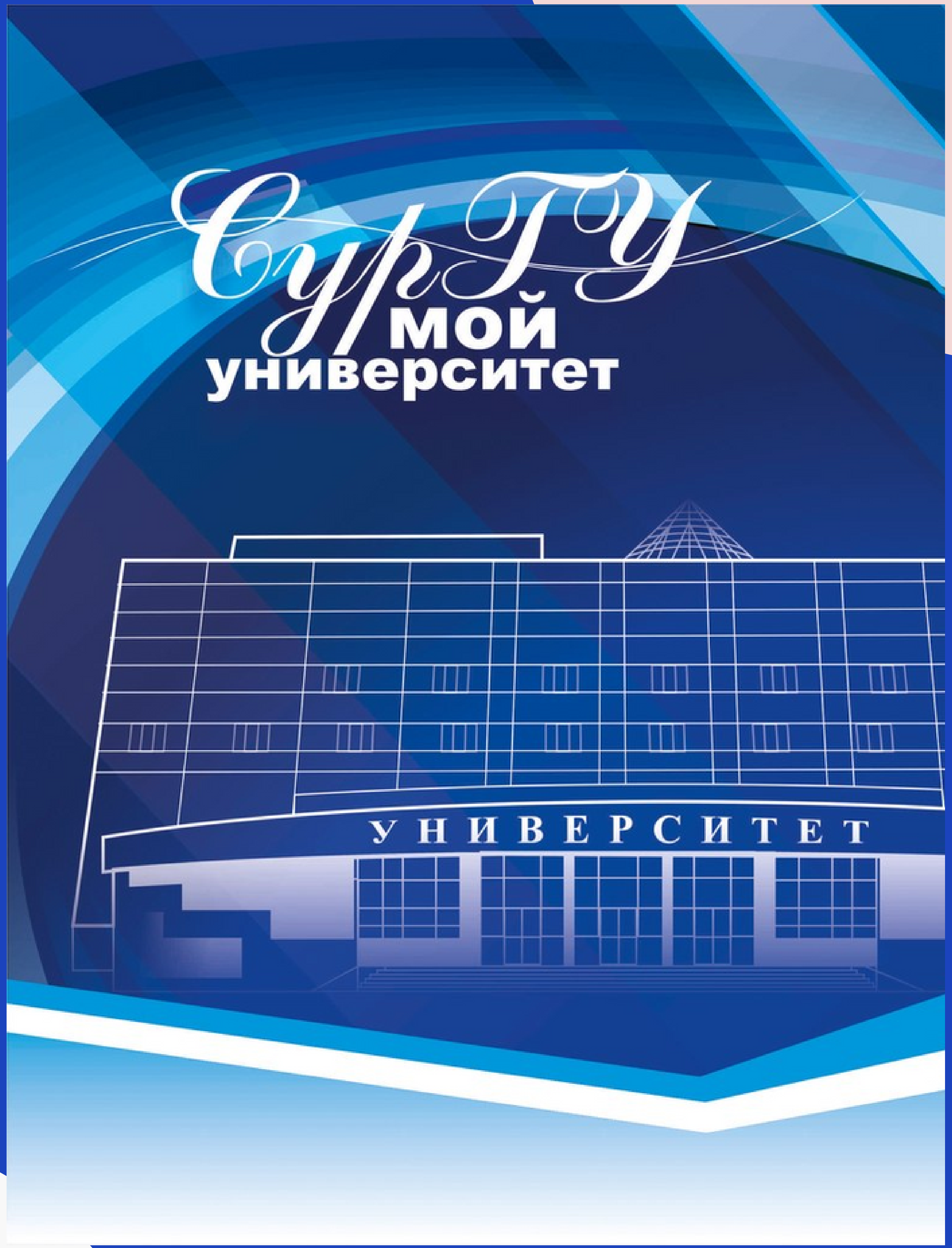
Findings:

- An organo-mineral composite PDI-TiO_2 was obtained by surface molecular imprinting using sol-gel technique;

- Characterization of the samples by **FTIR** showed the presence of template molecules (PDI-Taz-C_5OOH & EP-PDI) and the precursor of the sol-gel synthesis. By **laser diffraction** an increase in the MIP particle size compared with the NIP were shown. The **TGA&DSC** showed the mass loss MIP PDI-TiO_2 samples more than 13% and two-stage process of thermal oxidation at 250 and 450°C.

- The optical properties of MIP PDI-Taz-C_5OOH -TiO_2 were studied: a decrease in the band gap (ΔE_g = 0.47 eV) and an adsorption length shift in the visible spectral region ($\Delta\lambda$ = 72 nm) was shown. The adsorption kinetics of rebinding follows the pseudo-second order. The sorption capacity after template removal with ethanol has reached 0.75 μmol/g PDI-Taz-C_5OOH, and after calcination at 400°C - 1.8 μmol/g EP-PDI.

- The effectiveness of molecular imprinting and the possibility of the presence of molecular imprints of perylenediimide dye in the films on the surface of TiO_2 nanoparticles are shown: molecular imprinted (MIP) material can rebind 2 times more PDI-Taz-C_5OOH than unimprinted (NIP).



Yuliya Petrova

Institute of Natural & Technical Sciences Director

Surgut State University

☎ +7 (3462) 76 30 91

✉ PETROVA_JUJU@SURGU.RU

f YULIYA PETROVA