LIGHT 17 16-20 October 2017 Ringberg Castle

Organic materials development for fast photodetectors

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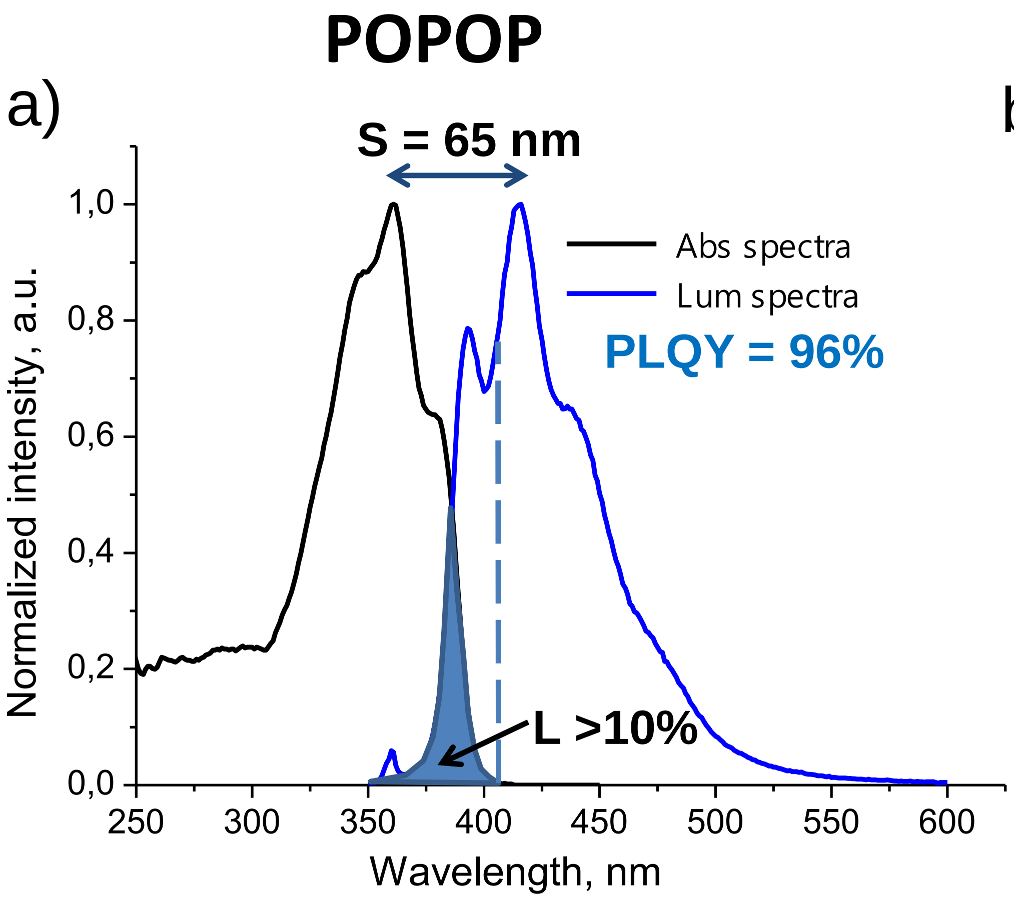
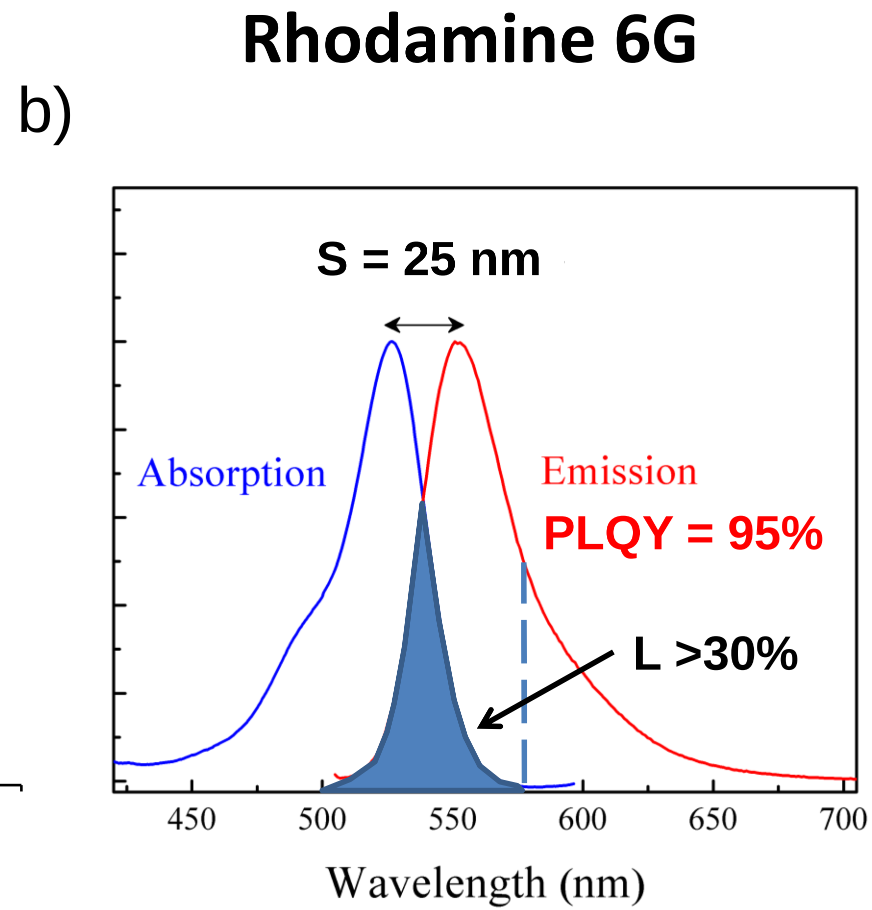
Outline

1. Can we improve the properties of organic luminophores?
2. Organosilicon nanostructured luminophores (NOLs) and their properties
3. Applications of NOLs in elementary particles photodetectors:
   a) plastic scintillators
   b) scintillating fibers
   c) VUV spectral shifters for noble gas detectors
   d) UV spectral shifters for pure CsI detectors, Cherenkov light and liquid scintillators
4. Other applications of NOLs
5. Conclusions

Optical properties of the best organic luminophores





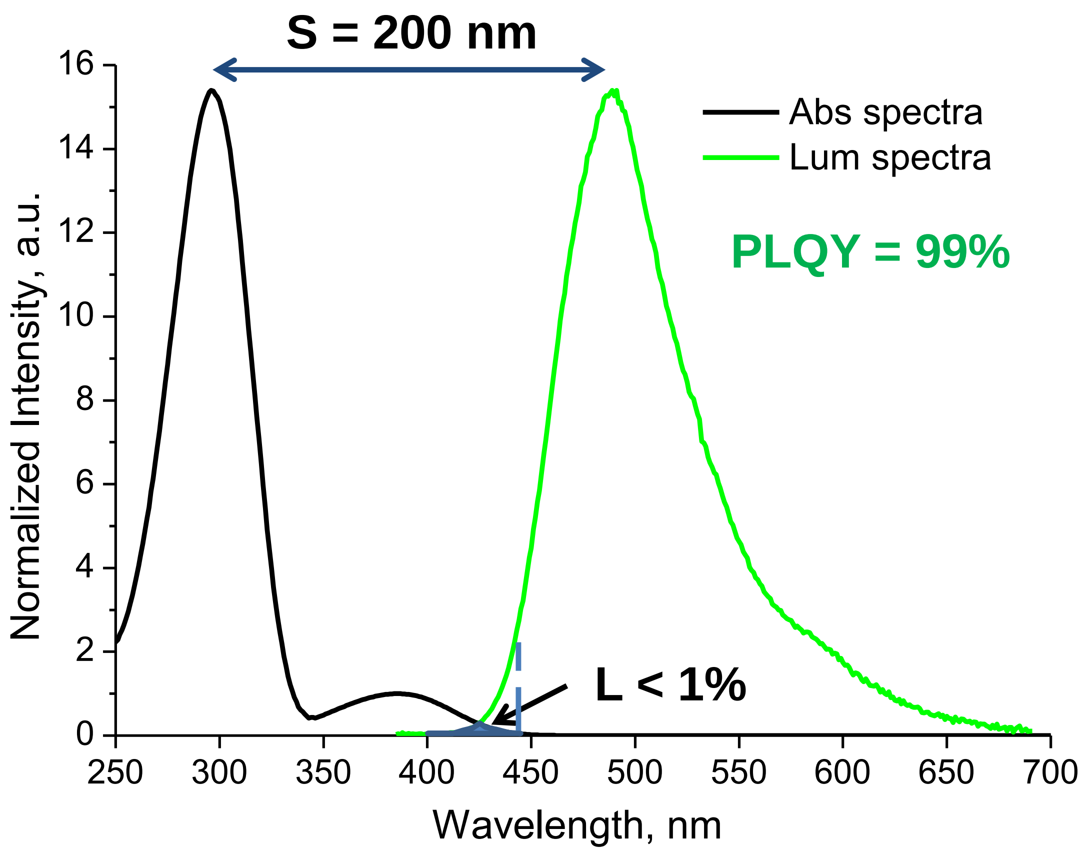
Main Drawbacks of Organic luminophores:

1) Small Stokes shift (S), 2) Large losses (L) of the luminescence due to self-absorption,

3) Luminescence quenching due to aggregation.

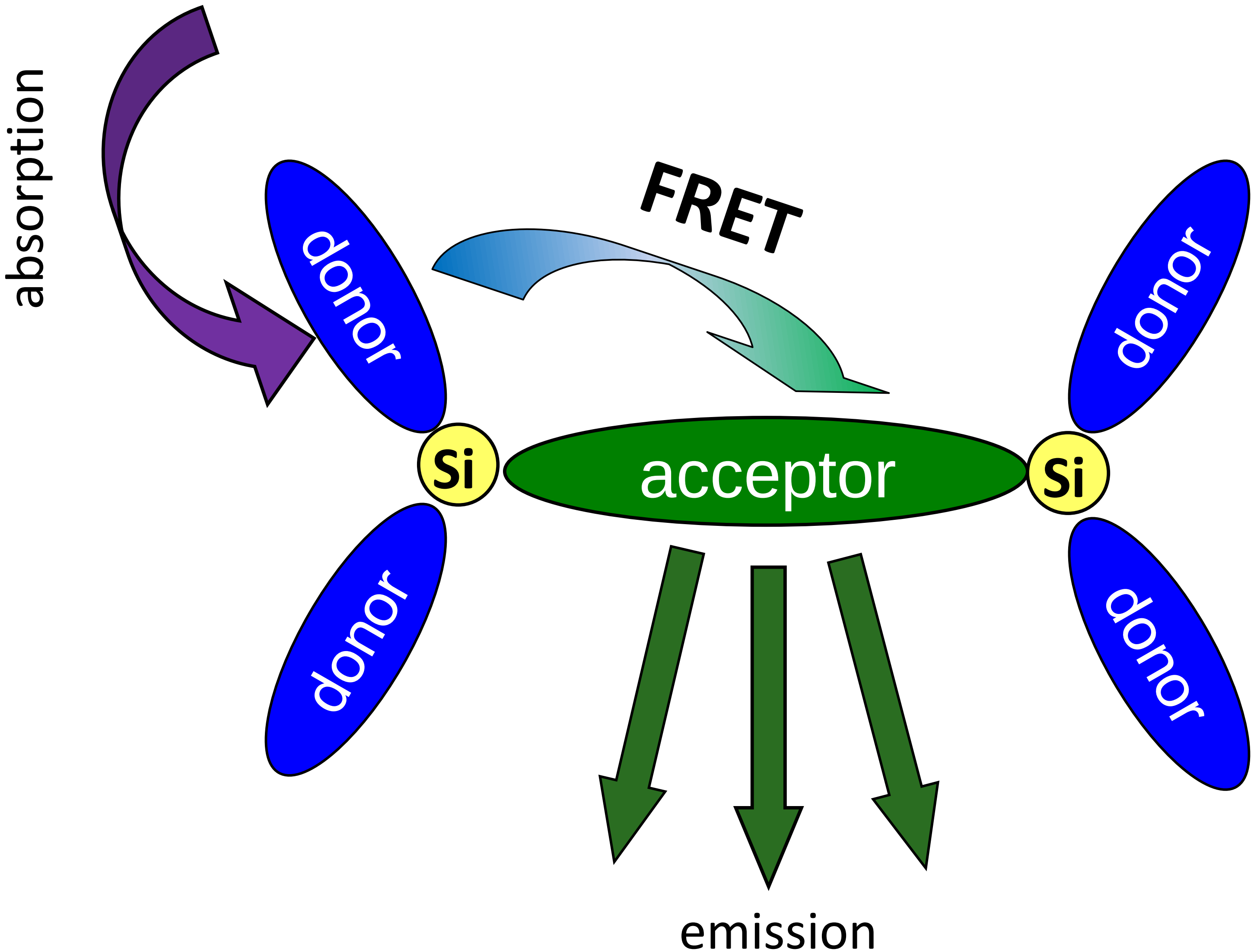
Can we improve the situation?

Can we improve the situation?
YES!

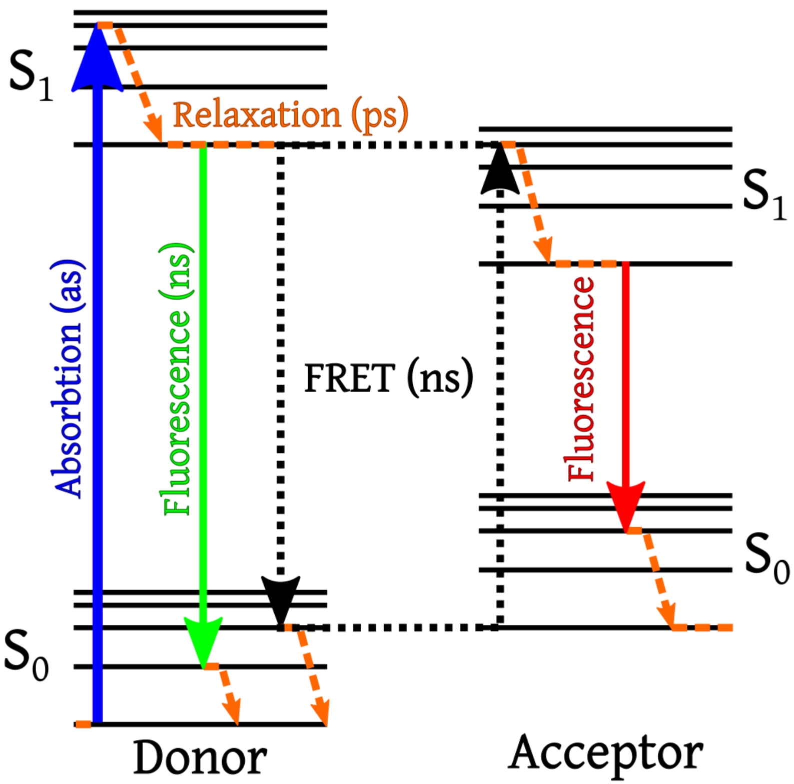


Spectral luminescence properties of nanostructured organosilicon luminophore (NOL)

NOL works as “Molecular antennae” based on efficient intramolecular energy transfer



Förster resonance energy transfer (FRET)



FRET conditions:

1) small **distance** between the luminophores

$$\left(\frac{\vec{R}_{DA}^{0}}{\vec{R}_{DA}}\right)^{6}$$

2) **spectra overlap**;

$$\left(\int_{0}^{\infty} f_D(\nu)\cdot\varepsilon_A(\nu)\frac{d\nu}{\nu^4}\right)^{1/6}$$

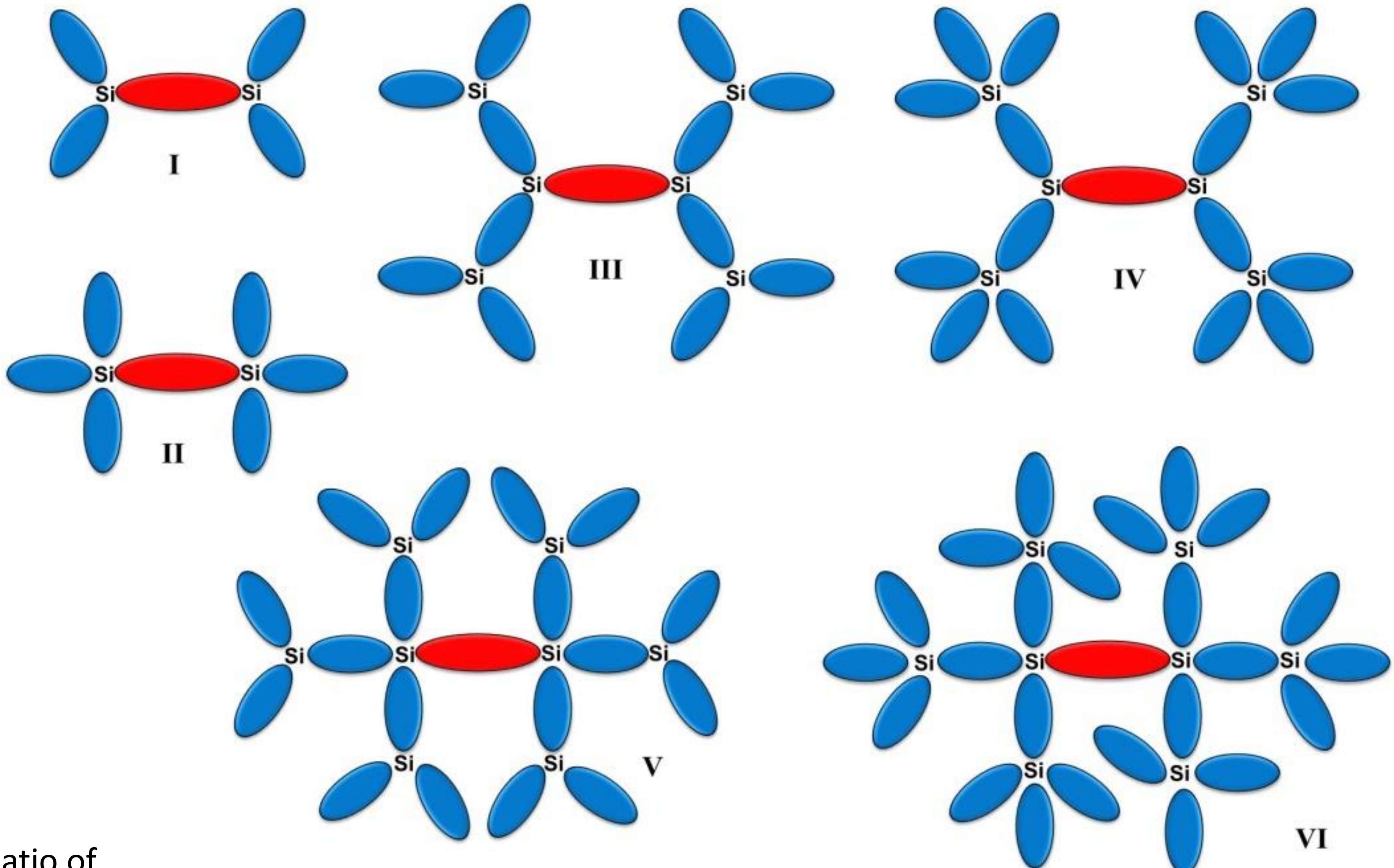
3) **orientation** of the luminophores.

$\vec{R}_{DA}$ – distance between the centers of the donor and acceptor fragments

$\vec{R}_{DA}^{0}$ – critical radius of the inductive-resonance energy transfer

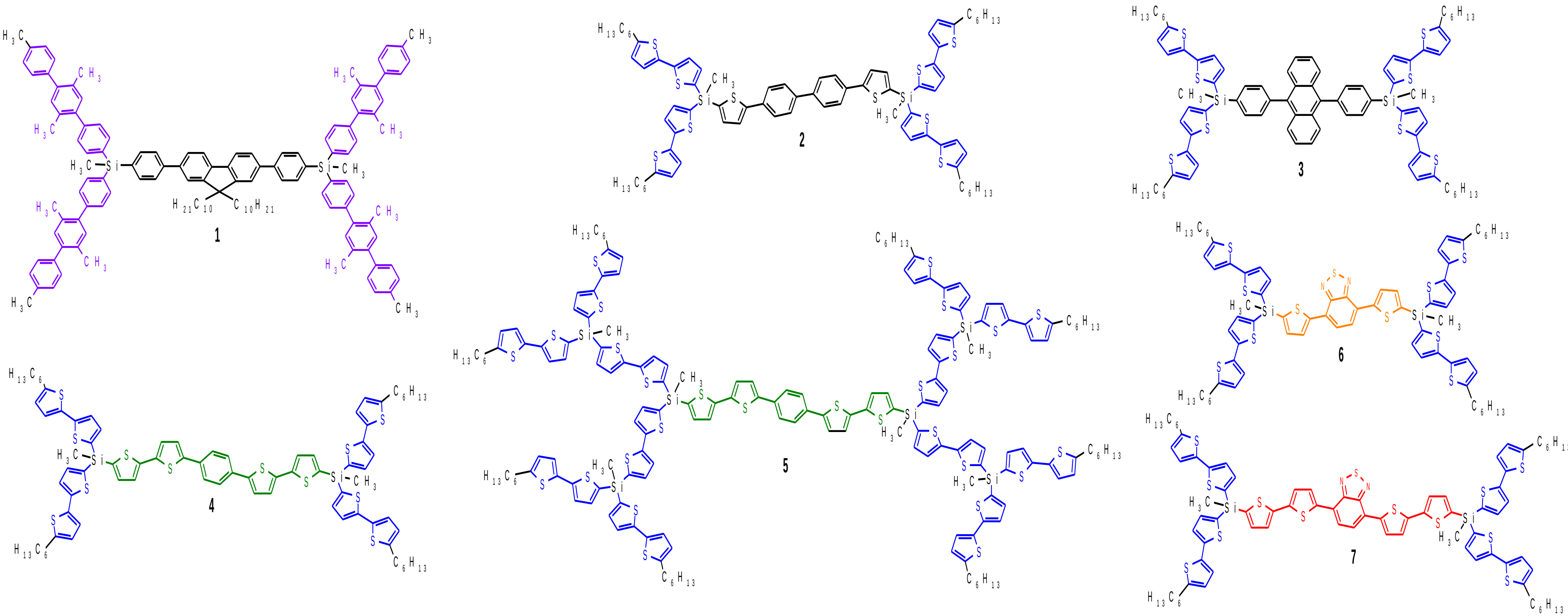
$\varepsilon_A(\nu)$ – acceptor absorption spectra, $f_D(\nu)$ – donor luminescence spectra

Schematic representation of NOLs with different topology

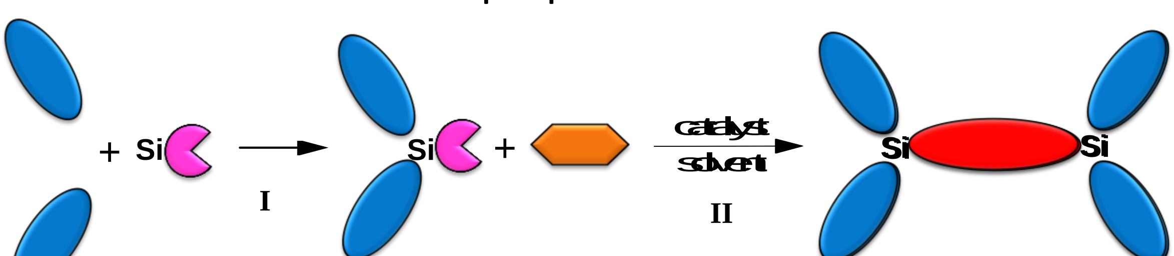


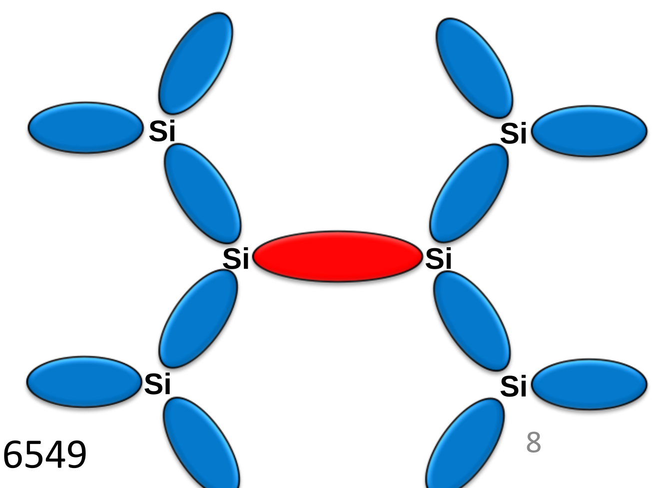
Ratio of
Donor (blue) to Acceptor (red) luminophores: 4 (**I**), 6 (**II**), 12 (**III**), 16 (**IV**), 18 (**V**) or 24 (**VI**)

Chemical structures of the first NOLs



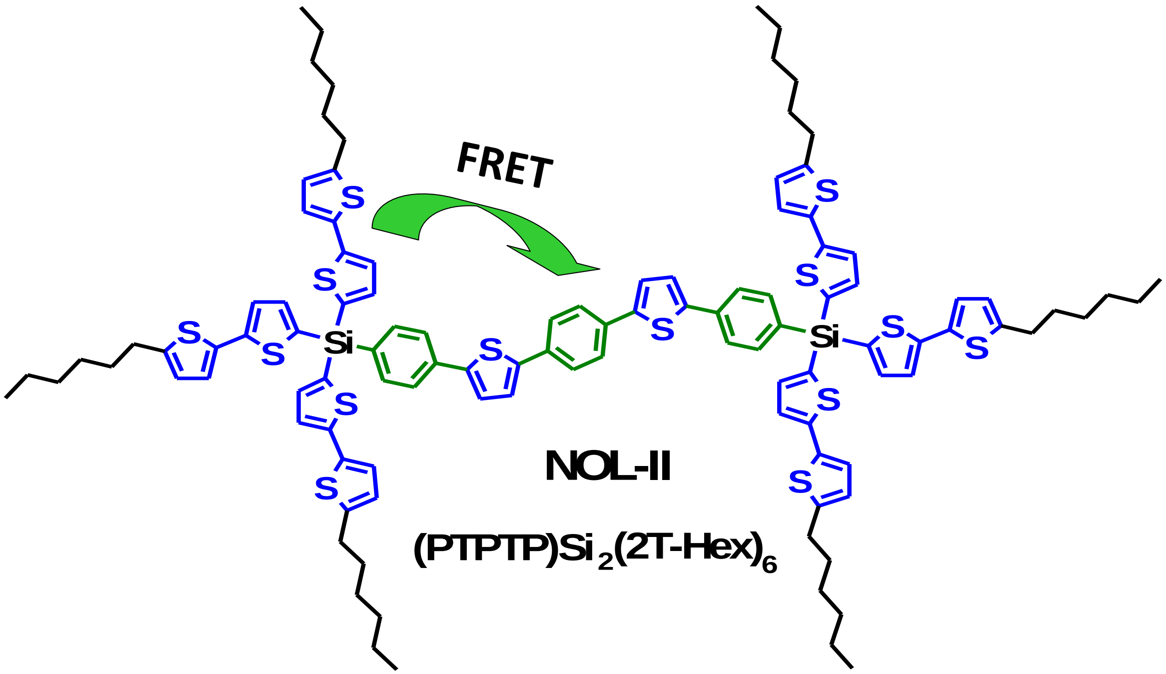
Schematic representation of the main synthetic steps for the preparation of NOLs.



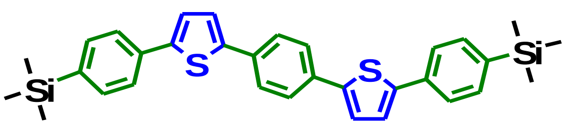


S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, et. al., ***Sci. Rep.* 2014**, *4*, 6549

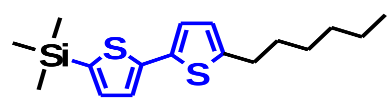
Modelling of electronic properties of NOLs



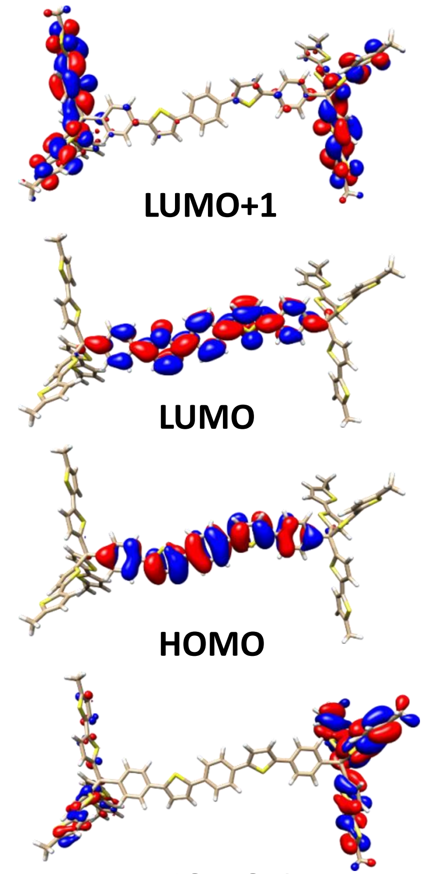
NOL-II
$(PTPTP)Si_2(2T\text{-}Hex)_6$



TMS-PTPTP-TMS



TMS-2T-Hex

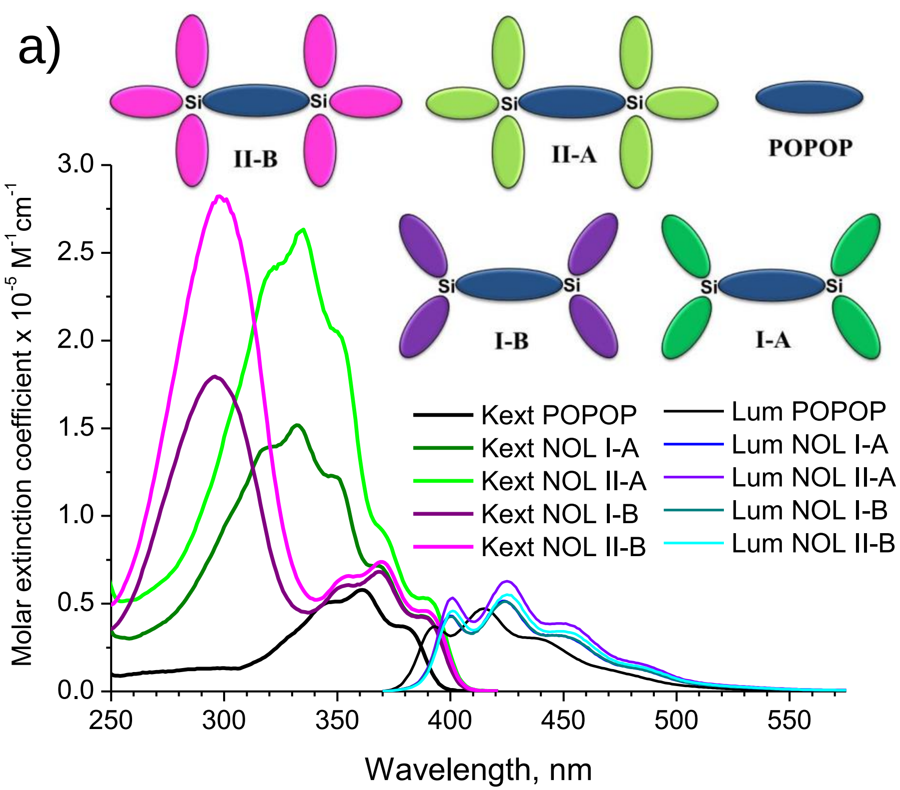


Luminophore	τ_{exp}/τ_{calc}, ns	$\tilde{\nu}^{exp}_{S_0-S_1}/\tilde{\nu}^{calc}_{S_0-S_1}$, cm^{-1}	$f^{exp}_{osc}/f^{calc}_{osc}$	ETE_{exp}/ETE_{calc}, %
NOL	0.90[b]/ -	-	-	97/98
	0.93[a]/0.88	23600/24800	2.85/2.77	
TMS-2T-Hex	≈0.17/1.53	28500/32900	0.89/0.90	
TMS-PTPTP-TMS	**1.01/0.95**	**23900/25600**	**2.46/2.41**	

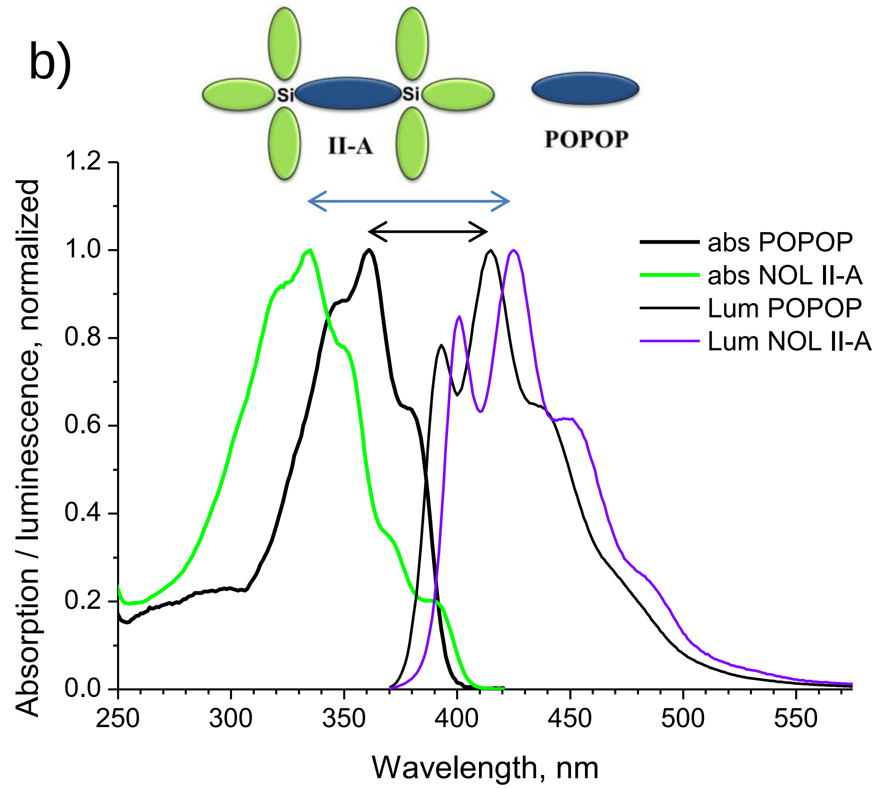
T. Starikova, N. Surin, O. Borshchev, et.al. ***J. Mater. Chem. C***, **2016**, 4, 4699

Tuning the absorption spectra of NOLs

Molar extinction coefficients



Normalized absorption



The higher is a donor-acceptor ratio in the NOL, the larger is its molar absorption coefficient.

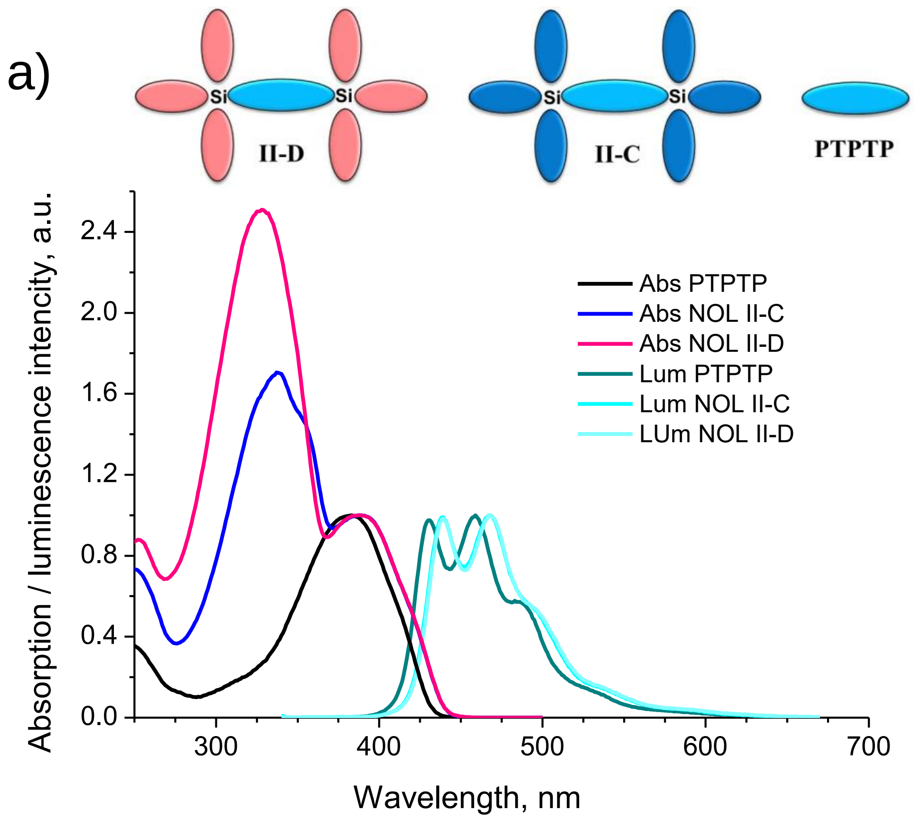
NOLs absorb the UV light more efficiently and can be used in smaller concentrations.

NOLs have increased Stokes shifts from S = 65 nm for POPOP to 115 nm for NOL I-A.

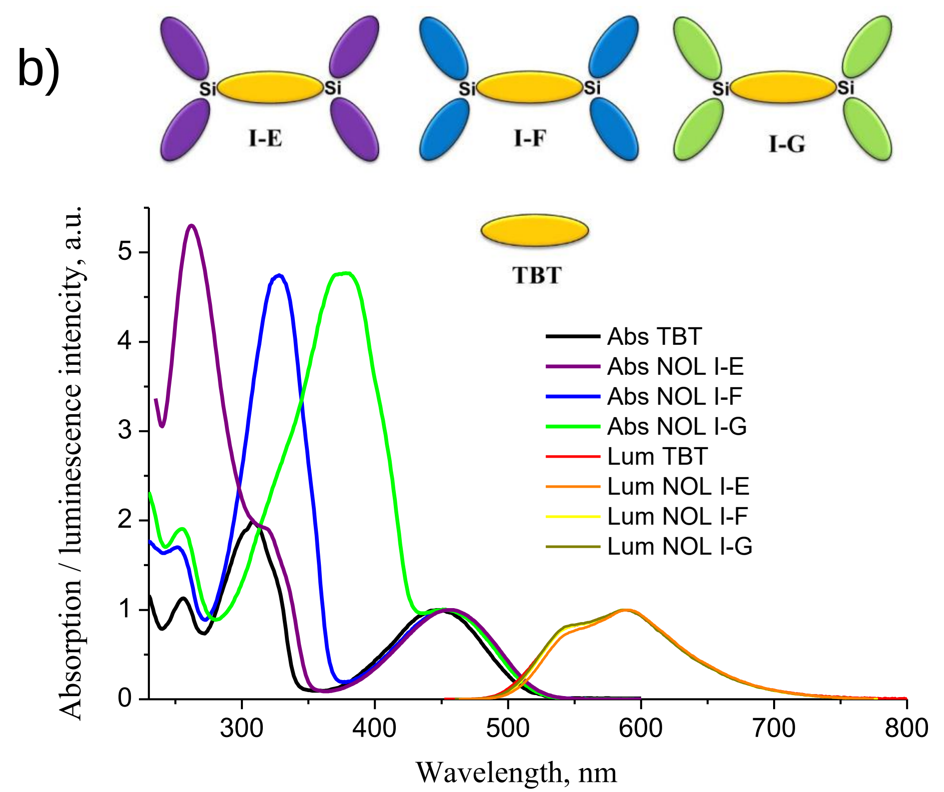
Ponomarenko S. A., Surin N. M., Borshchev O. V., at.al., ***Proc. SPIE* 2015**, 9545, 954509

Tuning the absorption spectra of NOLs

Green-emitting NOLs



Yellow-emitting NOLs



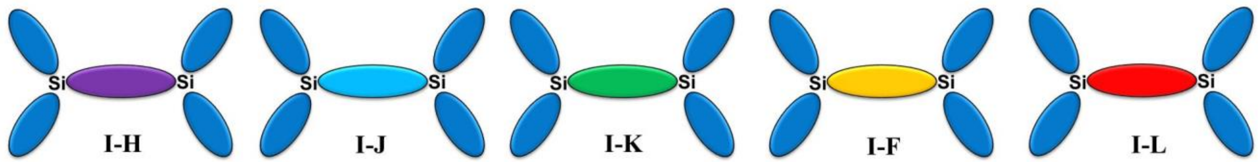
NOLs absorb the UV light more efficiently then the acceptor luminophores themself.

Blue-emitting NOLs have the pseudo Stokes shifts up to 110 nm.

Yellow-emitting NOLs have the pseudo Stokes shifts up to 330 nm!

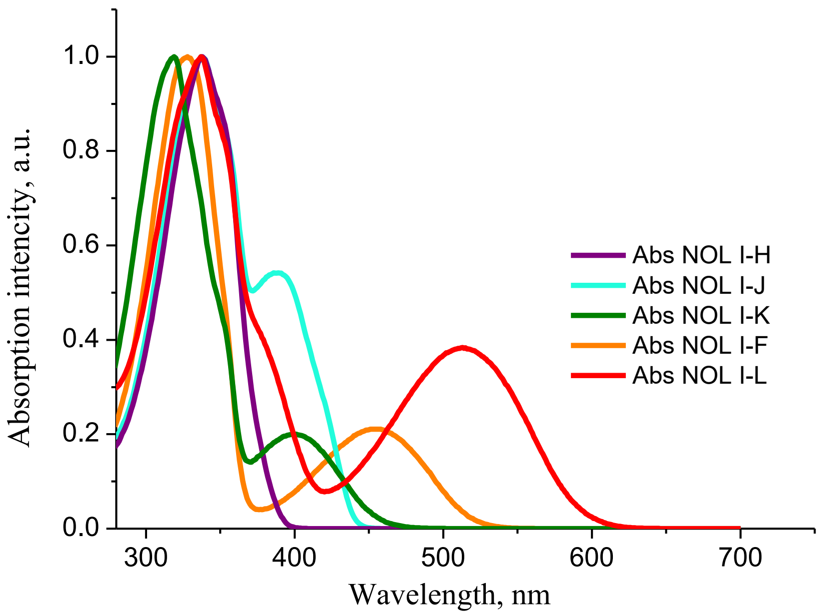
Ponomarenko S. A., Surin N. M., Borshchev O. V., at.al., ***Proc. SPIE* 2015**, 9545, 954509

Tuning the luminescence spectra of NOLs



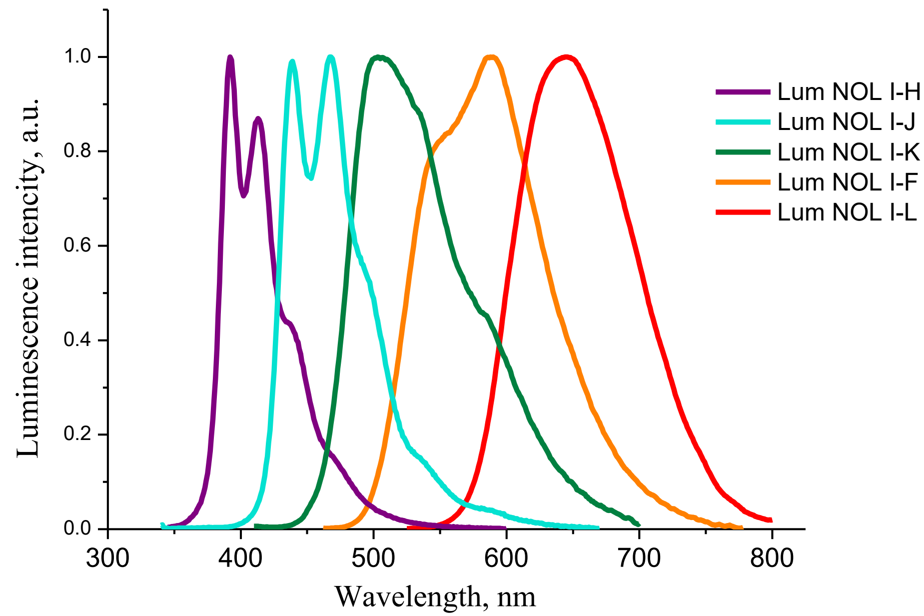
a)

Absorption spectra



b)

Luminescence spectra

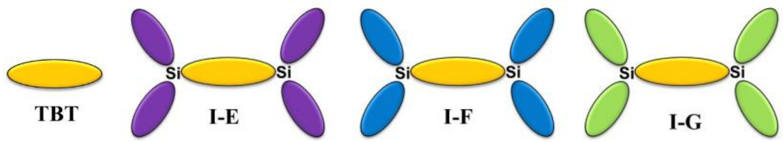


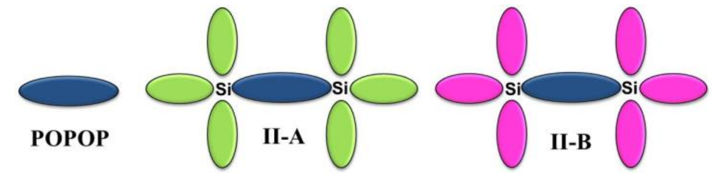
The main absorption maxima of NOLs are determined by the donor and lies in the UV range.

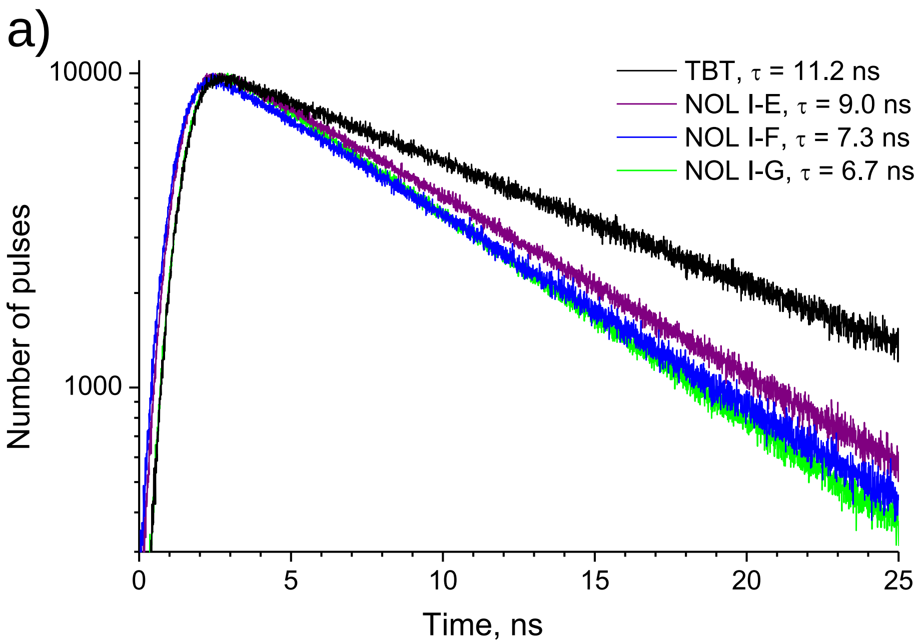
The luminescence spectra of NOLs are determined by the acceptor luminophore emissions, and can cover the whole visible spectral range – from violet to red.

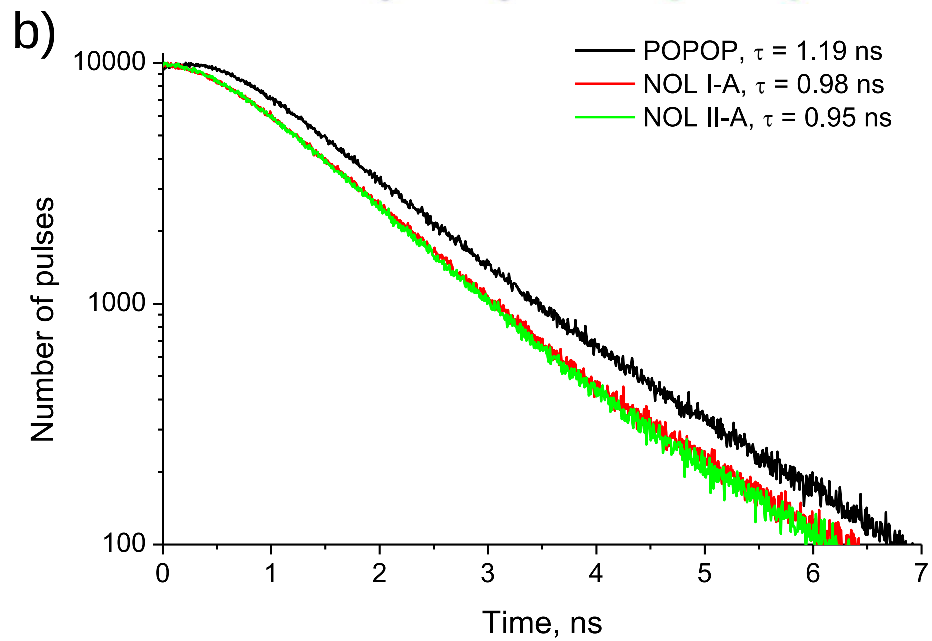
Ponomarenko S. A., Surin N. M., Borshchev O. V., at.al., ***Proc. SPIE* 2015**, 9545, 954509

Improving the luminescence decay time of the acceptor luminophore by NOLs









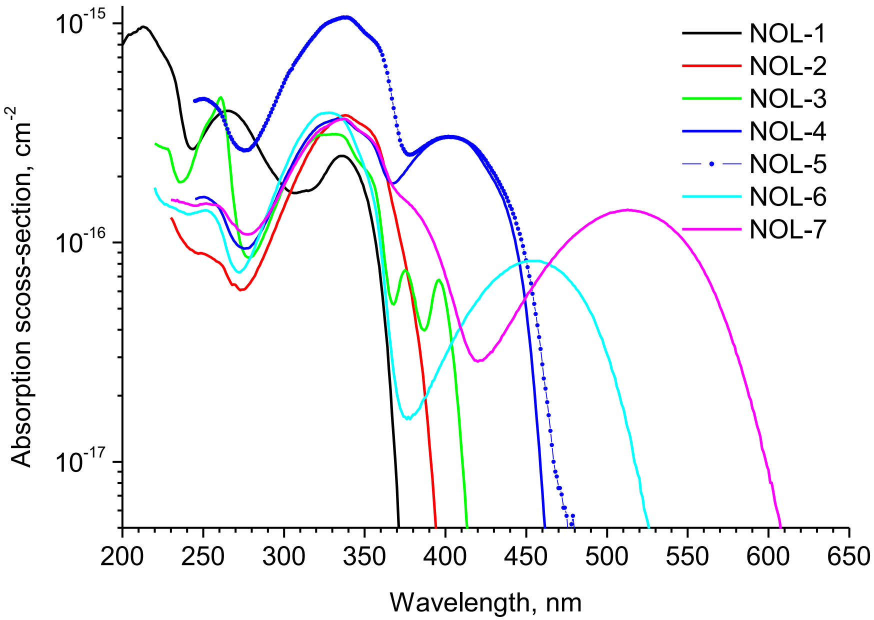
Yellow NOLs have 1.25 – 1.67 times faster luminescence than the TBT itself. Moreover, NOLs I-E and I-F have PLQY of 85 and 92%, respectively, which exceed 74% measured for TBT under the same conditions.

Blue NOLs have 1.21 – 1.25 times faster luminescence than the POPOP itself. Nevertheless, PLQY of these NOLs is essentially the same as POPOP, 96-98%.

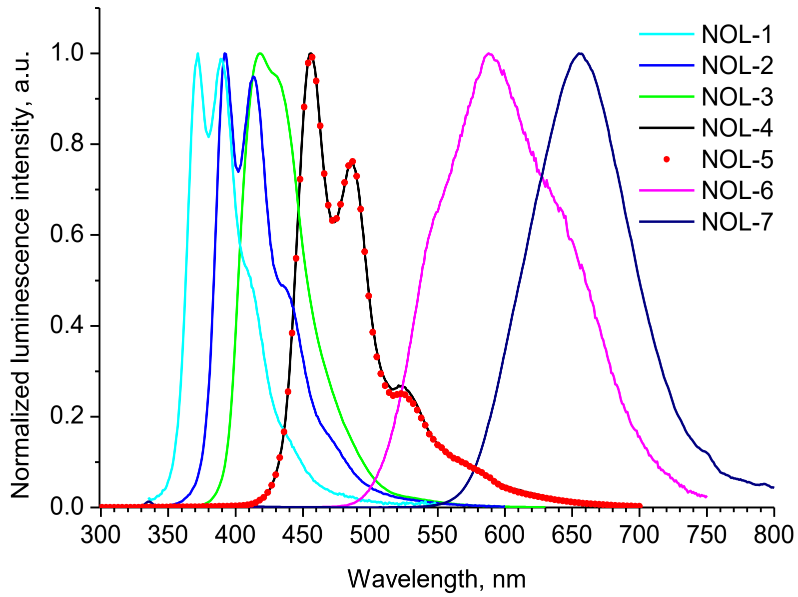
Ponomarenko S. A., Surin N. M., Borshchev O. V., at.al., ***Proc. SPIE* 2015**, 9545, 954509

Main advantages of NOLs

Spectral distributions
of absorption cross-sections



Luminescence spectra

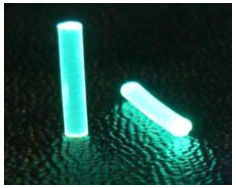


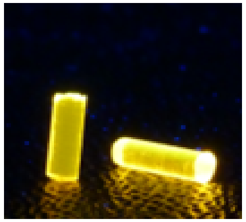
Main advantages of NOLs:

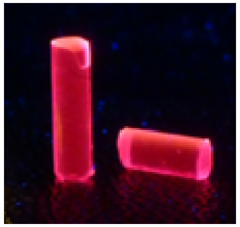
- ✓ absorption in a wide optical spectral region that can be tuned;
- ✓ 5-10 times higher absorption cross-sections as those of the best organic luminophores;
- ✓ high photoluminescence quantum yield (up to 99%);
- ✓ large pseudo Stokes shift (up to 250 – 330 nm);
- ✓ luminescence spectra in the required wavelength region;
- ✓ short luminescence lifetime;
- ✓ good solution processabilty.

A library of nanostructured organosilicon luminophores (NOLs)

	Absorption, λ_{max}, nm	Luminescence, λ_{max}, nm	Luminescence quantum yield Q_F, %
NOL 1	213, 262,342	390, 412	73
NOL 2	213, 262,366	390, 420	78
NOL 3	213, 262,335	373, 390	85
NOL 4	213, 262,367	396, 420	96
NOL 5	213, 262, 375, 396	416, 436	82
NOL 6	213, 262, 316, 457	588	87
NOL 7	296, 367	396, 419	96
NOL 8	337, 348	396, 419	85
NOL 9	327, 455	588	95
NOL 10	337, 513	655	78
NOL 11	332	396, 420	93
NOL 12	213, 262,342	396, 420	99
NOL 13	319, 400	502	83
NOL 14	302, 402	502	90
NOL 15	375, 455	588	65
NOL 16	296, 386	486	94
…	…	…	…
NOL 45	340	446	90



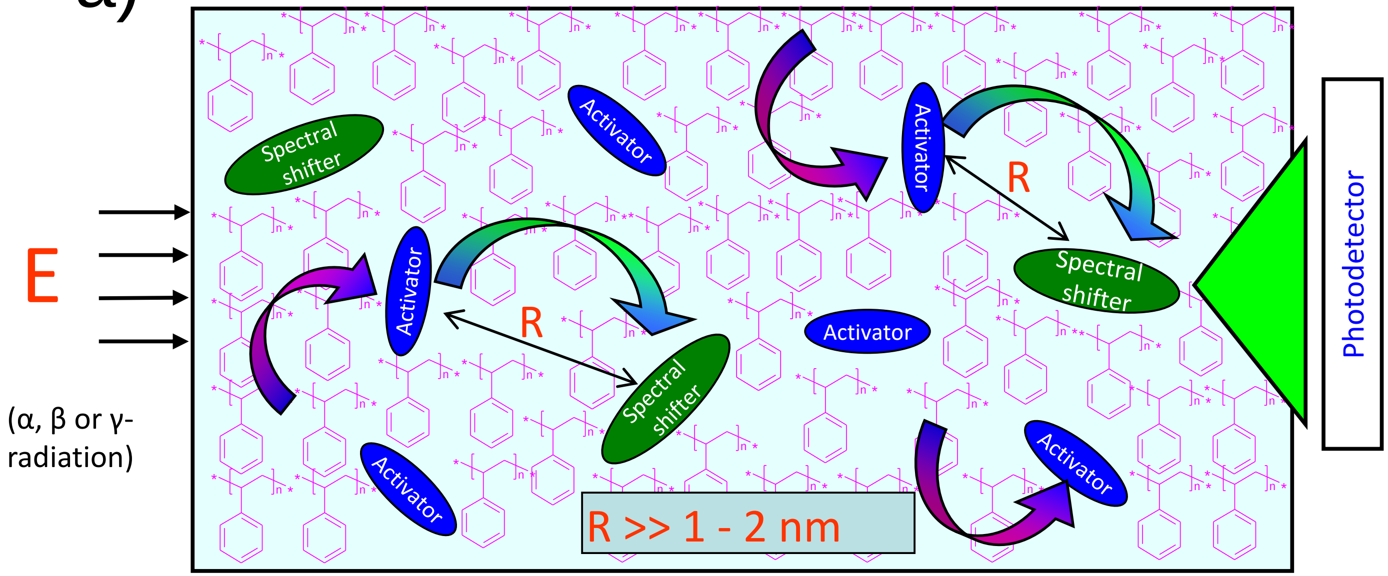




www.luminnotech.com

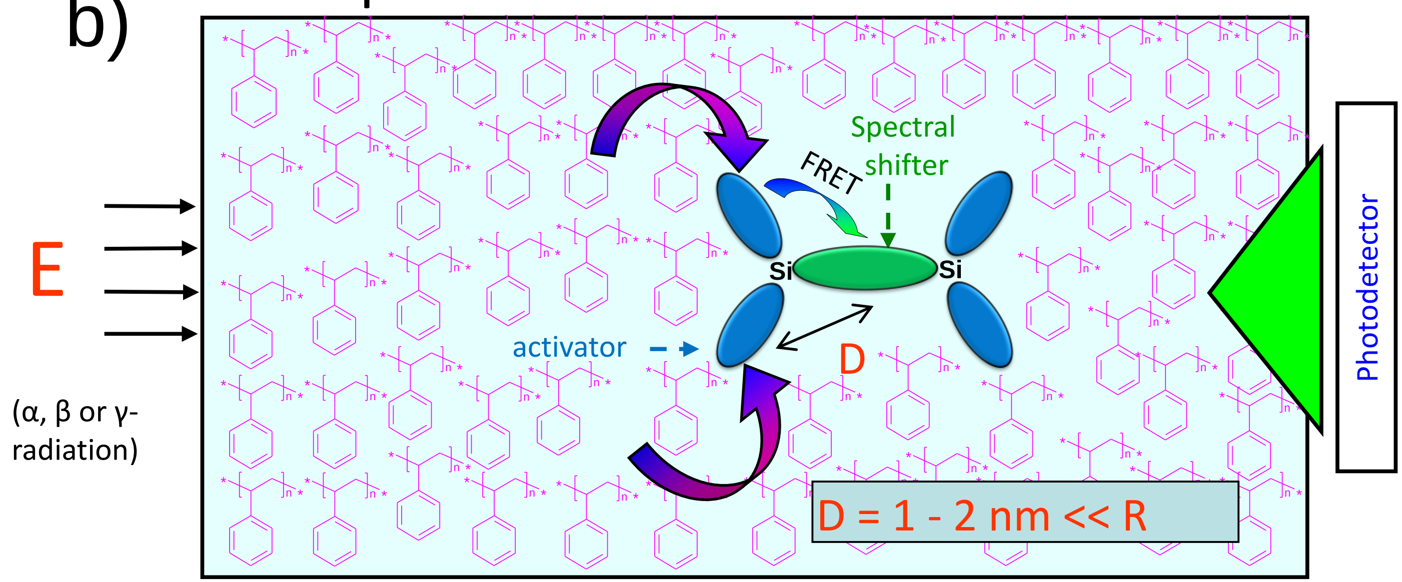
Application of NOLs in plastic scintillators

a) classical plastic scintillator



radiative energy transfer between the activator and spectra shifter

b) plastic scintillator based on NOLs

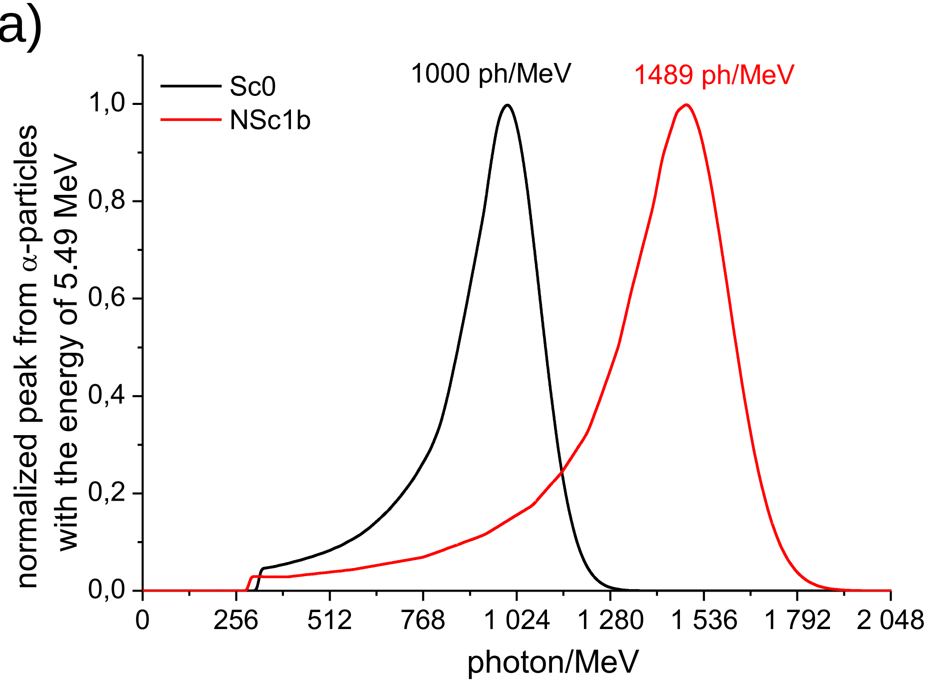


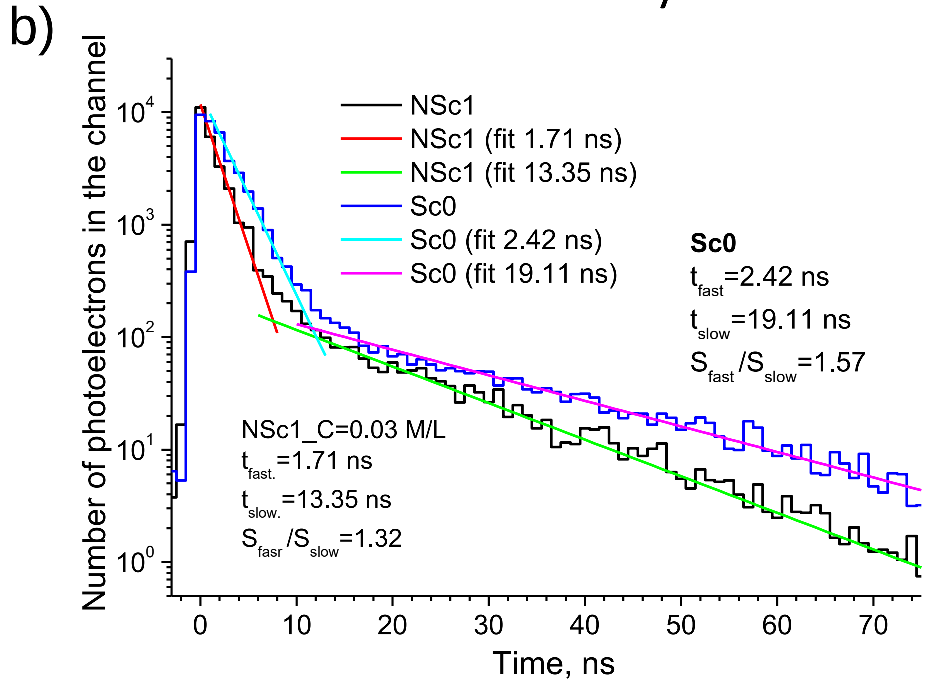
highly efficienct and fast FRET between the activator and spectral shifter!

Comparison of the standard (Sc0) and NOL-based (NSc1) plastic scintillators

amplitude spectra

scintillation decay time

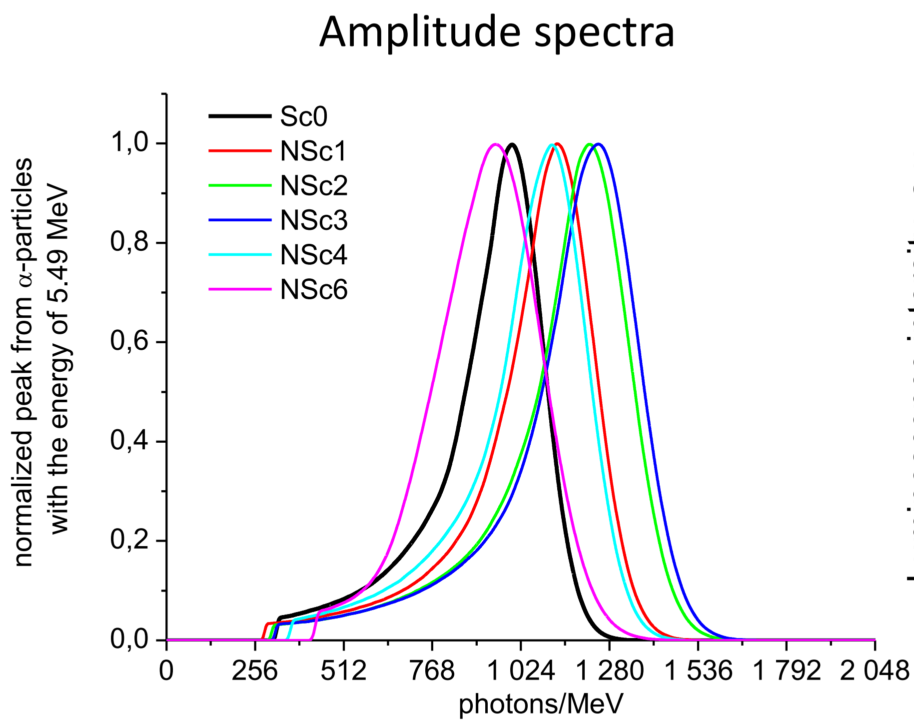


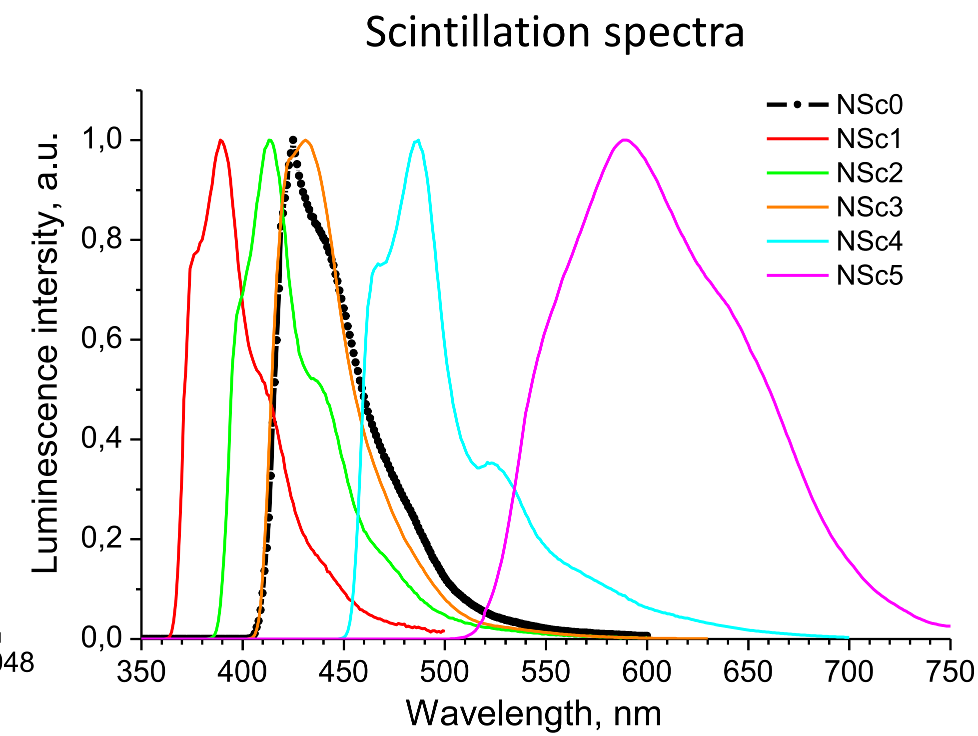


Using NOLs in plastic scintillators allows raising their scintillation light output on 50% as compared to the standard one, while their scintillation decay time can be improved on 40%.

S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, et. al., ***Sci. Rep.*** **2014**, *4*, 6549

Plastic scintillators with NOLs having different emission range

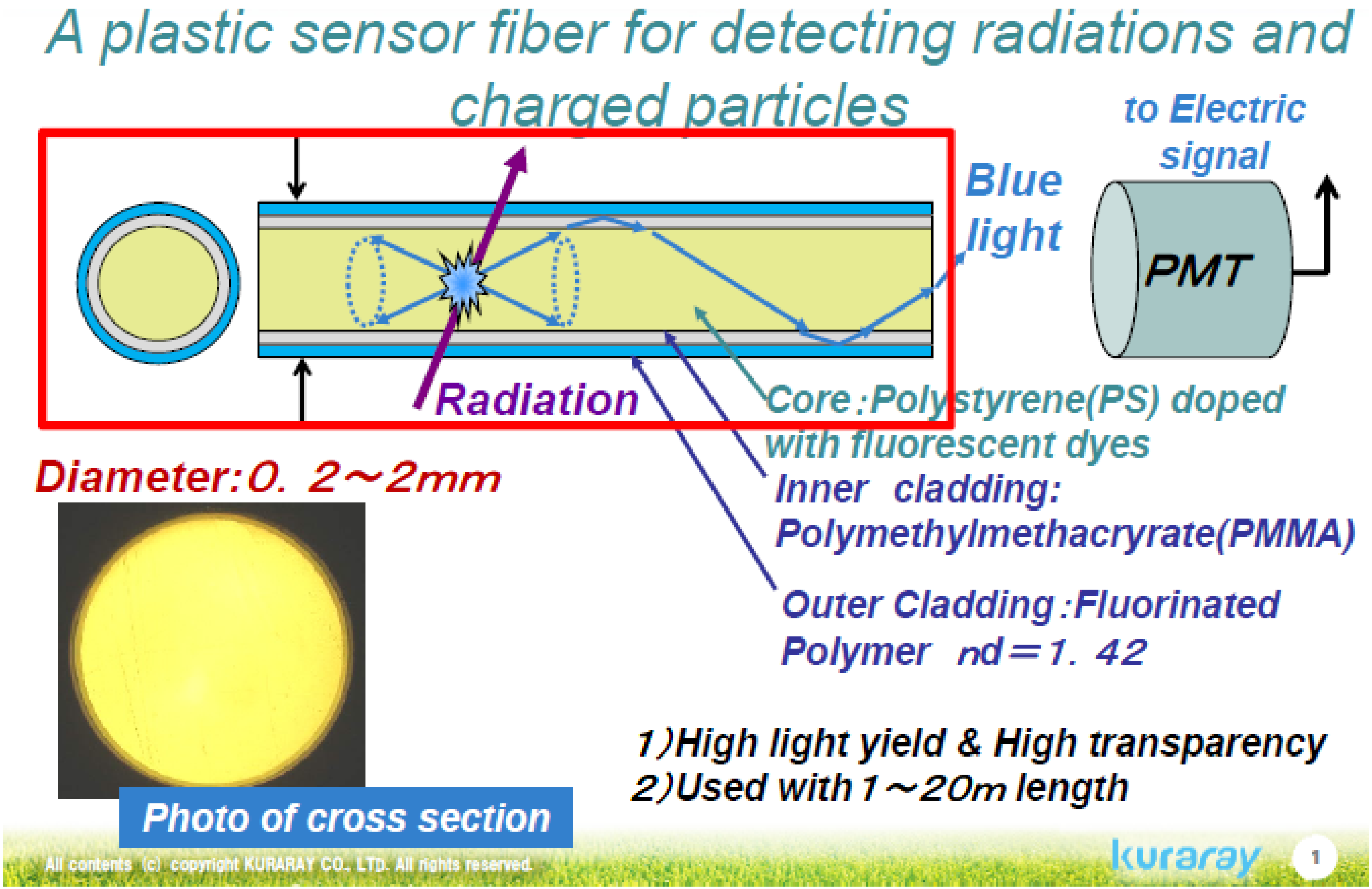




Plastic scintillators with NOLs are able emit light in any possible visible region, which allows to adopt plastic scintillators for any desired photodetector to reach the maximal efficiency of the elementary particles detections.

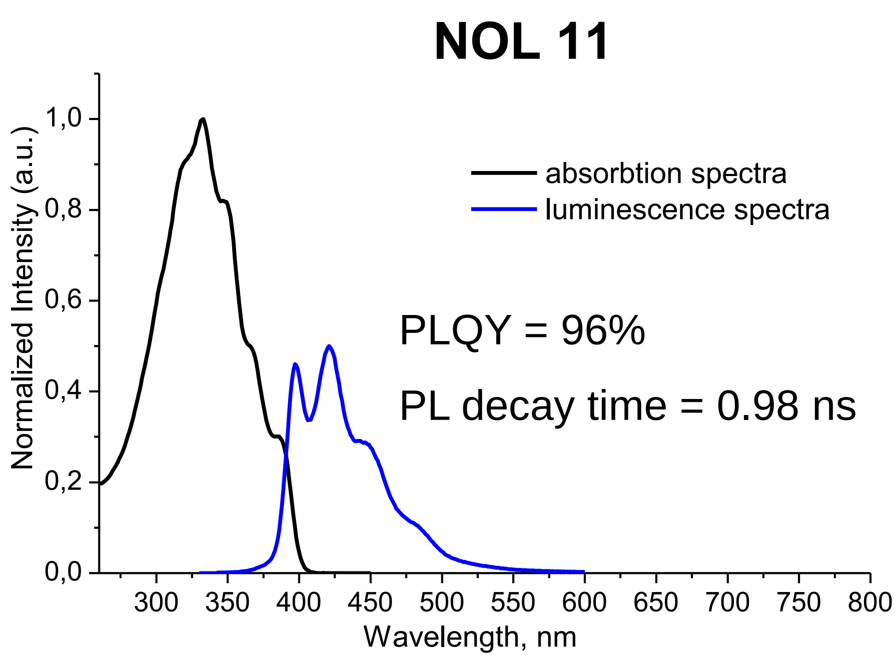
S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, et. al., ***Sci. Rep.*** **2014**, *4*, 6549

What is plastic scintillating fiber?

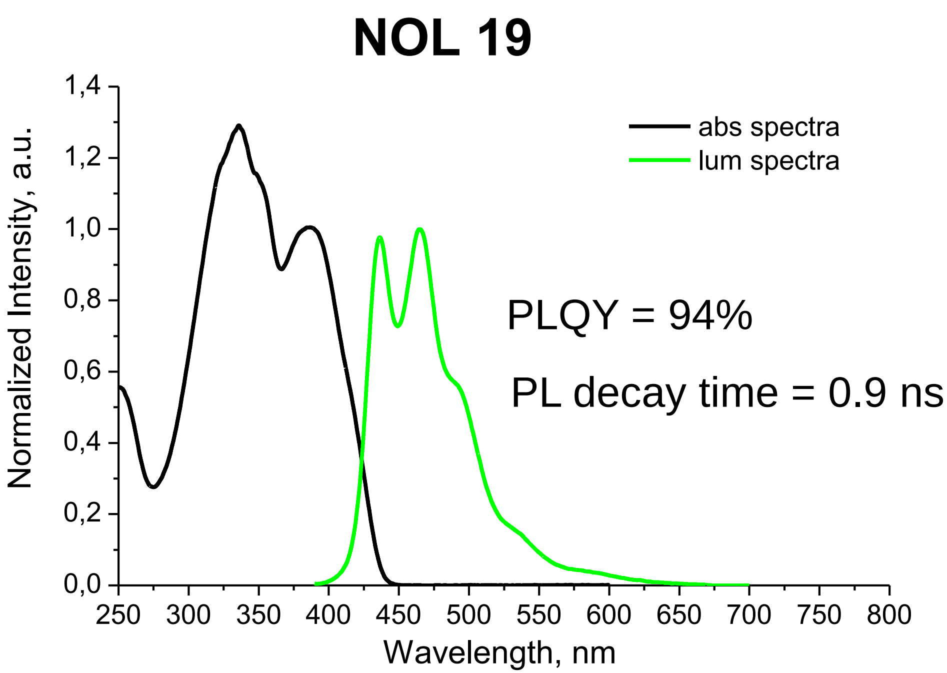


Absorption and emission spectra of NOLs used for initial preform synthesis

Blue-emitting NOL

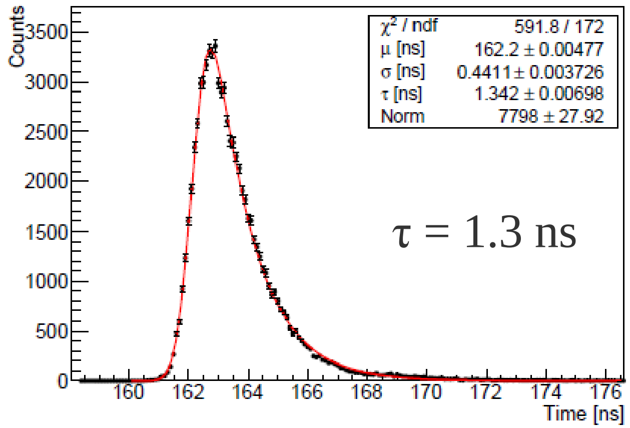


Green-emitting NOL

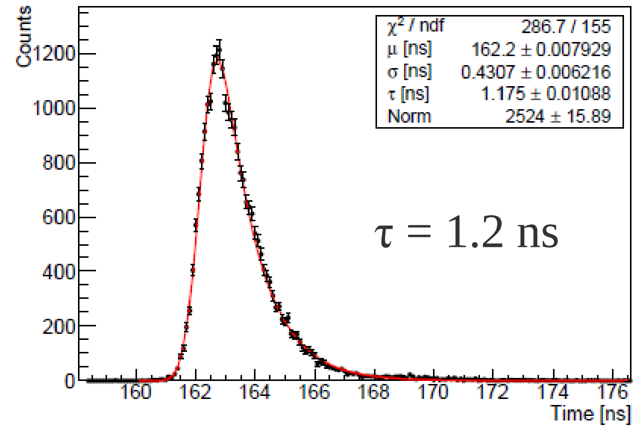


NOLs have good solubility in standard organic solvents, monomers used for plastic scintillation synthesis and in the polymers utilized as matrixes in plastic scintillators as well as in scintillating and wavelength shifting fibers.

Ultrafast plastic scintillators fibers



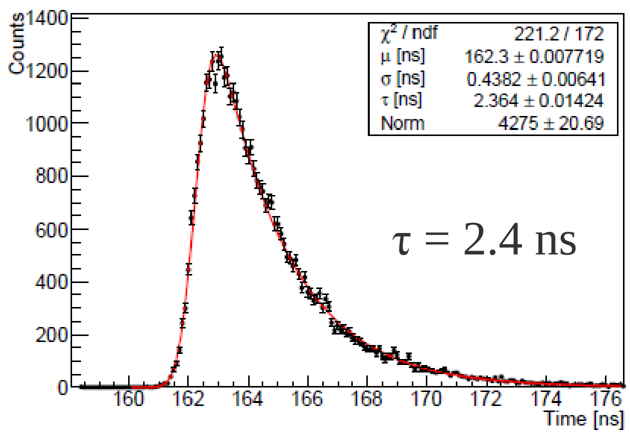
(a) BPF-11-1



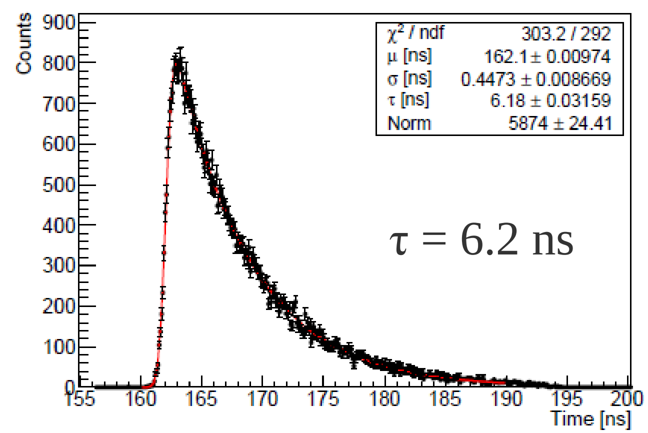
(b) GPF-19-1

Blue-emitting fibers

Green-emitting fibers



(c) SCSF-78

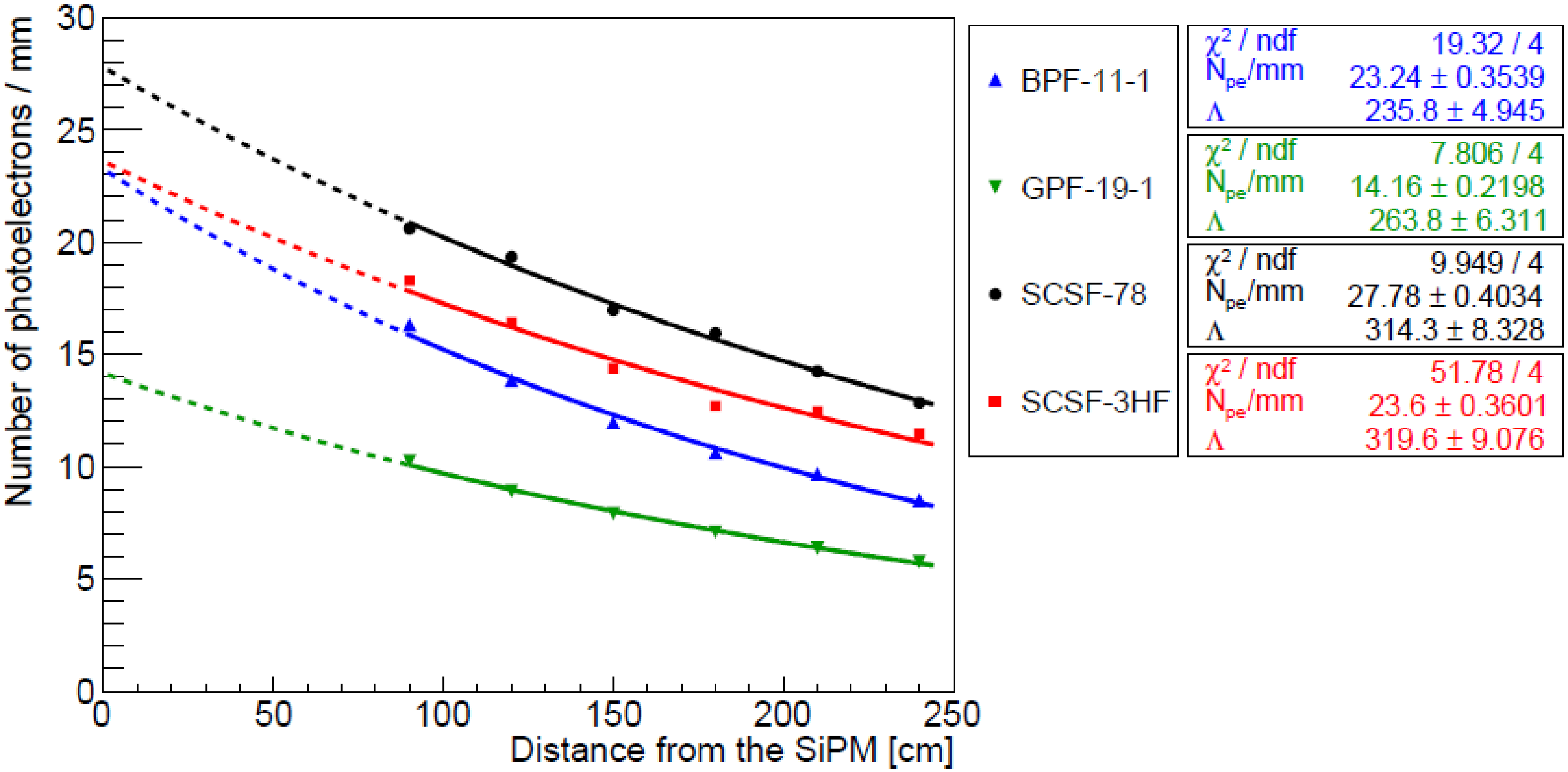


(d) SCSF-3HF

Decay time of NOL-based prototype fibers BPF-11-1 (a) and GPF-19-1 (b) as well as reference fibers SCSF-78 (c) and SCSF-3HF (d).

Borshchev, O., Cavalcante, A.B.R., Gavardi, at.al., *J. Instrum*. **2017,** 12, P05013

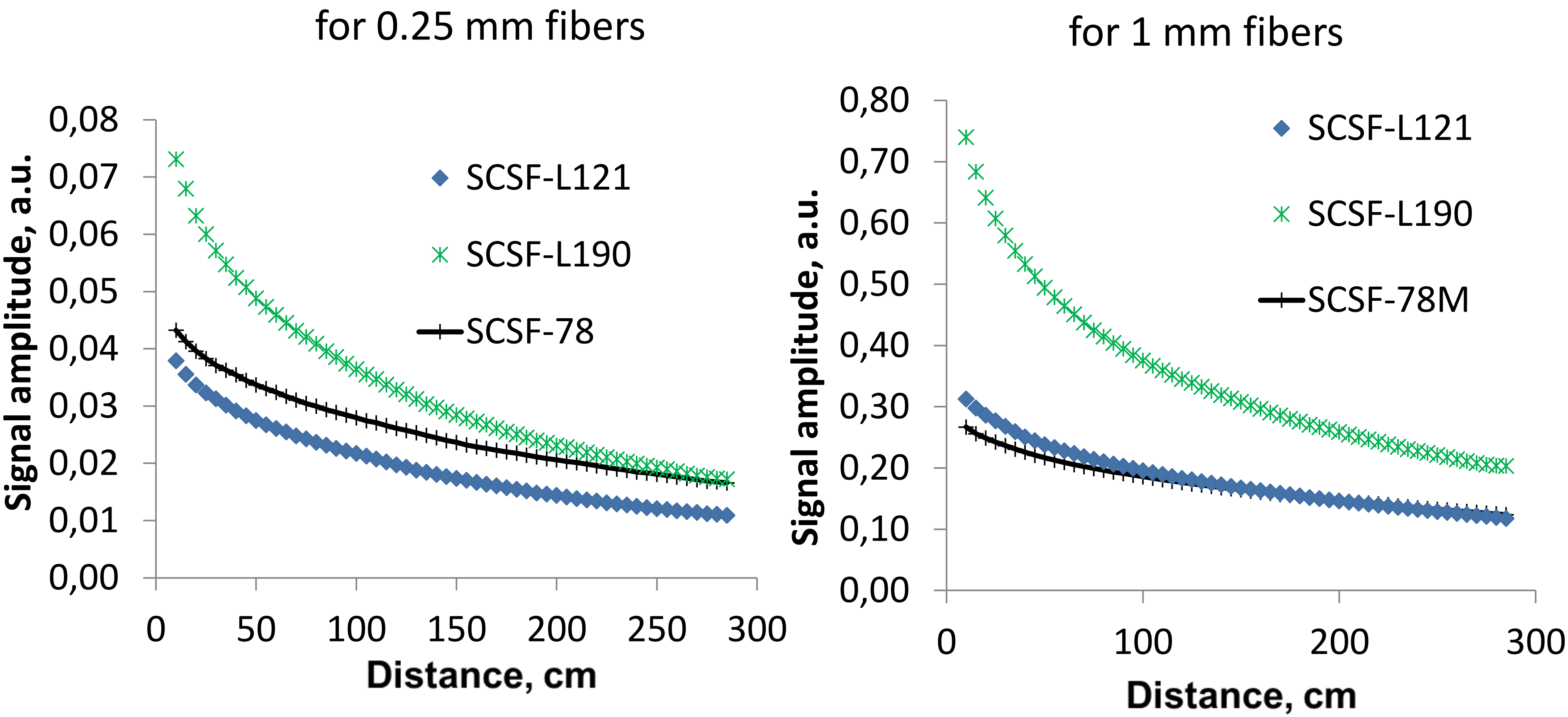
Ultrafast plastic scintillators fibers



Light yield of NOL-based prototype fiber samples and comparison to Kuraray standard fibers SCSF-78 and SCSF-3HF.

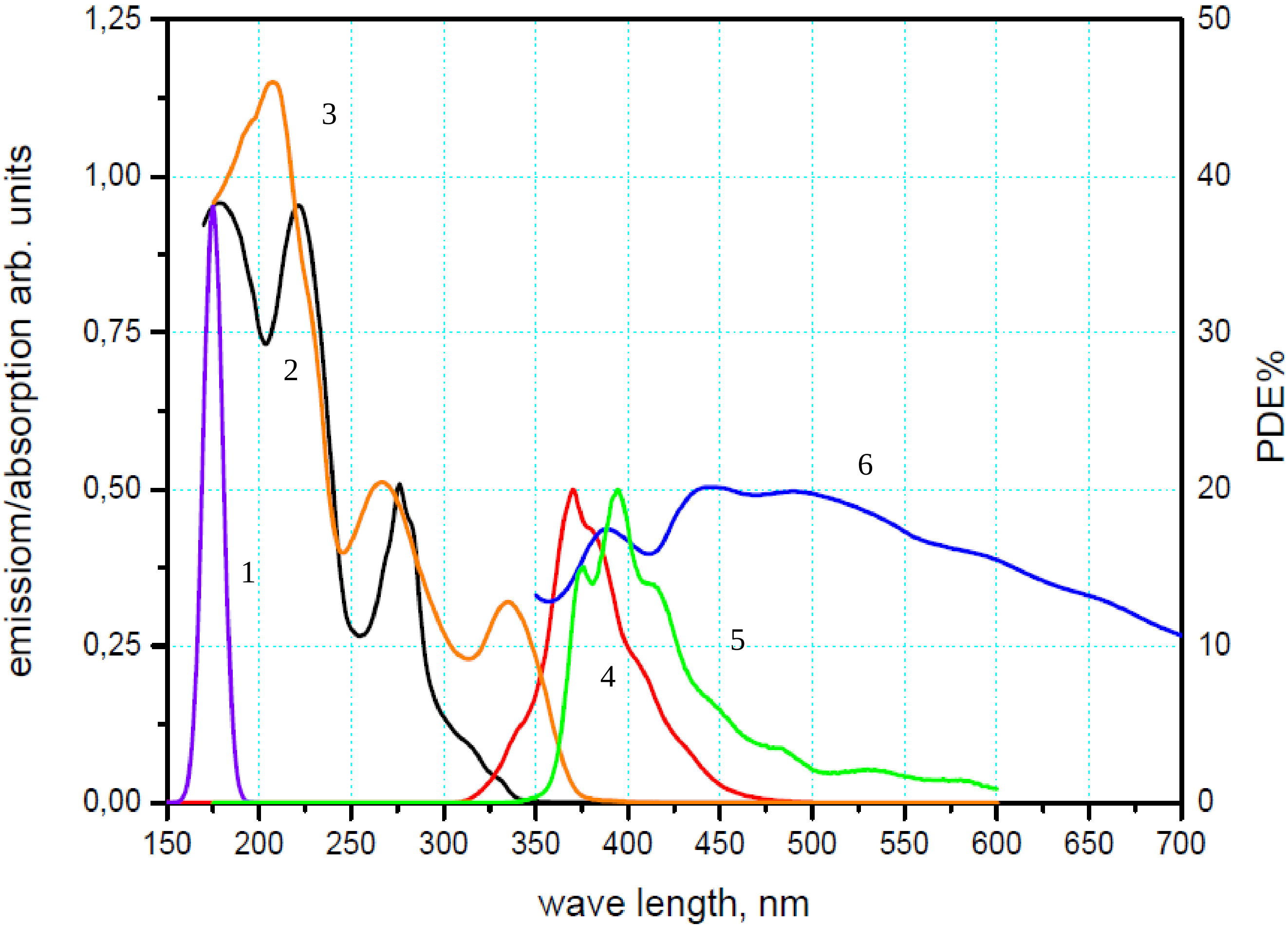
Borshchev, O., Cavalcante, A.B.R., Gavardi, at.al.**,** ***J. Instrum***. **2017,** 12, P05013

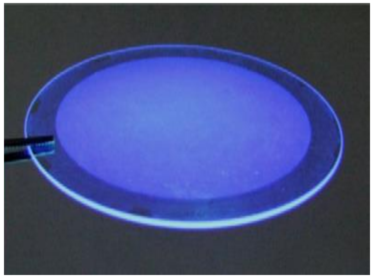
Attenuation length of the NOL-based fibers



Attenuation length measured using UV light from Hg lamp by Kuraray.
SCSF-L121 are the blue-emitting fibers. SCSF-L190 are the green-emitting fibers.
SCSF-78 are the standard blue-emitting fibers.

NOL-based VUV wavelength sifters for noble gas detectors





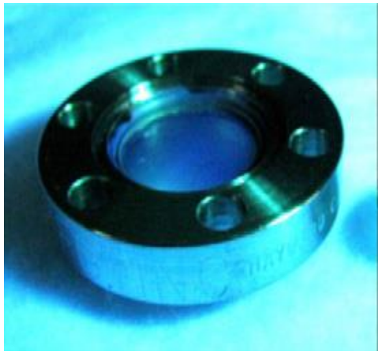
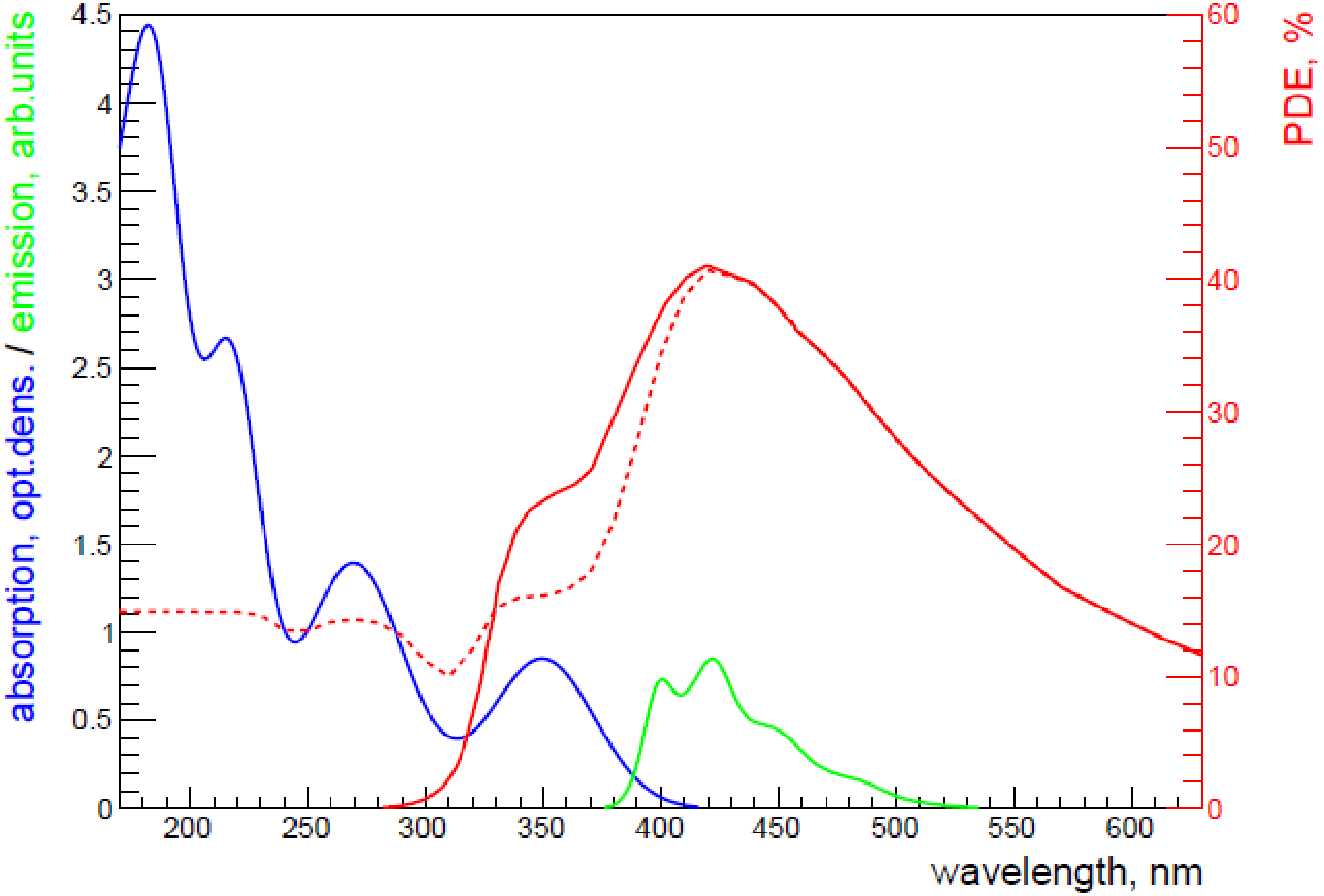
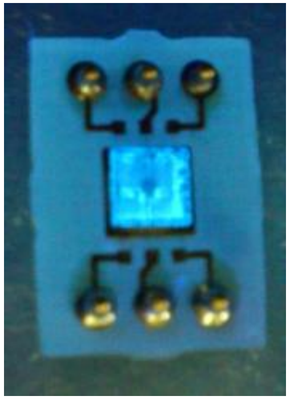


Fig 1. Emission spectrum of LXe (1), absorption spectrum of p-terphenyl (2), absorption spectrum of new WLS (3), emission spectrum of p-terphenyl (4), emission spectrum of new WLS (5), photon detection efficiency (PDE) of the CPTA “blue-sensitive” photodiode (6), right axis.

Akimov D.A., at. al., ***NIM A***, **2012**, *695*, 403-406.

NOL-based VUV wavelength shifters for noble gas detectors

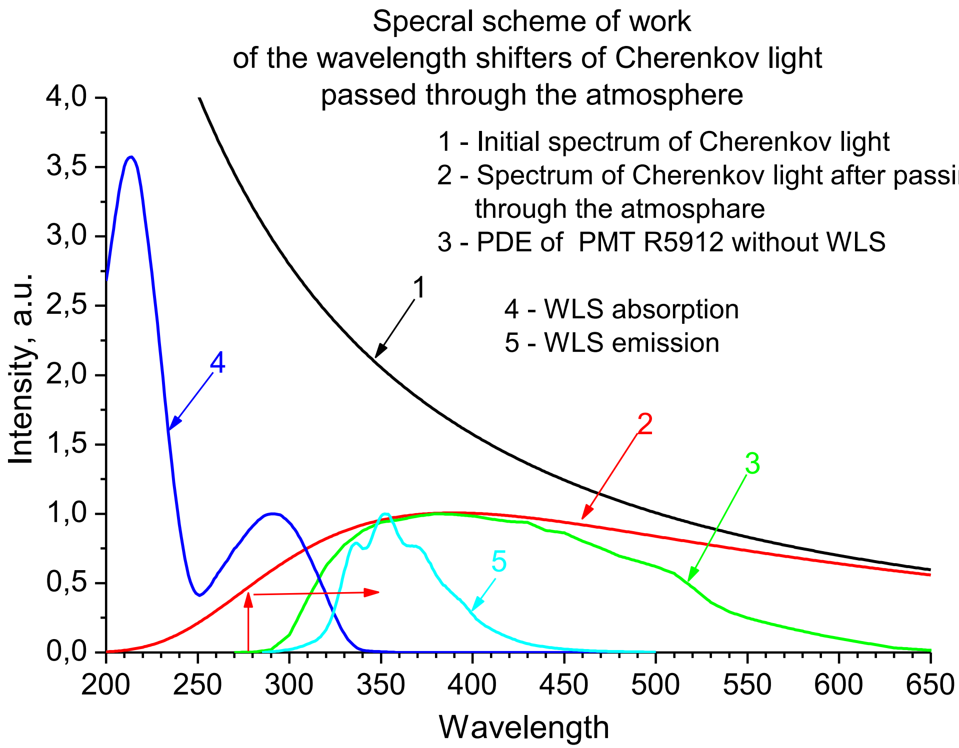


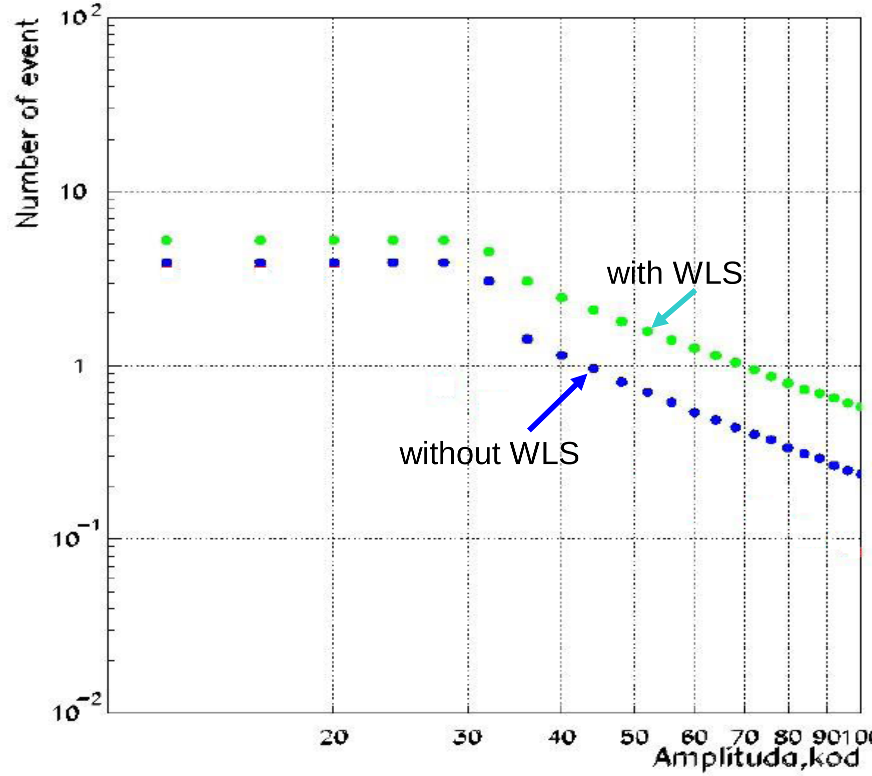


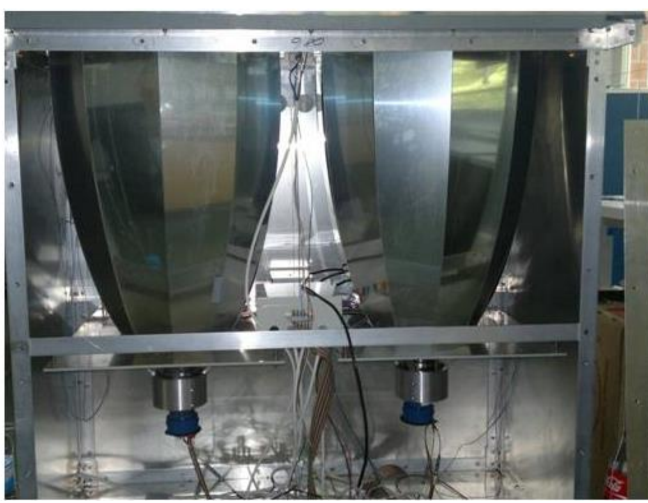
Absorption (blue) and luminescence (green) spectra of NOL-1, as well as spectral dependence of SiPM PDE without (red solid) and with (red dashed) 200 nm layer of NOL-1

Akimov D.A., at. al., ***J. Instrum.*** **2017**, 12, P05014

NOLs as effective wavelength shifters for TUNKA



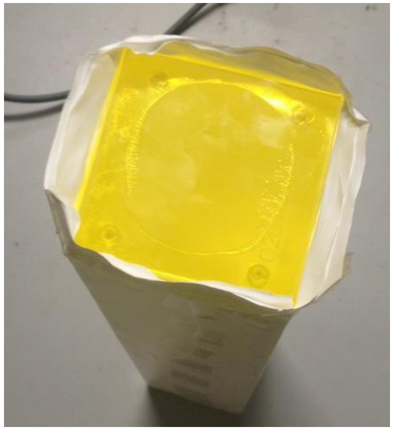


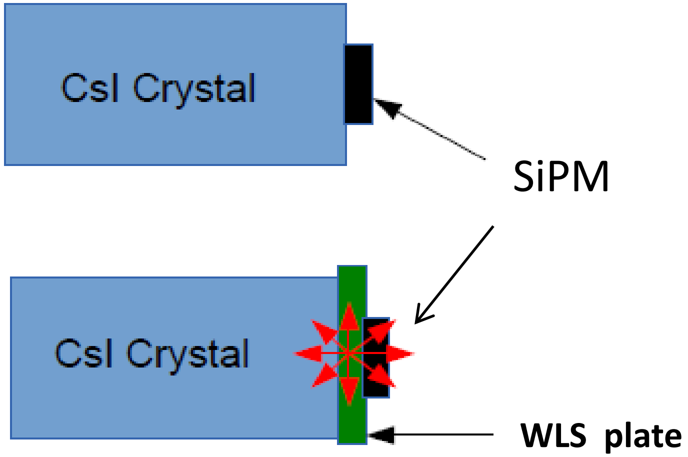


Photos of the optical station of TUNKA-HiSCORE and PMT R5912-TUNKA

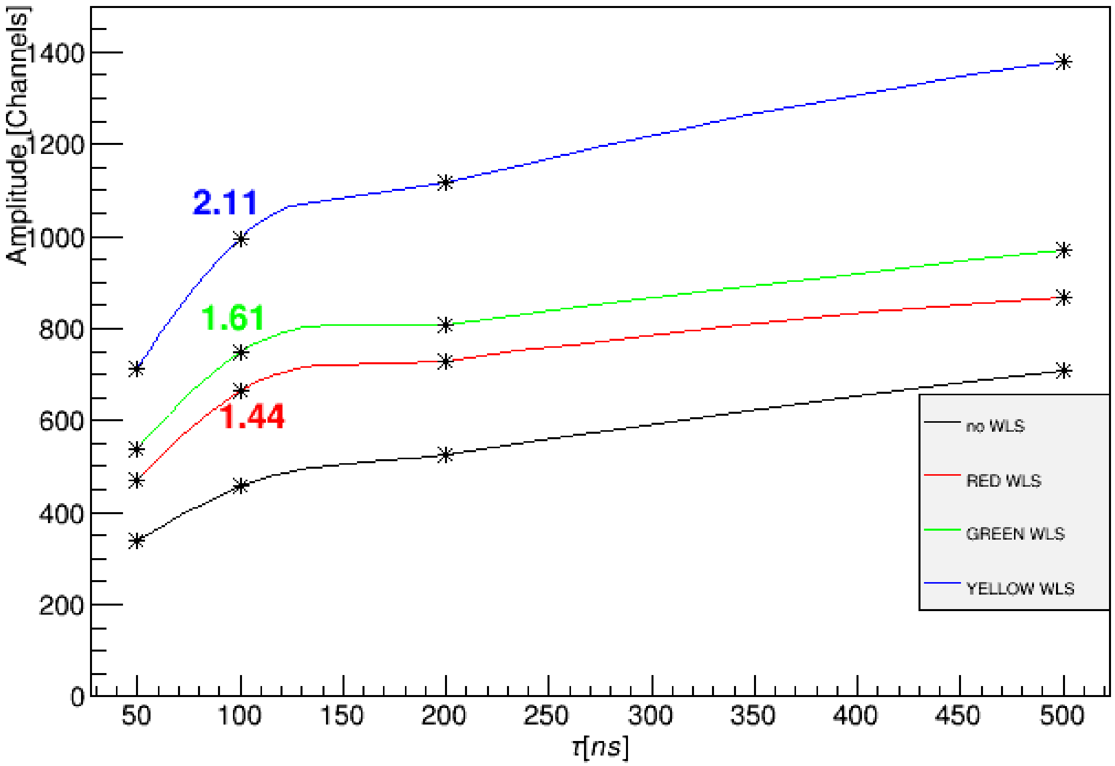
In collaboration with Bayarto Lubsandorzhiev (INR RAS, Moscow, Russia)

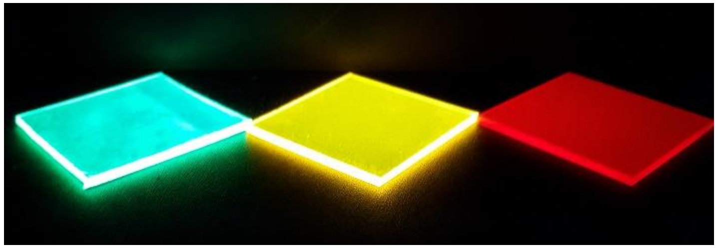
NOL-based VUV WLS plates for CsI single crystals





signal-shaping time

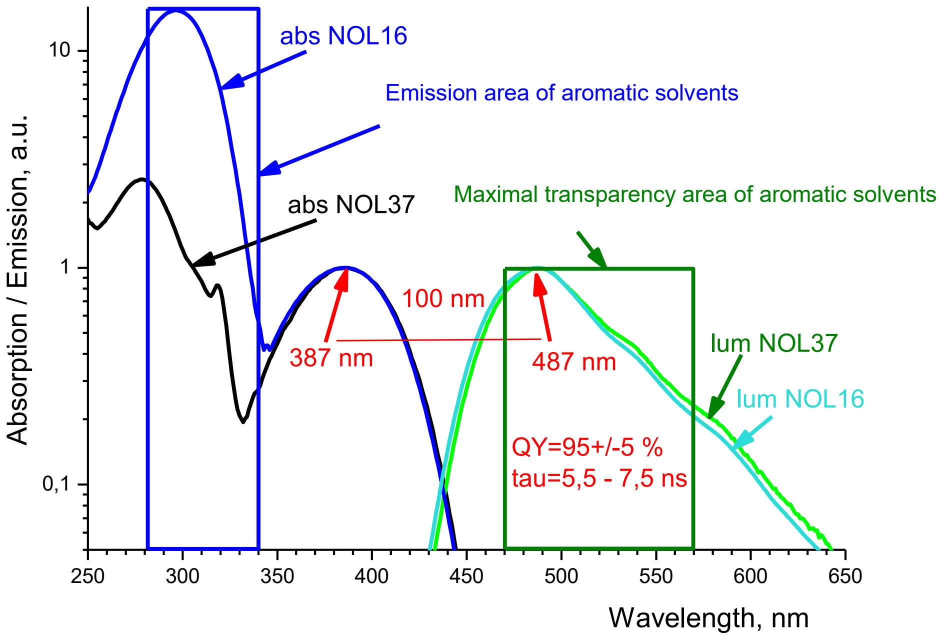




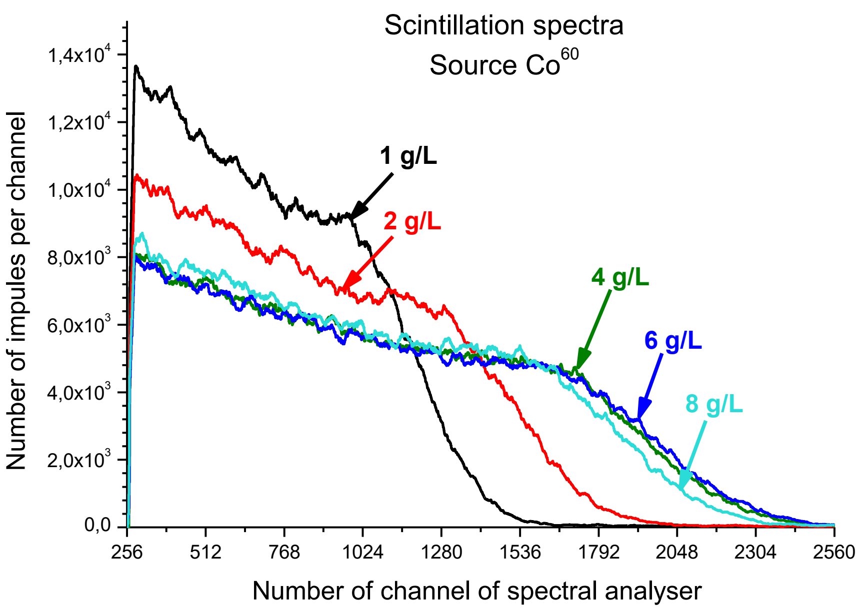
Usage of WLS plates based on NOLs allows 2-3 times to increase the detection efficiency

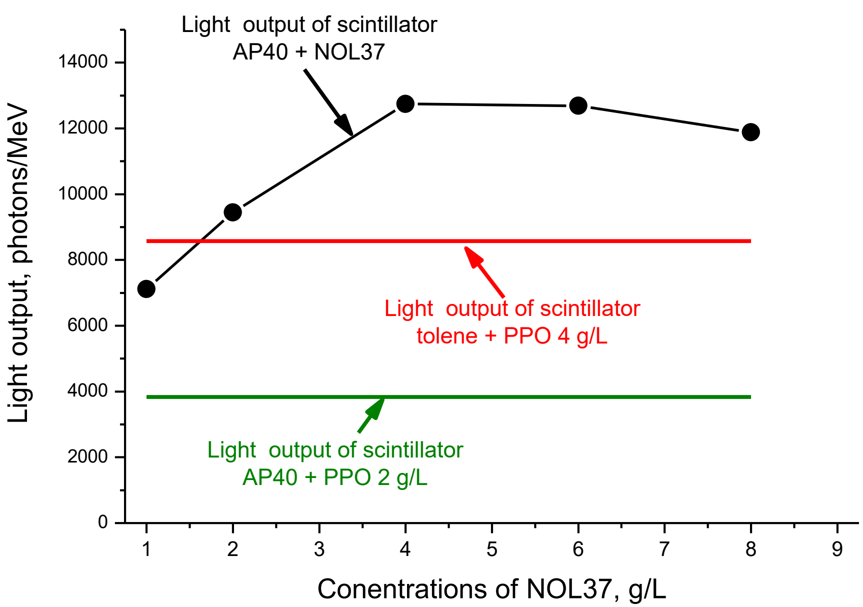
Jin, Y., Aihara, H., Borshchev, O.V., Epifanov, D.A., Ponomarenko, S.A., Surin, N.M., ***Nucl. Instr. Meth. Phys. Res. A***, **2016**, 824, 691-692

NOLs as effective wavelength shifters for liquid scintillators



Light output of liquid scintillator based on NOL 37 and aromatic solvent AP40 reaches **13000 photons**/MeV

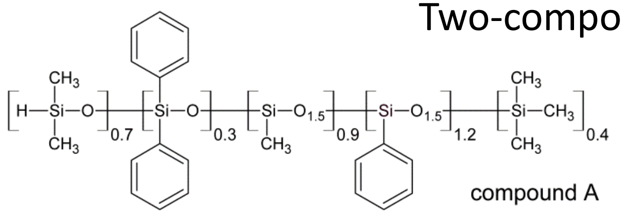


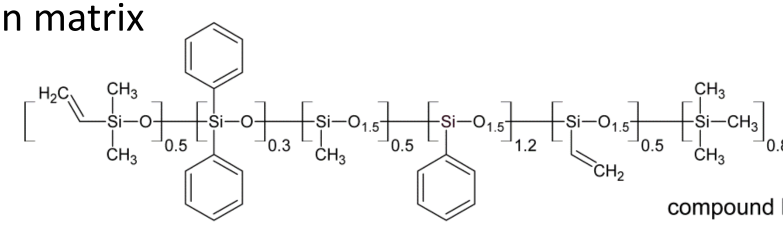


In collaboration with Bayarto Lubsandorzhiev (INR RAS, Moscow, Russia)

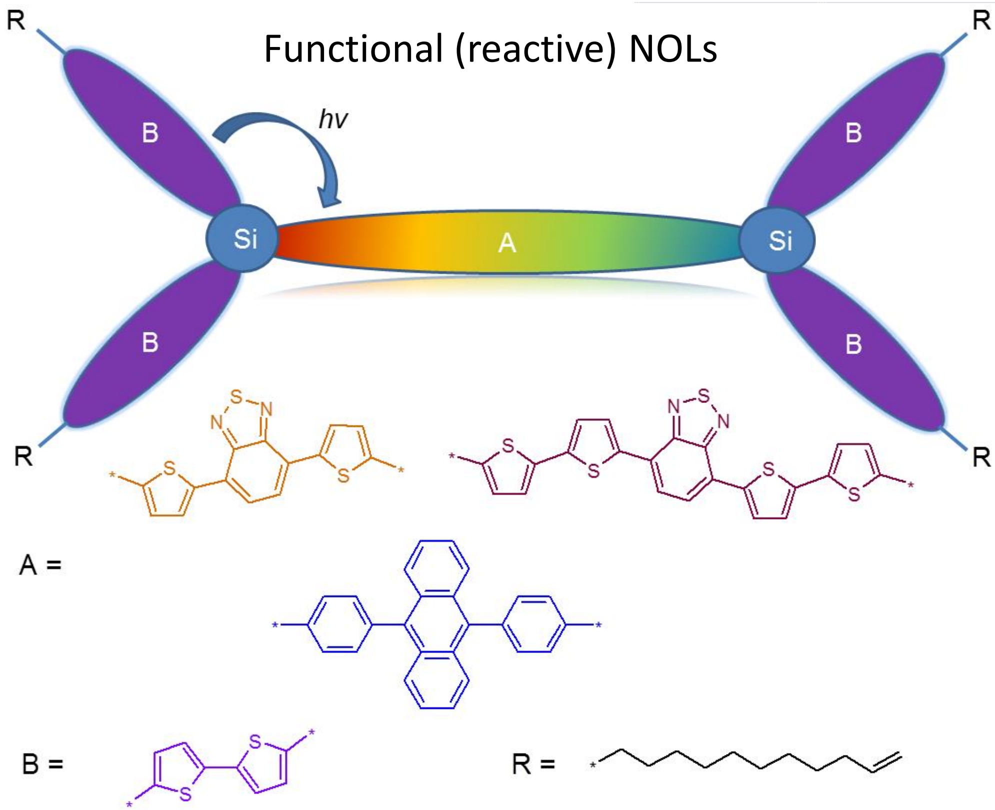
Functional NOLs compatible with organosilicon matrixes

Two-component organosilicon matrix





Functional (reactive) NOLs

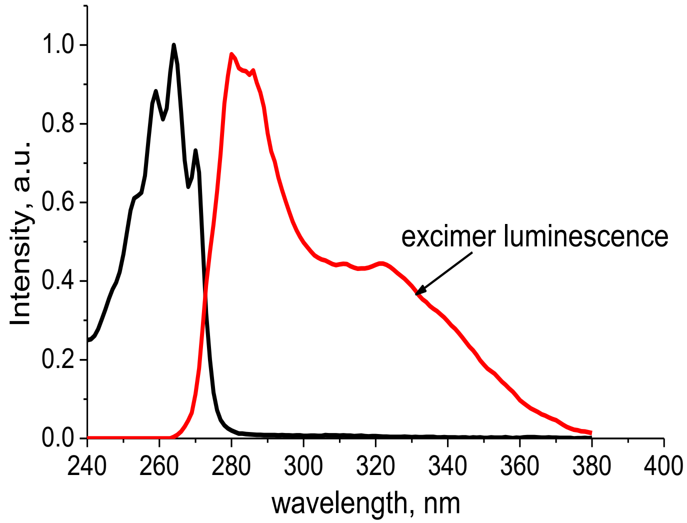


Composition of functional NOLs with two-component organosilicon matrix gives lacquer, which can be applied to a surface having any curvature and cross-linked to form a range of high temperature resistive and radiation stable plastic scintillators.

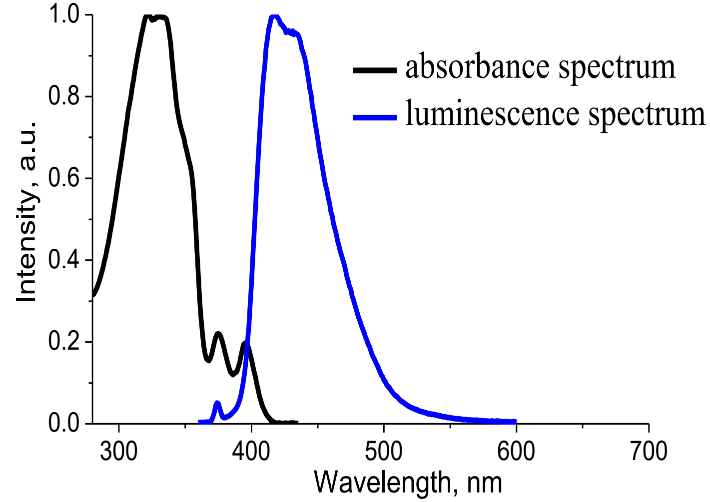
M.S. Skorotetcky, O.V. Borshchev, N.M. Surin et al., ***Silicon***, **2015**, **7**, 191-200

Functional NOLs compatible with organosilicon matrixes

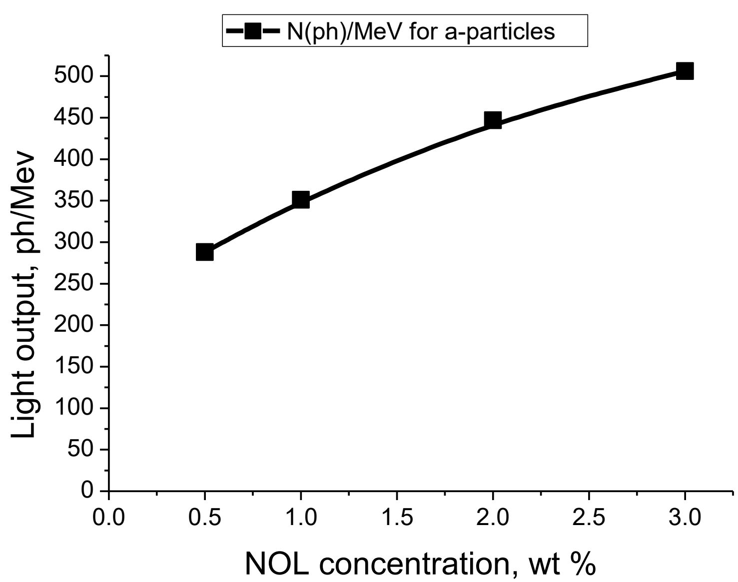
Absorbance and Luminescence spectra of organosilicon matrix



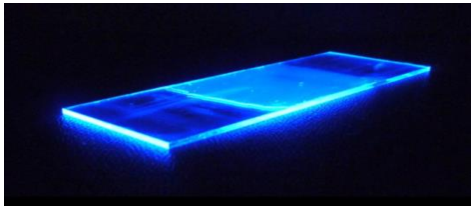
Absorbance and Luminescence spectra of NOL

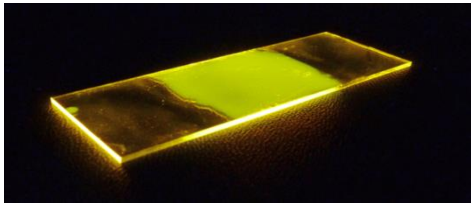


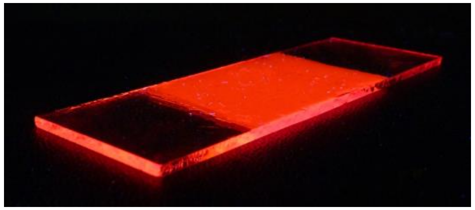
Scintillation efficiency



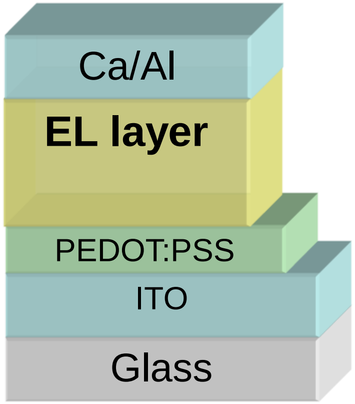
Photos of glass plates covered with thin organosilicon scintillating films under UV light

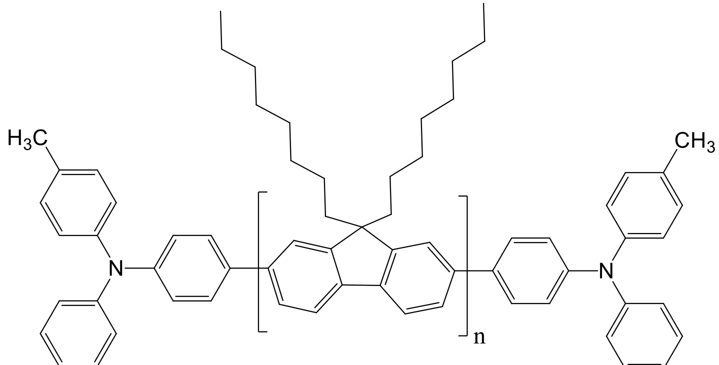






NOLs for effective light conversion in OLEDs



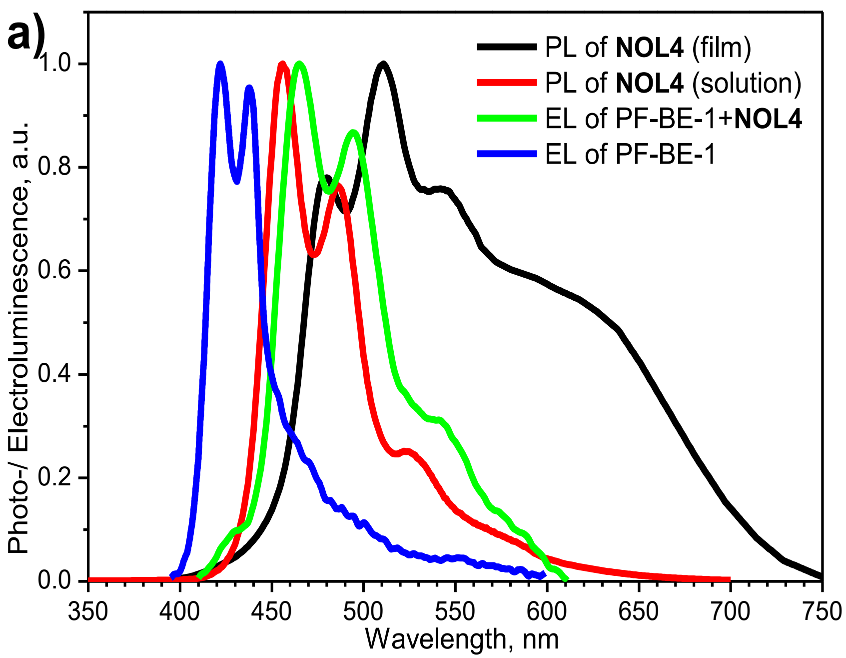


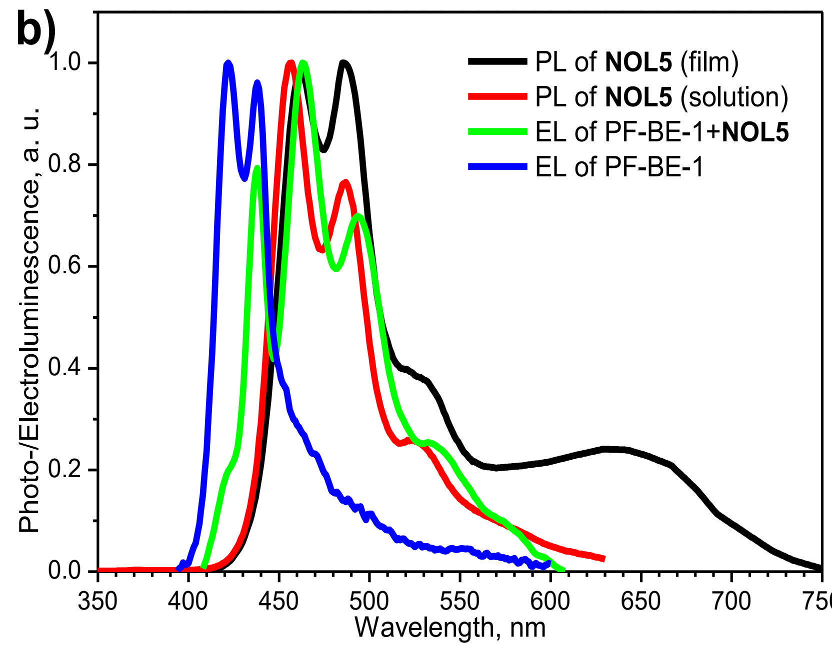
PF-BE-1

active layer	brightness
PF-BE-1	500 cd/m^2
PF-BE-1+ NOL4	1200 cd/m^2
PF-BE-1+ NOL5	1500 cd/m^2

(proof of principle)

PLQY (NOL4, NOL5) 50%

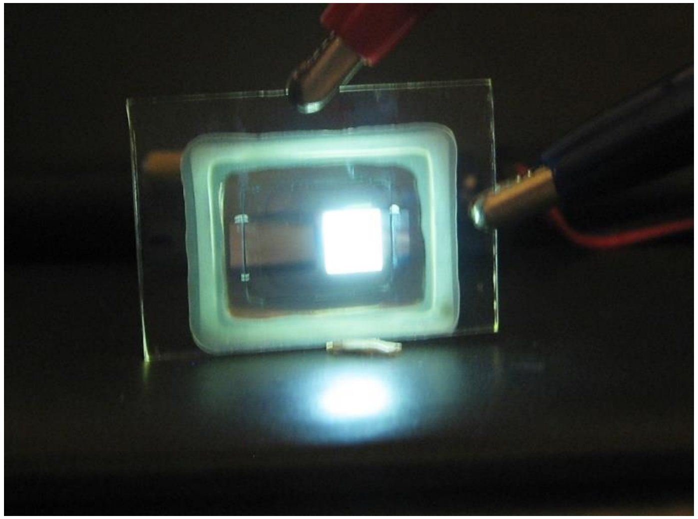




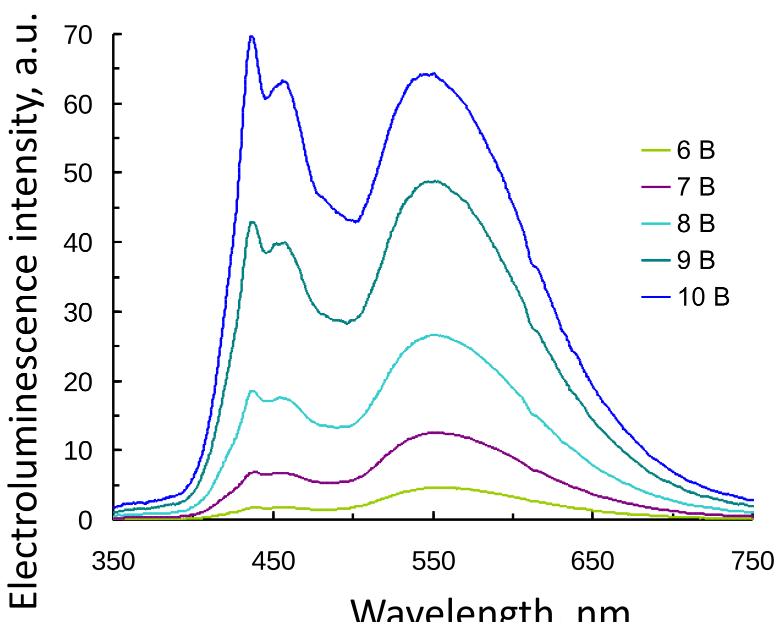
Y.N. Luponosov, N.M. Surin, D.K. Susarova et al., ***Org. Photonics Photovolt.,*** **2015**, **3**, 148-155

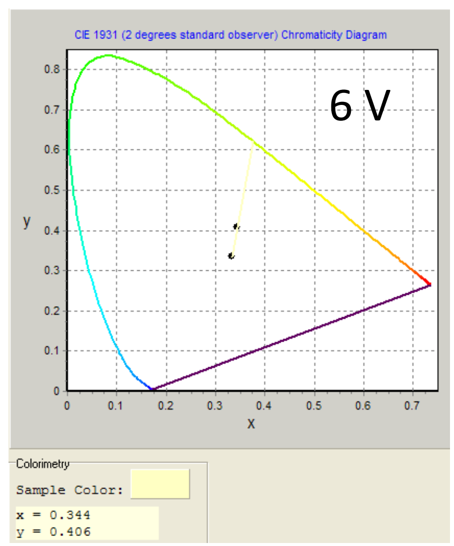
Solution-processible white OLEDs based on NOLs

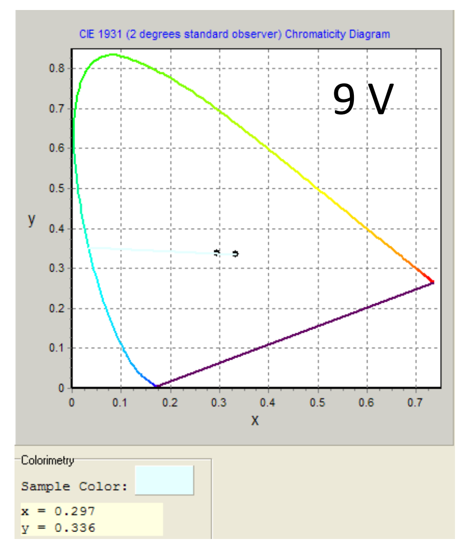
Photo of switched on OLEDs



- OLED structure: ITO/PEDOT(60 nm)/PVK (15 nm)/ PVK:NOL9 0.75%:PBD 30% (40 nm)/PF (15 nm)/ LiF/Al
- λ_{max} EL – 437, 457, 550 nm
- CIE x=0.297 , y=0.336 (U=9 V)
- Turn in voltage: $U_п$= 5.0 V
- Luminance: 450 Cd/m^2 at U= 12 V, J= 340 mA/cm^2 (S=0.25 cm^2)
- luminous efficiency: 0.24 Cd/A,
- luminous power efficiency – 0.15 Lm/W

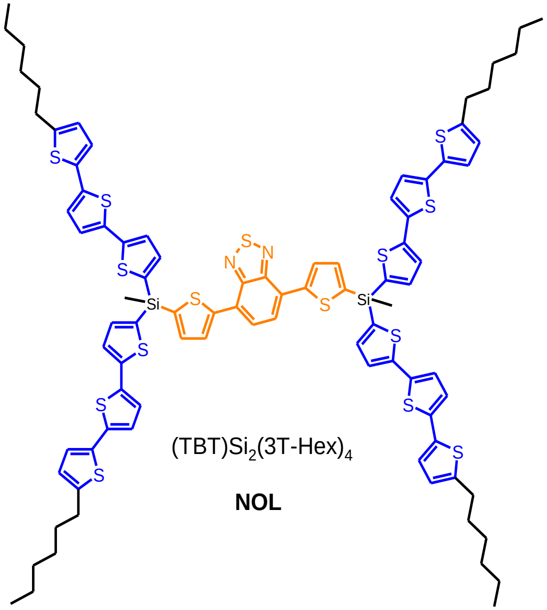






Patent RU 2555193 (2015)

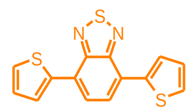
NOLs Luminescent Down Shifting Materials for Thin Film Photovoltaics



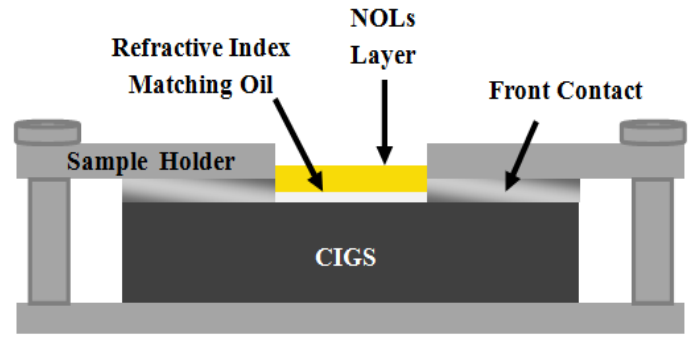
(TBT)Si_2(3T-Hex)$_4$

NOL

3T-Hex (donor)



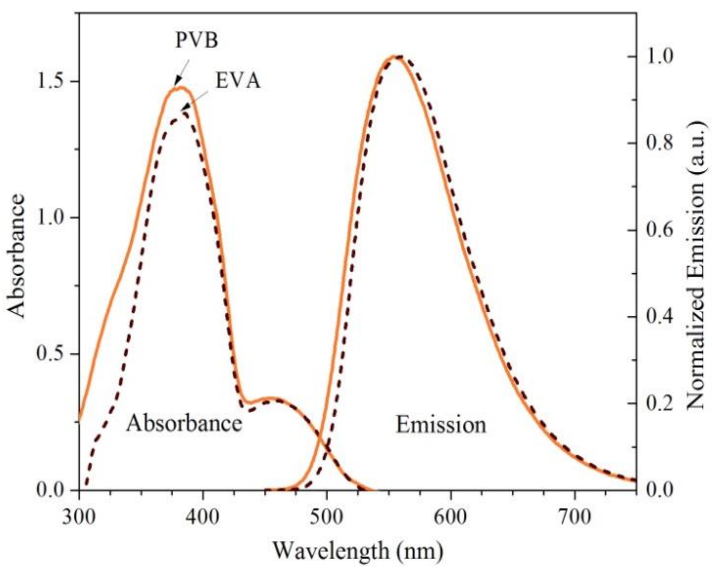
TBT (acceptor)

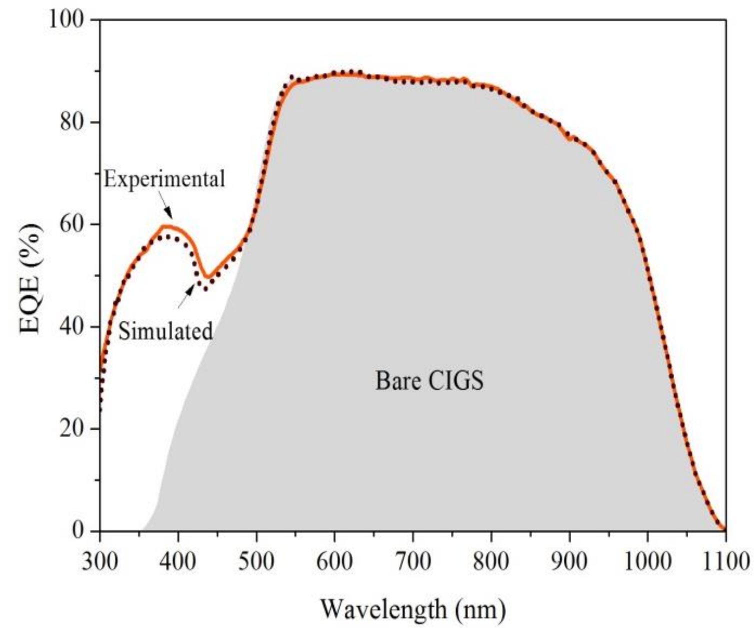


Increase of **EQE** at 360 nm from 1 % to 55 %

Relative increase of **Isc** and **η** are 3.2 – 4.3%

PLQY 80-92%

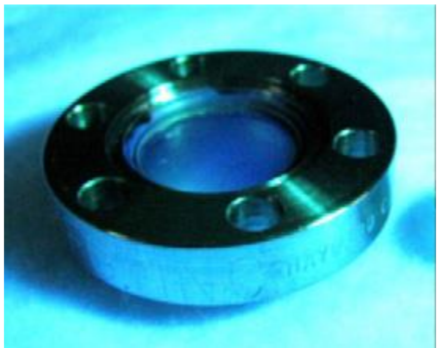




T. Uekert, A. Solodovnyk, S. Ponomarenko, at. al., ***Sol. Energy Mater. Sol. Cells*** **2016,** 155, 1-8

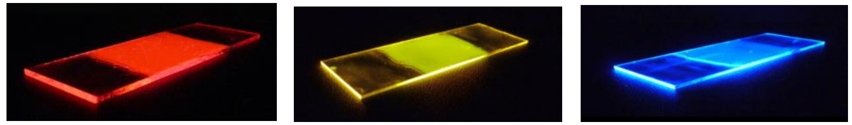
Summary of various application of NOLs

VUV wavelength shifters for noble gas detectors

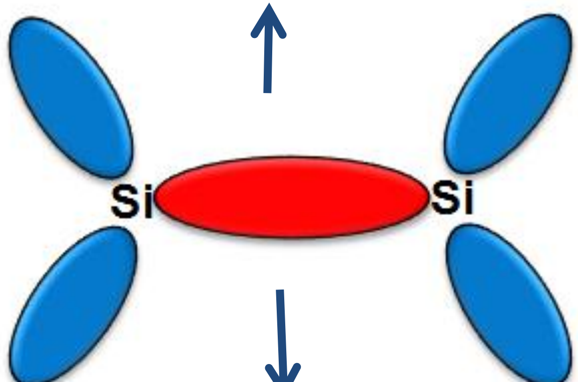


***NIM A*, 2012**, *695*
***J. Instrum.* 2017**, 12, P05014

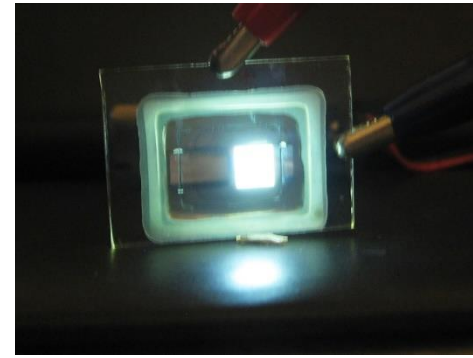
Organosilicon scintillators



***Silicon*, 2015, 7**, 191-200

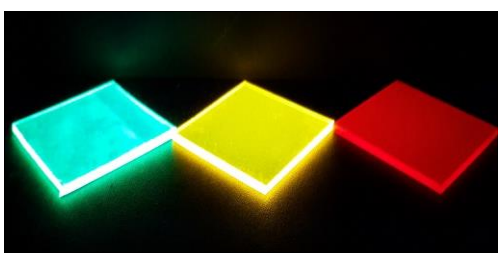


Wavelength shifters in OLEDs



***Org. Photonics Photovolts.*, 2015, 3**, 148-155

UV wavelength shifters for pure CsI detectors

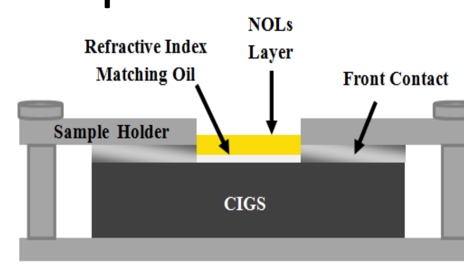


***NIM. A*, 2016,** 824, 691-692

Plastic scintillators, scintillating fibers

***Sci. Rep*. 2014**, *4*, 6549
***J. Instrum*. 2017,** 12, P05013

Wavelength shifters for photovoltaics



***Sol. Energy Mater. Sol. Cells* 2016,** 155, 1-8

Conclusions

Nanostructured Organosilicon Luminophores (NOLs) are a new class of nanomaterials with a combination of unique properties:

- ✓ large and tunable absorption in a wide optical spectral region
- ✓ tunable luminescence spectra in the visible spectral range
- ✓ high photoluminescence quantum yield (up to 99%)
- ✓ large «Stokes shift» (up to 330 nm)
- ✓ short luminescence lifetime
- ✓ good solution processabilty

Usage of NOLs can significantly increase the efficiency of different photonics devices used in high energy physics, such as plastics scintillators and scintillating fibers, Cherenkov light and Noble gas detectors, pure CsI scintillation detectors, liquid scintillators and other optoelectronic devices.

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