

1 **Synthesis and photostability of 1,4-bis(5-phenyloxazol-2-yl)benzene**
2 **(POPOP) structural isomers and their trimethylsilyl derivatives**

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1 In this work, a versatile synthetic method for preparation of linear phenyloxazoles and their
2 organosilicon derivatives under mild conditions via a combination of van Leusen and direct C-H
3 arylation reactions is reported. It was used for the synthesis of a novel trimethylsilyl (TMS)
4 derivative of blue laser dye 1,4-*bis*(5-phenyloxazol-2-yl)benzene (**POPOP**) and its structural
5 isomer 1,4-*bis*(2-phenyloxazol-5-yl)benzene (**isoPOPOP**) with and without TMS substituents. All
6 of the compounds demonstrated high photoluminescence quantum yields and large molar
7 extinction coefficients, which further increased for their TMS derivatives. Measurements of
8 accelerated photodegradation of the dyes in diluted THF solutions revealed that **POPOP**-type
9 compounds are twice more stable than their **isoPOPOP**-type isomers, independent of the
10 presence or absence of TMS substituents. Cyclic voltammetry (CV) investigations revealed that
11 **POPOP**-type dyes are more electrochemically stable as compared to their **isoPOPOP**-type
12 isomers. Quantum chemical TD DFT calculations of the frontier energy levels of the dyes were
13 in a good agreement with the experimental data obtained by CV. Single-crystal X-ray diffraction
14 experiments revealed significant structural differences between crystal lattices of the dyes. Due
15 to facile synthesis and excellent optical properties as well as high photo- and thermo- stability
16 the novel luminescent dyes may find wide application in organic photonics.

17

18 *Keywords:* phenyloxazole, direct C-H arylation, organosilicon luminophores, stability,
19 photodegradation, crystal structure

20

21 **1. Introduction**

22 Organic molecules emitting light in various spectral regions are widely used in many
23 fields of science and technology. Among them are aryl-substituted oxazoles, which are highly
24 efficient violet or blue emitting luminophores [1,2]. A burst of interest towards this class of
25 materials was triggered by their applicability as activators and spectral shifters in liquid and

1 plastic scintillators detecting elementary particles and ionizing radiation [3,4]. Moreover, they
2 are widely used as dyes for organic lasers [5,6] and spectral shifters in photonics [7]. Synthetic
3 approaches for preparation of phenyloxazoles are well known: after E. Fisher had synthesized
4 2,5-diphenyloxazole in 1896, a wide variety of techniques for the preparation of this compound
5 and its derivatives were reported [8]. Additional interest of researchers is drawn to biological
6 activity of oxazole as a structural moiety of various alkaloids as well [9].

7 In previous works we introduced a new class of highly efficient dyes – nanostructured
8 organosilicon luminophores (NOLs), which combine the best properties of quantum dots with
9 those of organic luminophores [10–13]. NOL molecule consists of two types of different organic
10 dyes covalently bonded to each other via silicon atoms, while one of the dyes has a wider and
11 the other – a lower bandgap relative to each other. Such structure ensures efficient
12 nonradiative intramolecular energy transfer (the so called “dendritic molecular antenna effect”
13 [14,15]), while the choice of organic dyes provides tunability of the optical properties of the
14 molecules such as the absorption and photoluminescence (PL) spectra lying within a desired
15 spectral region. One of the prospective organic dyes to be applied for NOLs architecting is a
16 blue-emitting luminophore 1,4-bis(5-phenyloxazol-2-yl)benzene (**POPOP**). It has a high
17 photoluminescence quantum yield (PLQY) along with a relatively large Stokes shift. The main
18 technique for its preparation is the Robinson-Gabriel synthesis using the corresponding ω -
19 amino methyl ketone and terephthaloyl chloride as the precursors, followed by dehydration in
20 concentrated sulfuric acid [16]. This method is yet not suitable for the preparation of **POPOP**
21 organosilicon derivatives as the latter are not stable in acidic conditions. At the same time, a
22 general approach for preparation of organosilicon derivatives of organic luminophores is based
23 on the reaction between organolithium precursors with corresponding chloro- or alkoxy-silanes
24 [17]. However, the oxazole ring undergoes decyclization in the presence of organolithium
25 reagents [18]. Therefore, the primary goal of this work was to develop a mild synthetic protocol

1 for preparation of organosilicon derivatives of **POPOP**, which would allow overcoming the
2 contradiction between the low stabilities of arylsilanes and oxazole cycle at strong acidic and
3 strong basic conditions, respectively. While doing this work, it was found that preparation of
4 1,4-*bis*(2-phenyloxazol-5-yl)benzene **iso-POPOP** and its organosilicon derivatives under mild
5 conditions can be achieved easily as the **POPOP** itself. Therefore, the secondary goal of this
6 work was to compare the properties, in particular photostability, of both isomers and their
7 TMS-derivatives.

8 **2. Experimental section**

9 *2.1. Materials*

10 Hexane solutions of 2.5 M *n*-butyllithium, toluenesulfonylmethyl isocyanide (TosMIC),
11 terephthaloyl aldehyde, anhydrous potassium carbonate, bromobenzene and 1,4-
12 dibromobenzene were obtained from Acros organics; *tetrakis*(triphenylphosphine)palladium (0)
13 Pd(PPh₃)₄, lithium *tert*-butoxide, 1,4-*bis*(5-phenyloxazol-2-yl)benzene (**POPOP**) scintillation
14 grade were obtained from Sigma-Aldrich and used as received. 1-Bromo-4-
15 (trimethylsilyl)benzene (**3**) was obtained by the method described previously [19]. Synthesis of
16 1,4-*bis*(1,3-oxazol-5-yl)benzene (**2**), 1-bromo-4-(trimethylsilyl)benzene (**3**) and 4-(trimethylsilyl)
17 benzaldehyde (**4**) is described in the results and discussion section. THF, 1,4-dioxane and
18 methanol were dried and purified according to the well-known techniques and then used as the
19 solvents.

20 *2.2. Characterization*

21 The ¹H NMR spectra were recorded on a Bruker WP250 SY spectrometer (250.13 MHz)
22 using the residual signal of CDCl₃ (δ 7.27 ppm) as the internal standard. The ¹³C NMR spectra
23 were recorded on a Bruker Avance II 300 spectrometer at 75 MHz. In the case of ¹H NMR
24 spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in CDCl₃.
25 In the case of ¹³C NMR spectroscopy, the compounds to be analyzed were taken in the form of

1 3-5% solutions in CDCl₃. The spectra were then processed on the computer using the ACD Labs
2 software. Mass-spectra (MALDI) were registered on the Autoflex II Bruker (resolution FWHM
3 18000), equipped with nitrogen laser (work wavelength 337 nm) and time-of-flight mass-
4 detector working in the reflections mode. The resulting spectrum was the sum of 300 spectra
5 obtained at different points of the sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and
6 α -cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as the matrices.

7 Elemental analysis of C, H, N elements was carried out using CHN automatic analyzer
8 CE1106 (Italy). Experimental error is 0.30–0.50 %. The burning was done in the Sheninger flask
9 using alkaline solution of hydrogen peroxide as an absorbent. Spectrophotometry technique
10 was used for the Si analysis.

11 Thermogravimetric analysis was carried out in dynamic mode in 30-800 °C interval using
12 Mettler Toledo TG50 system equipped with M3 microbalance allowing measuring the weight of
13 the samples in 1-150 mg range with 1 μ g precision. Heating/cooling rate was chosen to be 10
14 °C/min. Every compound was studied twice: in air and under nitrogen flow of 200 mL/min.
15 Polarization optical microscope Carl Zeiss Axioscop A40Pol with Linkam temperature controller
16 were used to determine the melting point and for the microphotographs of the crystals.

17 GPC analysis was performed on a Shimadzu instrument with a RID10A^{VP} refractometer
18 and a SPD-M10A^{VP} diode matrix as detectors using 7.8 \times 300 mm² Phenomenex columns (USA)
19 filled with the Phenogel sorbent with pore size of 500 Å and THF as the eluent. In the case of
20 column chromatography, silica gel 60 (“Merck”) was taken. For thin layer chromatography
21 (TLC), “Sorbfil” (Russia) plates were used. The solvents were removed under vacuum (1 mBar)
22 at 40 °C. All reactions, unless stated otherwise, were carried out in an inert atmosphere using
23 anhydrous solvents.

24 The absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer in
25 the standard 10 mm photometric quartz cuvette using THF solutions with the concentrations of

1 10^{-5} M. A scanning spectrofluorimeter ALS01M with registration in single photon counting
2 mode at successive time intervals and automatic adjustment of the intensity of the measured
3 emission was used for the measurements of PL spectra. Measurements were carried out for
4 several optical densities in the range from 0.06 to 0.12 absorbance units in 10 mm cuvette,
5 measurement geometry - 90° . The PLYQ was measured by comparing the integral PL intensity
6 of 10^{-6} M dilute solutions of luminophores in THF with the integral PL intensity of the standard
7 (**POPOP**) as described elsewhere [20].

8 Cyclic voltammetry (CV) measurements were carried out on films rubbed on the
9 electrode in acetonitrile using 0.1 M Bu_4NPF_6 as the supporting electrolyte. The scan rate was
10 200 mV/s. The glassy carbon electrode was used as a working electrode. A platinum plate was
11 used as the counter electrode. The potentials were measured relative to a saturated calomel
12 electrode (SCE). The standard potentials for quasireversible reduction and irreversible oxidation
13 processes were estimated as $\varphi_{\text{red}} = E_{\text{red}}^{1/2} = E_{\text{red}} + 0.06$ V and $\varphi_{\text{ox}} = E_{\text{ox}}^{1/2} = E_{\text{ox}} - 0.06$ V as
14 reported before [21]. CV curves of the luminophores investigated are shown in the Supporting
15 Information (Fig. S9).

16 2.3. Structure studies and molecular modeling

17 Quantum-mechanical calculations were performed using the Firefly software package
18 [22] with B3LYP5/6-31G[d] basis set and level theory [23]. Optimization of the singlet ground
19 state geometry was carried out without restriction on the symmetry. Adiabatic calculation of
20 excited states was carried out by TD DFT using Tamm-Dancoff approximation (TDA). In TD DFT
21 calculations 15 of the lower energy states were optimized.

22 Single-crystal X-ray diffraction was measured at the Swiss-Norwegian Beamlines of the
23 ESRF. The crystals for all compounds were formed during the recrystallization from toluene
24 solutions. The X-ray patterns were collected with a PILATUS2M pixel area detector. A
25 monochromatic beam at a wavelength of $\lambda = 0.69411$ Å was slit-collimated down to 100×100

1 μm^2 . The sample-to-detector distance and parameters of the detector were calibrated using a
2 LaB6 NIST standard. The detector images were recorded by phi-scans in shutter-free mode with
3 a 0.1 deg angular step. The data were preprocessed by SNBL Tool Box [24] and then by CrysAlis
4 Pro [25]. The crystal structures were solved with SHELXS and refined with SHELX [26].
5 CCDC1493771 and CCDC1493772 contain the supplementary crystallographic data for this
6 paper. The data can be obtained free of charge from The Cambridge Crystallographic Data
7 Centre via www.ccdc.cam.ac.uk/structures

8 *2.4. Synthesis of the phenyloxazoles*

9 **5-(4-trimethylsilylphenyl)-1,3-oxazole (5)**. 4-(trimethylsilyl)benzaldehyde (**4**) (2.5 g, 14
10 mmol, 1 equiv.) and TosMIC (2.87, g 14.7 mmol, 1.05 equiv.) were dissolved in methanol (50
11 mL), followed by addition of anhydrous potassium carbonate (3.8 g, 28 mmol, 2 equiv.) [Note:
12 during addition of potassium carbonate the reaction mixture may produce significant amounts
13 of heat]. The reaction mixture was heated to reflux for 2 h. The progress of the reaction was
14 monitored by TLC and GPC analyses. Then the reaction mixture was cooled to room
15 temperature (23 °C) and poured into water (150 mL) and diethyl ether (150 mL). The organic
16 phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent
17 was removed under reduced pressure on the Rotorvapor. The crude product was purified by
18 chromatography on silica gel using toluene as an eluent to give 2.71 g (yield 85.3%) of 96% pure
19 product **5** according to GPC analysis, which was used in the subsequent reactions without
20 additional purification. ^1H NMR (250 MHz, CDCl_3): δ [ppm] 0.29 (s, 12H), 7.37 (s, 1H), 7.60 (dd,
21 4H, $J_1 = 17.39$ Hz, $J_2 = 8.20$ Hz), 7.92 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ [ppm] -1.23, 121.63,
22 123.51, 127.91, 133.84, 141.48, 150.47, 151.61. Calcd (%) for $\text{C}_{12}\text{H}_{15}\text{NOSi}$: C, 66.31; H, 6.96; N,
23 6.44; Si, 12.92. Found: C, 66.12; H, 7.07; N, 6.20; Si, 12.65.

24 **1,4-bis(2-phenyloxazol-5-yl)benzene (isoPOPOP)**. Solutions of lithium *tert*-butoxide
25 (0.94 g, 12 mmol, 5 equiv.), 1,4-bis(1,3-oxazol-5-yl)benzene (**2**) (0.5 g, 2.4 mmol, 1 equiv.),

1 bromobenzene (0.89 g, 5.6 mmol, 2.3 equiv.) and Pd(PPh₃)₄ (54 mg, 0.047 mmol, 2%) in
2 1,4-dioxane (60 mL) was heated to boiling. The reaction mixture was refluxed for 1 h. Progress
3 of the reaction was monitored by GPC analysis. After completeness of the reaction, the reaction
4 mixture was cooled to room temperature (23 °C) and poured into water (200 mL), filtered off
5 and thoroughly washed with water and acetone. The crude product was passed over a short
6 column of silica gel in toluene: ethyl acetate 10:1 mixture to remove the rest of the catalyst.
7 The product was purified by recrystallization from toluene to give a pure compound (686 mg,
8 yield 80%) as yellowish needle crystals, mp. 238-240 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 7.53
9 (8H, overlapping peaks), 7.82 (s, 4H), 8.15 (4H, overlapping peaks). ¹³C NMR (75 MHz, CDCl₃): δ
10 [ppm] 124.12, 124.65, 126.38, 127.29, 127.78, 128.89, 130.53, 150.69, 161.45. Calcd (%) for
11 C₂₄H₁₆N₂O₂: C, 79.11; H, 4.43; N, 7.69. Found: C, 78.93; H, 4.53; N, 7.53. MALDI MS: found *m/z*
12 364.39; calculated for [M]⁺ 364.396.

13 **1,4-bis{2-[4-(trimethylsilyl)phenyl]-1,3-oxazol-5-yl}benzene (TMS-isoPOPOP-TMS)**. This
14 compound was obtained by the method described above for **isoPOPOP** using lithium *tert*-
15 butoxide (0.75 g, 9.4 mmol, 5 equiv.), 1,4-bis(1,3-oxazol-5-yl)benzene (**2**) (0.4 g, 1.9 mmol, 1
16 equiv.), 1-bromo-4-(trimethylsilyl)benzene (**3**) (1.3 g, 5.6 mmol, 3 equiv.) and Pd(PPh₃)₄ (43 mg,
17 0.04 mmol, 2 %) in 1,4-dioxane (50 mL). The product was purified by recrystallization from
18 toluene to give pure compound (709 mg, yield 74%) as yellowish plate-like crystals, mp. 267-
19 269 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 0.33 (s, 18H), 7.52 (s, 2H), 7.66 (d, 4H, J = 8.55 Hz),
20 7.81 (s, 4H), 8.10 (d, 4H, J = 8.55 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] -1.27, 124.12, 124.60,
21 125.34, 127.35, 127.73, 133.73, 143.80, 150.61, 161.52. Calcd (%) for C₃₀H₃₂N₂O₂Si₂: C, 70.82; H,
22 6.34; N, 5.51; Si, 11.04. Found: C, 71.07; H, 6.43; N, 5.39; Si, 11.09. MALDI MS: found *m/z*
23 508.75; calculated for [M]⁺ 508.758.

24 **1,4-bis{5-[4-(trimethylsilyl)phenyl]-1,3-oxazol-2-yl}benzene (TMS-POPOP-TMS)**. This
25 compound was obtained by the method described above for **isoPOPOP** using lithium *tert*-

1 butoxide (1.7 g, 21 mmol, 5 equiv.), 1,4-dibromobenzene (1 g, 4.2 mmol, 1 equiv.), 5-(4-
2 trimethylsilylphenyl)-1,3-oxazole (**5**) (2.21 g, 10 mmol, 2.4 equiv.) and Pd(PPh₃)₄ (98 mg, 0.085
3 mmol, 2 %) in 1,4-dioxane (100 mL). The product was purified by recrystallization from toluene
4 to give pure compound (1.78 g, yield 83%) as yellowish plate-like crystals, mp. 269-271 °C. ¹H
5 NMR (250 MHz, CDCl₃): δ [ppm] 0.32 (s, 18H), 7.52 (s, 2H), 7.62 (d, 4H, J = 7.94), 7.73 (d, 4H, J =
6 7.94), 8.24 (s, 4H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] -1.24, 123.40, 123.99, 126.61, 127.94,
7 128.71, 133.87, 141.51, 151.80, 160.43. Calcd (%) for C₃₀H₃₂N₂O₂Si₂: C, 70.82; H, 6.34; N, 5.51;
8 Si, 11.04. Found: C, 70.56; H, 6.24; N, 5.51; Si, 10.84. MALDI MS: found *m/z* 508.75; calculated
9 for [M]⁺ 508.758.

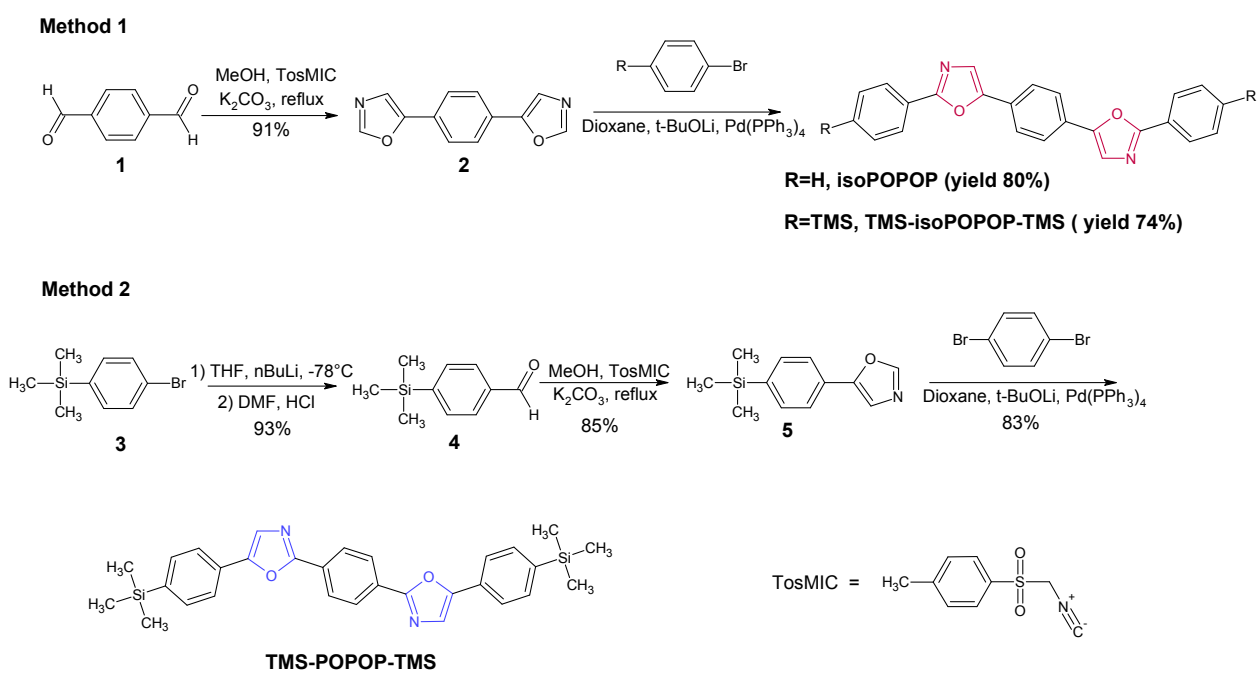
10 **3. Results and discussion**

11 *3.1. Synthesis*

12 The novel method developed for the synthesis of **POPOP**-like luminophores is described
13 in details below. It comprises a step-by-step upbuilding of a phenyloxazole fragment, leading to
14 the formation of **POPOP** luminophore structure. The method is based on the preparation of
15 5-substituted oxazoles starting from aldehydes under Van Leusen conditions [27] as well as on
16 the palladium complexes catalyzed direct C-H arylation [28], which has been widely used for the
17 synthesis of various conjugated oligomers and polymers with atomic precision [29]. The latter
18 method is especially important for oxazoles due to the lack of the need to synthesize reactive
19 organolithium, organomagnesium, organozinc, organoboron or organotin precursors leading to
20 a reduced number of reaction steps, and since the direct C-H arylation may lead to the products
21 of selective substitution at 2 or 5 positions in a given asymmetric heterocycle depending on the
22 reaction conditions and the catalyst used [30].

23 Two synthetic schemes were suggested based on the methods described above (Fig.1).
24 It was found that preparation of the **POPOP** isomer – 1,4-*bis*(2-phenyloxazol-5-yl)benzene (**iso-**
25 **POPOP**), which differs from the **POPOP** solely by the position of oxazole rings relative to the

1 central 1,4-phenylene unit, comprises fewer reaction steps (**method 1**) as compared to the
 2 synthesis of the exact **POPOP** structure (**method 2**). At the same time, **method 1** is preferable
 3 for further development of corresponding NOL preparation approach, since it allows direct
 4 using of already available 4-bromophenylsilyl functional luminophore precursors [10]. However,
 5 we were surprised to find out that almost no data is available in the literature regarding to this
 6 **iso-POPOP** structure. The only description of this **POPOP** isomer preparation was reported in
 7 1979 [31]. In this case 1,4-bis(2-phenyloxazol-5-yl)benzene was obtained via Lewis acid (boron
 8 fluoride) catalyzed decomposition of the corresponding α -diazoketophenone in excess of
 9 benzonitrile in 80% yield. However, this method is not applicable for the synthesis of
 10 organosilicon derivatives due to sophisticated procedures of the starting materials preparation
 11 and high affinity of silicon to fluoride ion.



12 **TMS-POPOP-TMS**

13 **Fig. 1.** Scheme of the synthesis of 1,4-bis(2-phenyloxazol-5-yl)benzene (**isoPOPOP**), 1,4-bis{2-[4-
 14 (trimethylsilyl)phenyl]-1,3-oxazol-5yl}benzene (**TMS-isoPOPOP-TMS**) and 1,4-bis{5-[4-
 15 (trimethylsilyl)phenyl]-1,3-oxazol-2-yl}benzene (**TMS-POPOP-TMS**).

16

1 At the first stage of the isomeric luminophores synthesis a symmetric center 1,4-*bis*(1,3-
2 oxazol-5-yl)benzene (**2**) [32] was prepared from terephthaloyl aldehyde (**1**) and
3 tosylmethylisocyanate (TosMIC) under Van-Leusen conditions. The reaction was performed in
4 boiling methanol as a solvent. Unexpectedly, it was found that usage of ethanol instead of
5 methanol does not lead to the target product formation. Nevertheless, a mixture of methanol
6 and THF may be applied for aldehydes, which have poor solubility in methanol. **IsoPOPOP** and
7 its trimethylsilyl derivative, 1,4-*bis*{2-[4-(trimethylsilyl)phenyl]-1,3-oxazol-5yl}benzene (**TMS-**
8 **isoPOPOP-TMS**), were obtained at the following stages under direct C-H arylation conditions
9 starting from the corresponding bromides. This reaction was initially carried out under
10 microwave synthesis conditions (according to the original method [28] the reaction was
11 performed in sealed tubes above the boiling point of the solvent). However, it was found that
12 regular boiling leads to a rapid (30 min according to GPC analysis) reaction progress in a high
13 yield (74-83%) as well. Both compounds obtained were purified by means of recrystallization
14 from toluene.

15 The second method demonstrates synthesis of the molecule identical to that of **POPOP**
16 luminophore bound to trimethylsilyl substituents - 1,4-*bis*{5-[4-(trimethylsilyl)phenyl]-1,3-
17 oxazol-2-yl}benzene (**TMS-POPOP-TMS**). In this case, 1-bromo-4-(trimethylsilyl)benzene (**3**) was
18 lithiated at the first stage at low temperature in THF to yield corresponding organolithium
19 derivative, which was reacted with DMF. The salt obtained formed the aldehyde via
20 acidification by the stoichiometric amount of 1 M HCl. 4-(Trimethylsilyl)benzaldehyde
21 synthesized (**4**) [33] was transformed into 5-substituted 4-(trimethylsilyl)phenyloxazole (**5**)
22 under Van-Leusen conditions. At the last stage the latter was subjected to direct C-H arylation
23 with 1,4-dibromobenzene. Although this method comprises more steps, all of them are
24 sufficiently selective and proceed in high yields (83-93%). Moreover, purification at some of the
25 stages is not mandatory as the impurities do not affect the following reactions, and their

1 solubility differs significantly from that of the final product, which can thus be easily isolated by
2 means of recrystallization.

3 All the target compounds synthesized are yellowish crystals. It is worth to note that
4 **POPOP** and **isoPOPOP** form needle-shaped crystals, while in the case of trimethylsilyl
5 derivatives formation of plate-like crystals was observed (see Fig. S19 in ESI). Chemical
6 structure and purity of all intermediates and final compounds were confirmed by means of ¹H
7 and ¹³C NMR as well as mass spectroscopy along with analytic GPC and elemental analysis (see
8 Experimental part and Fig. S1 – S12 in ESI).

9

10 3.2. Thermal behaviour

11 Investigation of the thermal stability using thermogravimetric analysis revealed that
12 decomposition (5% weight loss) of **POPOP**, **isoPOPOP**, **TMS-POPOP-TMS**, **TMS-isoPOPOP-TMS**
13 oligomers in the air occurs at 294, 260, 317 and 318 °C respectively (see Fig. S13 in ESI). The
14 decomposition temperatures (5% weight loss) for **POPOP** and **isoPOPOP** under nitrogen flow
15 were found to be lower than those in the air and amount to 284 and 254 °C respectively. This
16 may be related to the partial sublimation under inert atmosphere. The thermal stability of **TMS-**
17 **POPOP-TMS** and **TMS-isoPOPOP-TMS** compounds under nitrogen flow and in the air were
18 almost the same. These results highlight the positive influence of trimethylsilyl substituents on
19 the thermostability of the phenyloxazoles. The residual weights do not exceed 2% at heating up
20 to 700 °C under nitrogen. Thus, **isoPOPOP** seems to be the most thermally unstable compound
21 among the oligomers investigated, while both TMS derivatives are the most and equally
22 thermostable.

23 3.2. X-ray measurements

24 To analyze the structure of the POPOP isomers and their TMS derivatives, single-crystal
25 X-ray diffraction experiments were carried out. Table 1 compares the unit cell parameters

1 found for **isoPOPOP** and **TMS-isoPOPOP-TMS** with the cell parameters of the known **POPOP**
2 luminophore [34].

3 The single crystals exhibit preferential growing direction, which can be explained from
4 the X-ray data by stacking of the aromatic rings and formation of the layered structures similar
5 to the rod-like oligomers such as quinquethiophenes [35]. Despite some similarities, the
6 molecules in the successive layers in the unit cells of **POPOP**, **isoPOPOP** and **TMS-isoPOPOP-**
7 **TMS** crystals are packed differently.

8

9 **Table 1.** Summary of the unit cell parameters of the studied POPOP structural isomers.

Compound	a (Å)	b (Å)	c (Å)	α	β	γ	sym	Z ^b	Angle	Interplane
									between	distance ^d
									layers ^c (deg)	(Å)
POPOP ^a	9.14	5.25	19.20	90	91.81	90	P 2 ₁ /c	2	82.12	3.410
isoPOPOP	5.08	10.54	17.32	90	97.93	90	P 2 ₁ /n	2	52.01	3.312
TMS-isoPOPOP-TMS	6.46	8.28	25.26	90	94.96	90	P 2 ₁ /c	2	45.86	3.224

10 ^aLiterature data [34]

11 ^b number of molecules per unit cell

12 ^c dihedral angle measured between the mean planes in the adjacent molecular layers

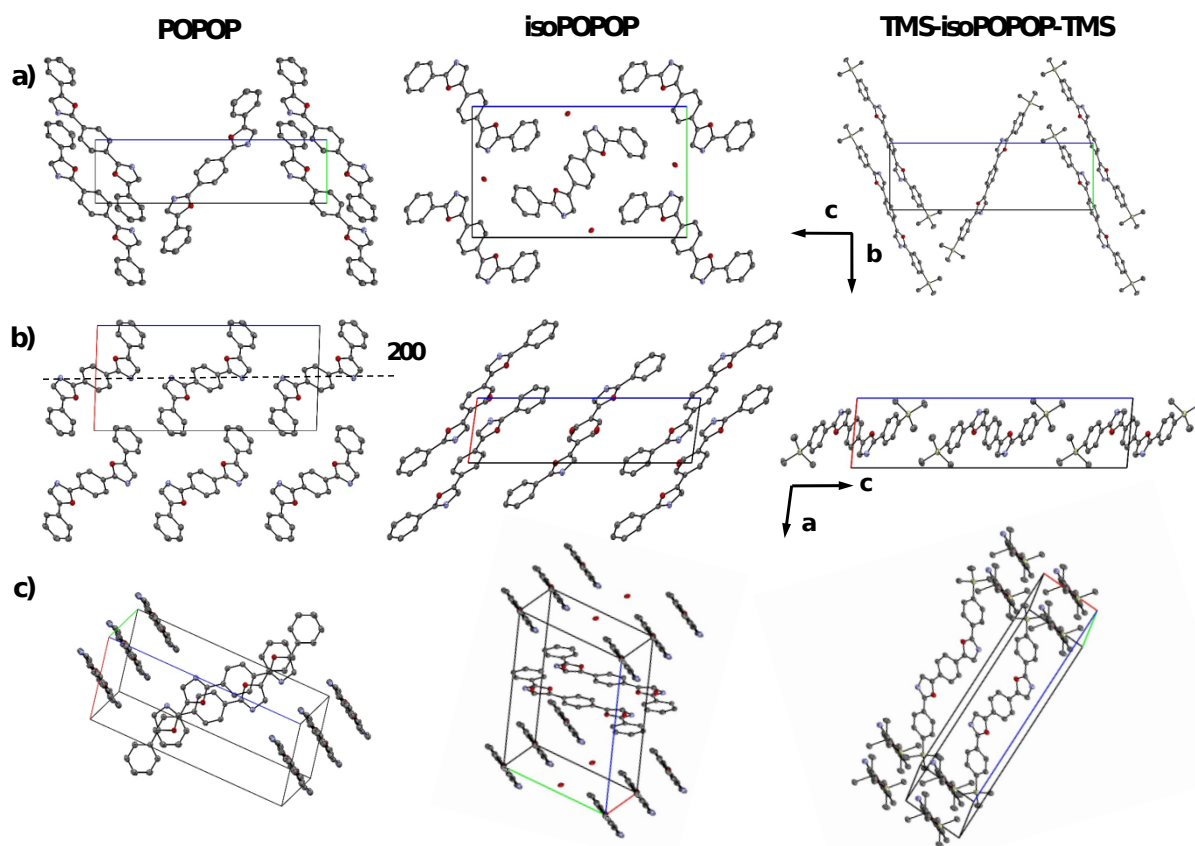
13 ^d distance measured between the mean planes in the adjacent molecular layers

14

15 Figure 2 allows appreciating important structural differences in the molecular packing.

16 Table 1 summarizes the values of the angles and distances between the adjacent molecular
17 planes in the layers. First of all, the molecular planes in the unit cell of **POPOP** are running
18 almost orthogonal to each other in the successive layers. The angle between the molecular
19 planes is approx. 82 deg (see Table 1). By contrast, in the unit cell of **iso-POPOP**, the molecules
20 are inclined to each other less strongly, with the angle between the molecular planes being only

1 of about 52 deg. Surprisingly, the introduction of bulky TMS side groups almost does not affect
 2 this angle. For **TMS-isoPOPOP-TMS** it equals ca. 46 deg. The distance between mean planes in
 3 the adjacent molecular layers decreases with the angle from 3.41 to 3.22 Å. Also, an important
 4 difference between the crystals consists in the positions of the nitrogen atoms. Thus, in the
 5 **POPOP** crystals, all nitrogen atoms are located within one plane, which is 200. In the case of
 6 **isoPOPOP**, the nitrogen atoms are split about the *bc* plane, being offset at a distance of 1.453
 7 Å. For the lattice of **TMS-isoPOPOP-TMS**, this distance is increased to 2.957 Å, which could
 8 explain different thermal stability of these materials.



9

10 **Fig. 2.** (a-b) ORTEP views along *a* (top) and *b* (middle) axis of the **POPOP**, **isoPOPOP** and **TMS-isoPOPOP-**
 11 **TMS** unit cells. For **POPOP** all the nitrogen atoms (given in blue) are positioned within (200) plane. (c)
 12 Projection showing the stacks of the molecular planes with angle between the molecular planes in the
 13 successive layers reducing from 82.12 to 45.86 deg and interplane distance decreasing from 3.41 to 3.22
 14 Å for **POPOP** and **TMS-isoPOPOP-TMS**, respectively. Hydrogens are omitted for clarity.

3.3. Optical properties

Optical properties of all four compounds were investigated in diluted THF solutions. The corresponding absorption and PL spectra are shown in Fig. 3. The absorption and PL spectra of the compounds synthesized are very similar to those of **POPOP**, but slightly shifted as compared to the latter. Table 2 summarizes the absorption and emission maxima wavelength positions (nm), 0-0 transition energy (eV), PLQY and molar extinction coefficients (ϵ) corresponding to the absorption maxima.

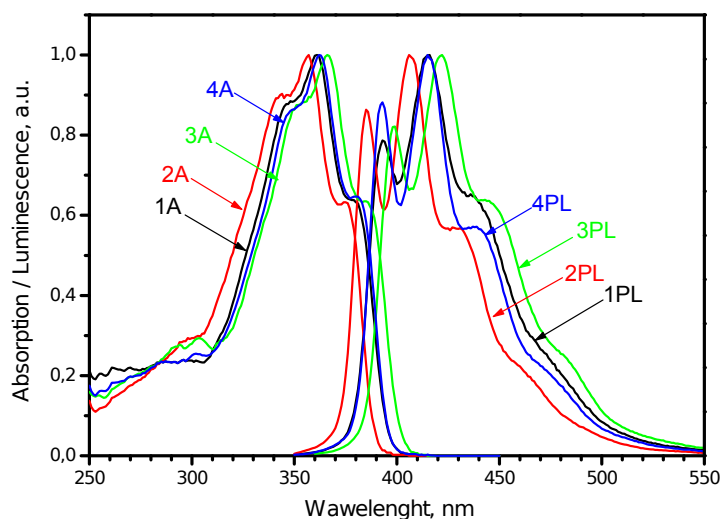


Fig. 3. Absorption (A) and photoluminescence (PL) spectra of the compounds investigated in diluted THF solutions: 1A, 1PL - **POPOP**; 2A, 2PL - **isoPOPOP**; 3A, 3PL - **TMS-POPOP-TMS**; 4A, 4PL - **TMS-isoPOPOP-TMS**.

The **isoPOPOP** structure demonstrates a slight blue shift of the absorption (4 nm) and emission (7 - 10 nm) maxima as compared to **POPOP**. Introduction of trimethylsilyl substituents, on the contrary, leads to a slight red shift of the absorption (5 nm) and emission (6 - 9 nm) spectra as compared to the unsubstituted dyes. In the case of **TMS-isoPOPOP-TMS** the two trends compensate each other, and as a result its absorption and emission spectra are nearly identical to those of **POPOP**. It is also worth noting that molar extinction coefficients of

1 TMS-substituted dyes is ca. 10-20% higher as the corresponding values for the unsubstituted
 2 dyes. All four dyes investigated show high PLQY in the range of 85-96%.

3

4 **Table 2.** Spectral characteristics of diluted THF solutions of the dyes investigated and their
 5 cyclic voltammetry (CV) data.

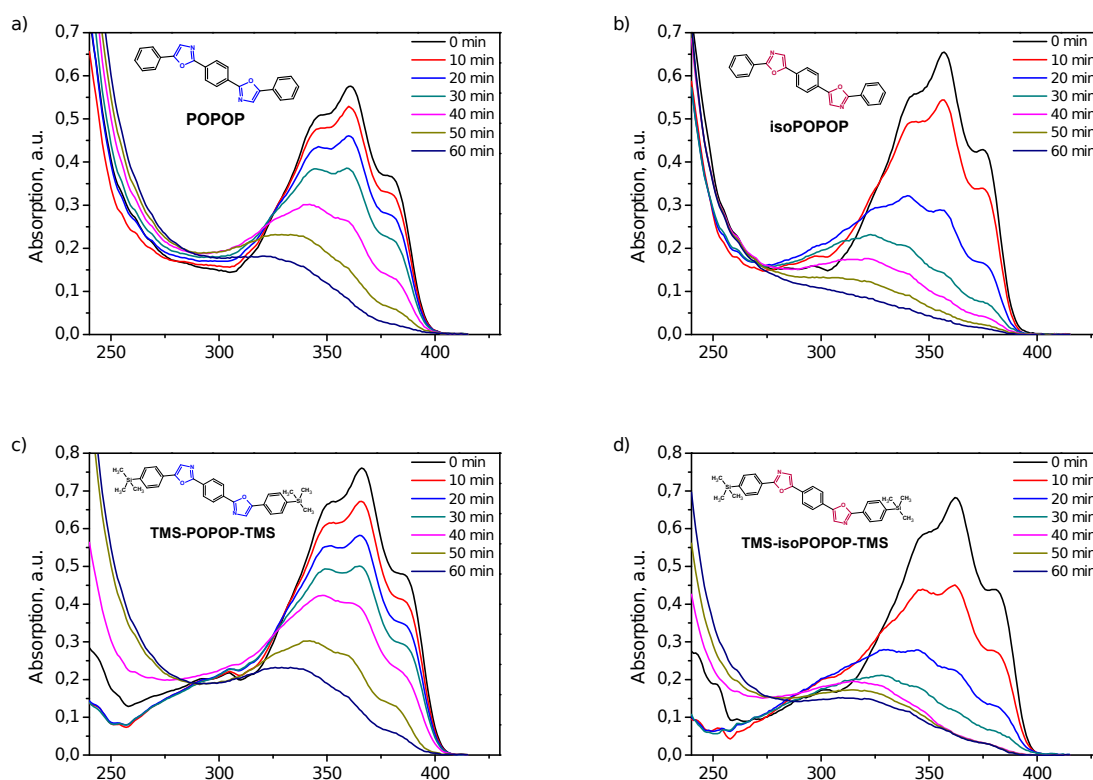
	Abs	PL	E_g^{opt}	PLQY,	ϵ ,	CV		
	λ_{max} , nm	λ_{max} , nm	eV	%	$10^3 \cdot M^{-1} \cdot cm^{-1}$	$\varphi_{ox}(HOMO)$ (V)/(eV)	$\varphi_{red}(LUMO)$ (V)/(eV)	E_g^{EC} (eV)
POPOP	348, 361,379	393, 416, 438	3.20	96	57.2	1.48/-5.88	-1.87/-2.53	3.35
isoPOPOP	344, 357, 375	385, 406, 427	3.25	85	65.2	1.34/-5.74	-2.05/-2.35	3.39
TMS-POPOP-TMS	352, 366, 385	399, 422, 443	3.15	89	69.1	1.49/-5.89	-1.84/-2.56	3.33
TMS-isoPOPOP-TMS	348, 362, 381	393, 415, 439	3.20	91	70.2	1.35/-5.75	n.d.	n.d.

6 Notes: Abs - absorption maximum, PL - photoluminescence maximum, E_g^{opt} - optical energy
 7 gap, PLQY - photoluminescence quantum yield, E - molar extinction coefficient, CV - cyclic
 8 voltammetry data, φ_{ox} - standard oxidation potential, φ_{red} - standard reduction potential, E_g^{EC} -
 9 electrochemical energy gap. Excitation of the PL was made at the respective maximum of the
 10 absorption band. Accuracy of the absolute value of PL reported is +/-7. Relative error of the PL
 11 measurements is 0.5%.

12 3.4. Photooxidation stability

13 In order to estimate photooxidation stability of the dyes in THF solution, accelerated
 14 photostability tests with a help of 150W xenon lamp having a maximum emission at 300-400
 15 nm wavelength range was performed. Fig. 4 shows plots of changes in the absorption spectra of
 16 the dyes as a function of irradiation time. As can be seen from the data presented, under
 17 continuous UV irradiation the long-wavelength absorption peaks at 300-400 nm dramatically
 18 decrease, while absorption in the short-wavelength region (below 300 nm) simultaneously
 19 increases. Such results indicate on destruction of the conjugated system of the phenyloxazoles

1 investigated. Moreover, it was found that the compounds containing **POPOP**-like fragment are
2 more resistant to degradation than the corresponding **isoPOPOP** derivatives (Fig. 5). The
3 estimated half-life time of **TMS-isoPOPOP-TMS** and **isoPOPOP** dyes was found to be 19+/-4 and
4 21+/-4 min respectively. Whereas the half-life time of **POPOP** and **TMS-POPOP-TMS** dyes was
5 twice longer and reached 37+/-4 and 39+/-4 min, respectively. Thus, introduction of
6 organosilicon substituents does not have any significant influence on the photooxidation
7 stability, which is mainly defined by the conjugated core structure (**POPOP** or **isoPOPOP**). THF
8 was chosen as a solvent as one of the most aggressive for photooxidation stability
9 investigations that allows to reach the maximal photo bleaching of the dyes for a minimum
10 time.



11

12

13 **Fig. 4.** UV-vis absorption spectral changes of the dyes investigated in THF at 296 K as a function
14 of irradiation time upon exposure to light from 150 W xenon lamp in the presence of air.

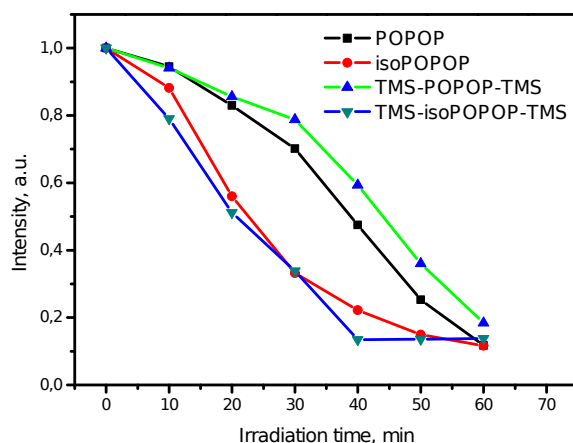


Fig. 5. Changes in absorption (at their peak values) of the phenyloxazoles over irradiation time.

3.5. Electrochemical properties

Electrochemical properties of **POPOP** and **isoPOPOP**-based dyes synthesized were studied using cyclic voltammetry (CV) technique (Table 2, Fig. S14 in ESI). For all the compounds irreversible oxidation peaks were observed. **POPOP** was the only oligomer capable to undergo further oxidation, but its CV curve demonstrates two irreversible anodic peaks. The data presented in Table 2 shows that the first oxidation potentials of both **isoPOPOP** and **TMS-isoPOPOP-TMS** isomers, as well as those of **POPOP** and **TMS-POPOP-TMS** are close to each other and do not depend on the presence or absence of trimethylsilyl groups. At the same time, the latter couple of compounds are oxidized as at higher potentials (140 mV) as compared to their isomeric analogs.

The reduction of **POPOP** and **TMS-POPOP-TMS** proceeds in one quasireversible step at close potentials (-1.84 ... -1.87 V), while **isoPOPOP** is irreversibly reduced at quite large negative potentials (-2.05 V), and the CV of **TMS-isoPOPOP-TMS** did not demonstrate any reduction peaks up to the background discharge potentials. Based on the CV oxidation and reduction potentials, values of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) were calculated using the equations 1 and 2 [36]:

$$E(\text{HOMO}) = -e(\phi_{\text{ox}} + 4.40) \text{ (eV)} \quad (1)$$

$$E(\text{LUMO}) = -e(\phi_{\text{red}} + 4.40) \text{ (eV)} \quad (2)$$

Thus, the electrochemical data evidence the ability of **POPOP** and **TMS-POPOP-TMS** dyes to undergo reversible reduction and stable anion-radical formation as opposite to their isomers **isoPOPOP** and **TMS-isoPOPOP-TMS**. Presence of the terminal trimethylsilyl groups does not virtually affect the oxidation and reduction potential values and CV shapes.

3.5. Theoretical calculations

In order to confirm the trends revealed, computer modelling based on the method of time-dependent density functional theory (TD DFT) using Tamm-Dancoff approximation (TDA), was performed (Table 3). For all the four compounds investigated two structural shapes close in full energy were found (Fig. S15-S18 in ESI). One of the shapes is polar (C_{2v} symmetry group), while the other has a zero dipole moment due to the C_{2h} symmetry group. Dipole moments of the main (μ_0) and the first excited (μ_1) states were calculated. Since the dipole moment in this case is orientated along the main axis of symmetry, the table represents its projection up to the sign. In **isoPOPOP** type structures dipole moment of the excited state of C_{2v} symmetry is opposite in direction to the dipole moment of the main state, while on **POPOP**-type structures electronic density change under excitation is less significant.

Table 3. Calculated parameters for the phenyloxazoles using TD DFT computer modeling.

	ΔE_{01} , eV	$\Delta\lambda_{01}$, nm	Symmetry type	E_0 , Hatree	μ_0 (μ_1), Debye	E(HOMO), eV	E(LUMO), eV	E_g^{DFT} , eV	Oscillator strength
POPOP	3.31	375	C_{2h}	-1183.4278134	3.014	-5.30	-1.80	3.5	2.014
			C_{2v}	-1183.4276984	(3.788)				1.796
isoPOPOP	3.32	373	C_{2h}	-1183.4280159	1.793	-5.25	-1.75	3,5	2.071
			C_{2v}	-1183.4280163	(-0.255)				1.869
TMS-POPOP-TMS	3.22	385	C_{2h}	-2000.4718386	3.375	-5.27	-1.81	3,46	2.312
			C_{2v}	-2000.4716688	(3.967)				1.993
TMS-isoPOPOP-TMS	3.23	383	C_{2h}	-2000.4716896	2.192	-5.22	-1.76	3,46	2.355
			C_{2v}	-2000.4717083	(-0.168)				2.055

1

2 The calculated energies of $S_0 - S_1$ electronic transitions (Table 3) are approximately 0.1
3 eV larger as compared to the energies of 0-0 transitions evaluated from the THF solutions
4 spectra (Table 2). Increasing the values of the oscillator strengths calculated during the
5 transition to trimethylsilyl derivatives are in a good agreement with enlarging the molar
6 extinction coefficient data measured for THF solutions of these compounds. A general trend of
7 the reduction in energy of the molecular orbital levels for compounds of **POPOP**-type structure
8 as compared to their isomers and constriction of the energy gap for trimethylsilyl derivatives
9 are in a good agreement with the experimental data. On the other hand, similar energy gaps
10 calculated for the isomers well as their HOMO and LUMO energy levels, which are
11 overestimated by ca. 0.6 eV, does not correlate well with the experimental data. This
12 contradiction may be assigned to a low precision of the computer model applied, according to
13 which electronic properties of single molecules in vacuum were calculated.

14 **4. Conclusions**

15 In this work two novel organosilicon derivatives of phenyloxazole luminophores were
16 synthesized under mild conditions using Van Leusen reactions and palladium complexes
17 catalyzed regioselective direct C-H arylation. All the reactions used were highly selective and led
18 to excellent yields. Moreover, they allow preparation of **POPOP** and its isomer **iso-POPOP**
19 derivatives, which are unstable under acidic conditions. Investigation of their spectral
20 luminescent properties revealed that all of them possess high PLQYs and high molar extinction
21 coefficients up to $70.2 \times 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$, while their absorption and emission maxima vary within
22 357-366 nm and 406-422 nm, respectively. Cyclic voltammetry showed that the molecules with
23 the **POPOP** structure are more stable to oxidation as compared to their isomers, while presence
24 of the TMS substituents does not affect the values of the oxidation or reduction potentials.
25 Single-crystal X-ray diffraction experiments revealed important structural differences between

1 the lattices of the isomers: the angle between the molecular planes and positions of the
2 nitrogen atoms is different for **POPOP** and **isoPOPOP** structures. Quantum mechanical
3 parameters of these oligomers calculated via TD DFT method (HOMO and LUMO energy values,
4 energy gap and oscillator strength) correspond well to the optical spectroscopy and cyclic
5 voltammetry experimental data. The novel trimethylsilyl derivatives of phenyloxazoles reported
6 in this work may find applications in organic photonics due to their high PLQY, large molar
7 extinction coefficients as well as high photo- and thermo- stability.

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13 and DCS measurements.

14 **Supplementary material**

15 Supplementary data contain ^1H and ^{13}C NMR spectra, MALDI MS spectra, GPC and CV curves,
16 TGA data, pictures of frontier molecular orbitals for the dyes calculated by DFT B3LYP/6-31G[d]
17 method, microphotographs of the crystals and single-crystal X-ray diffraction data (CCDC:
18 1493771-1493772). Supplementary data associated with this article can be found in the online
19 version at doi: 10.1016/

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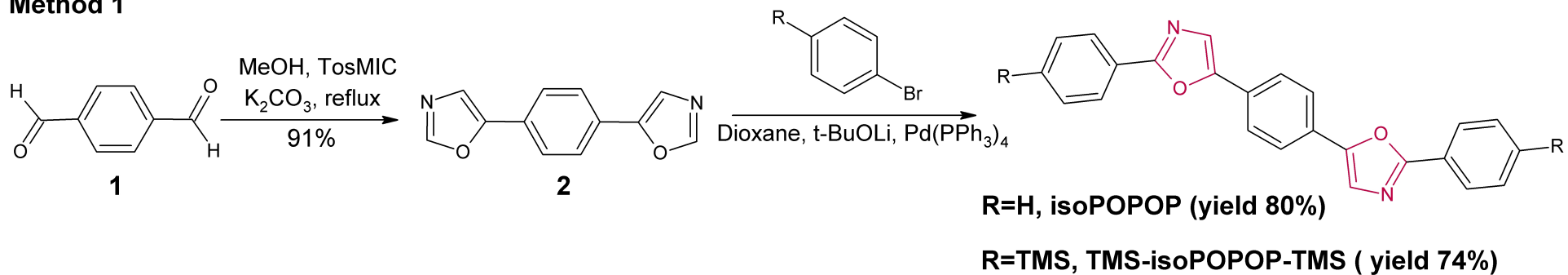
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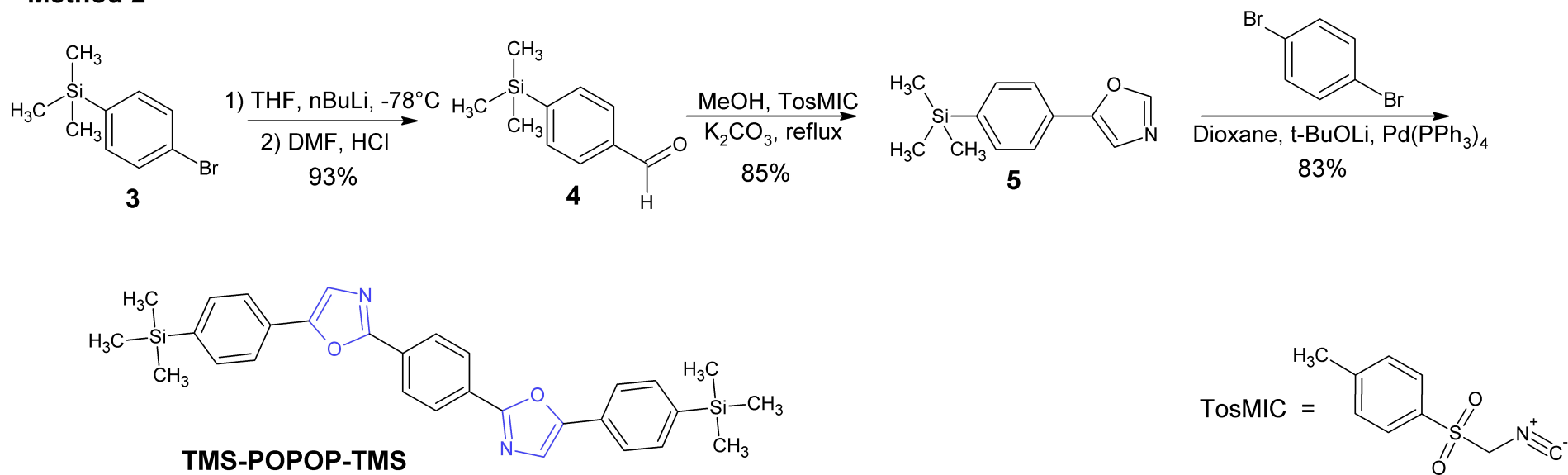
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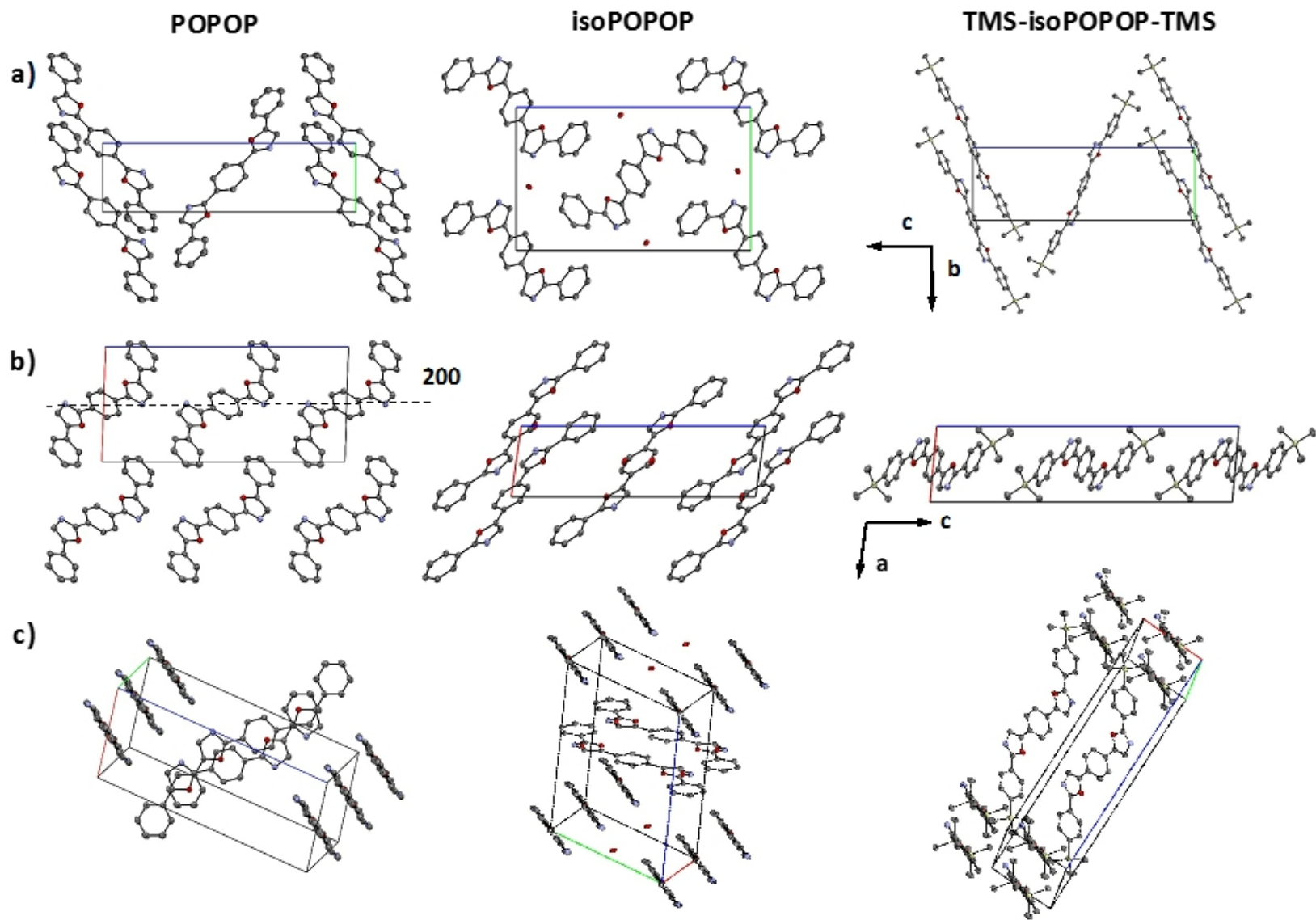
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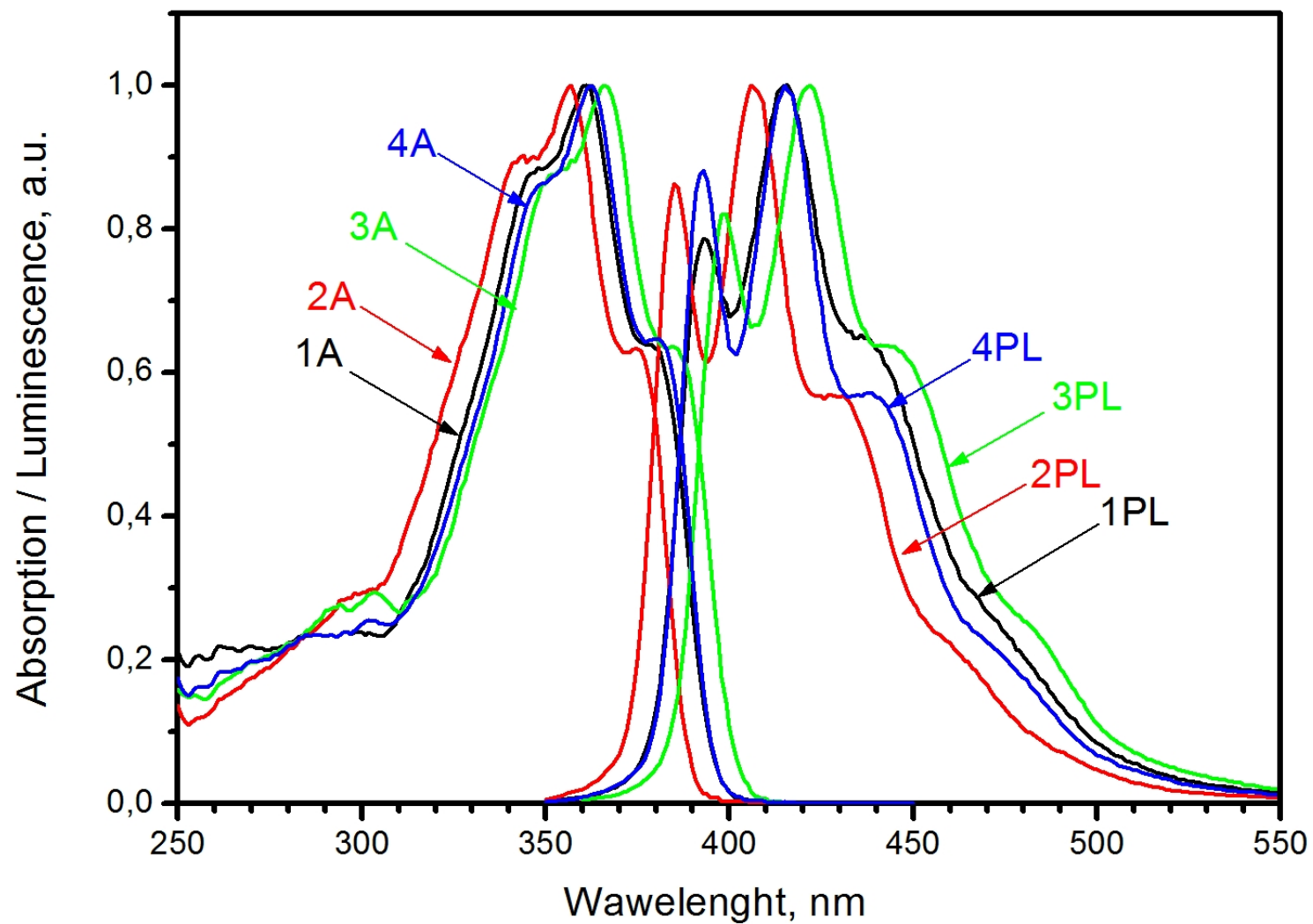
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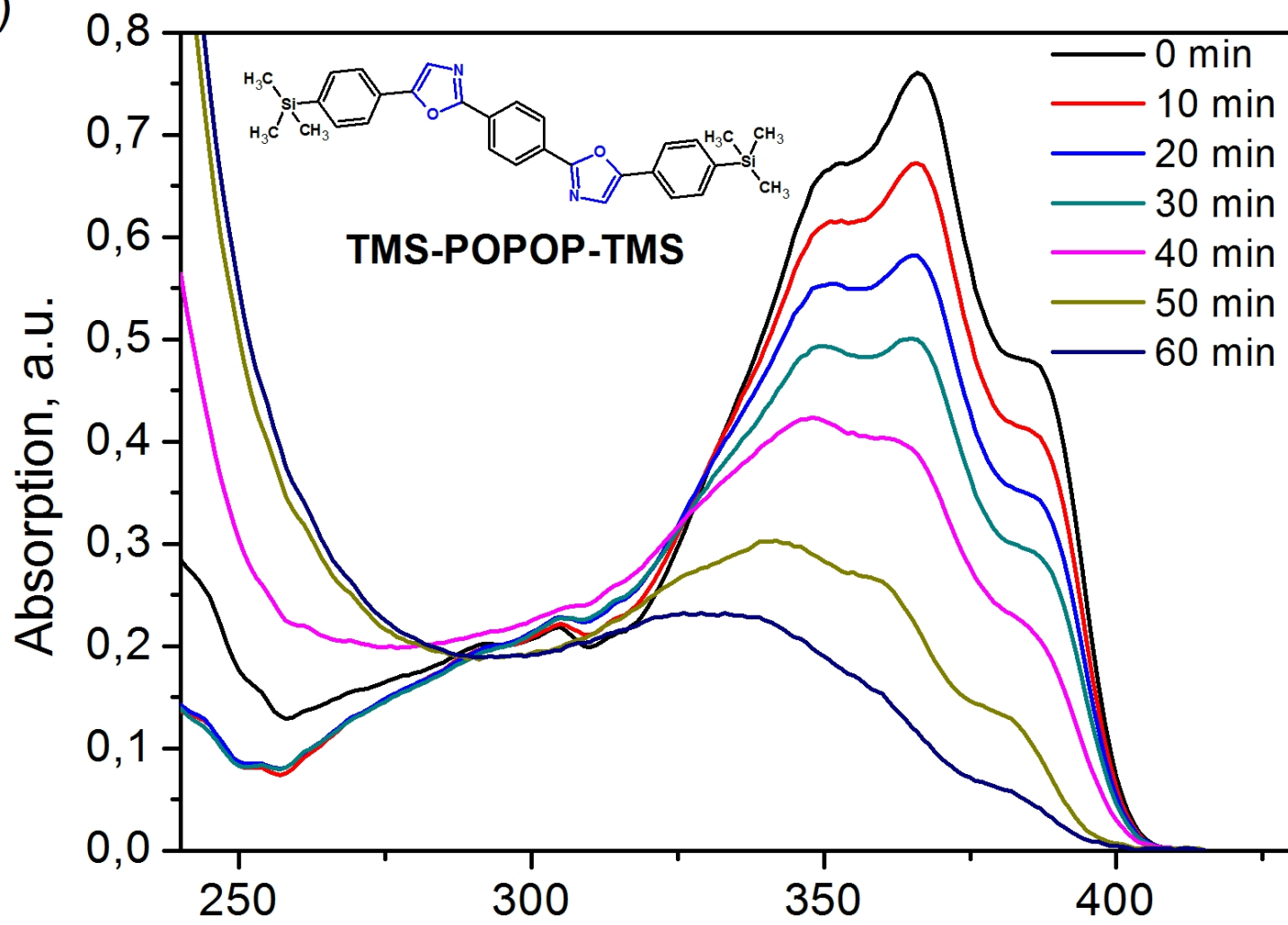
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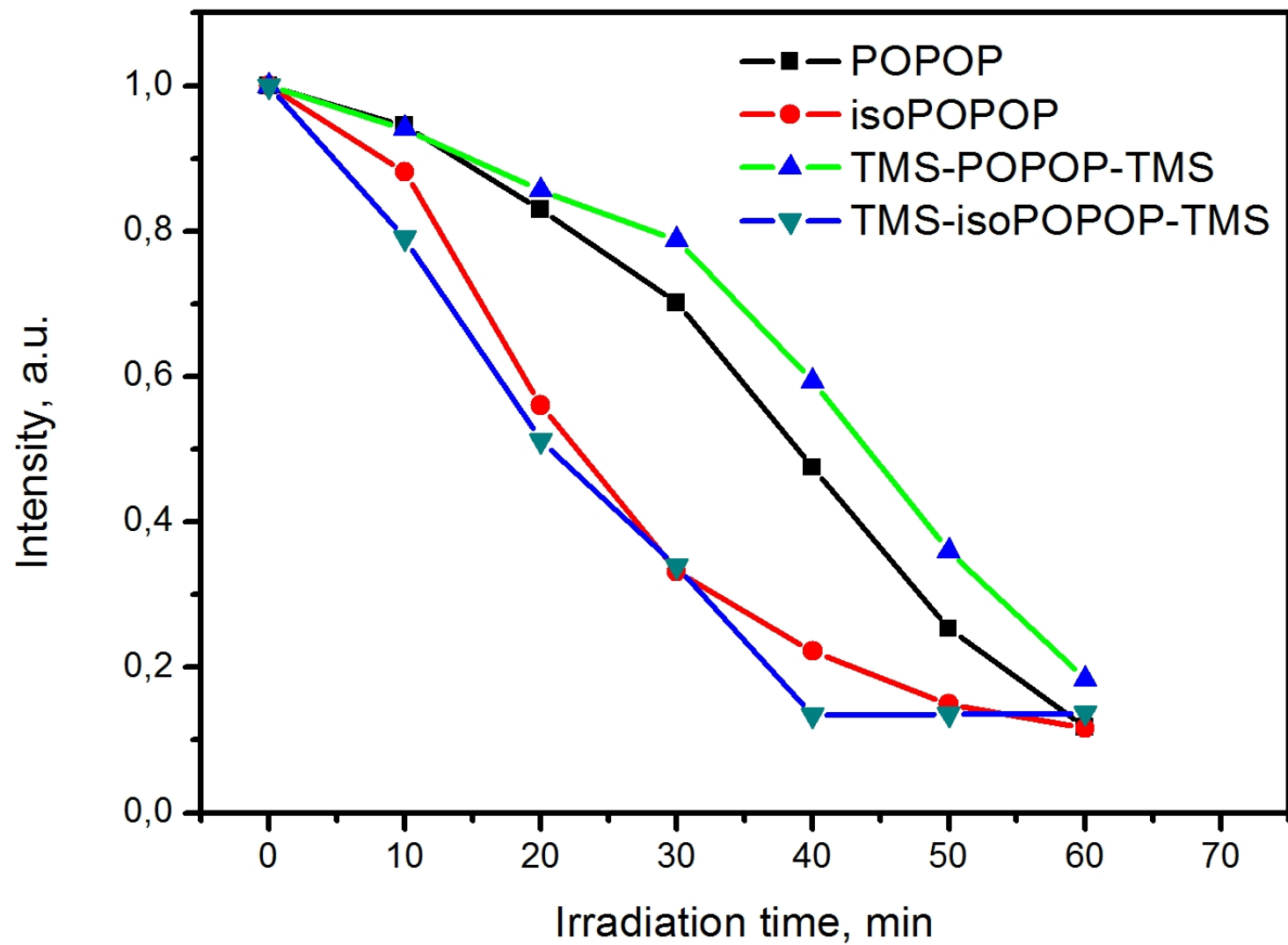






c)





checkCIF/PLATON report

Structure factors have been supplied for datablock(s) isoPOPOP

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: isoPOPOP

Bond precision:	C-C = 0.0020 A	Wavelength=0.70135	
Cell:	a=5.08300(14)	b=10.54100(18)	c=17.3178(4)
	alpha=90	beta=97.929(2)	gamma=90
Temperature:	100 K		
	Calculated	Reported	
Volume	919.02(4)	919.02(3)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C24 H16 N2 O2, 0.842(H2 O)	C24 H16 N2 O2, 0.842(H2 O)	
Sum formula	C24 H17.68 N2 O2.84	C24 H17.68 N2 O2.84	
Mr	379.56	379.63	
Dx,g cm-3	1.372	1.372	
Z	2	2	
Mu (mm-1)	0.087	0.087	
F000	396.8	397.0	
F000'	397.00		
h,k,lmax	6,13,21	4,13,21	
Nref	1888	1364	
Tmin,Tmax	0.990,1.000	0.471,1.000	
Tmin'	0.970		

Correction method= # Reported T Limits: Tmin=0.471 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.722 Theta(max)= 25.984

R(reflections)= 0.0397(1317) wR2(reflections)= 0.1092(1364)

S = 1.089 Npar= 143

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level A

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.766 Note

Author Response: Measurement was performed by a 360 degree phi-scan on an one-axis goniometer.

Alert level B

PLAT911_ALERT_3_B Missing # FCF Refl Between THmin & STh/L= 0.600 238 Report

Author Response: Measurement was performed by a 360 degree phi-scan on an one-axis goniometer.

Alert level C

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

colourless,

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

strongly

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

birefringent

CRYSC01_ALERT_1_C No recognised colour has been given for crystal colour.

PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. Please Check

PLAT088_ALERT_3_C Poor Data / Parameter Ratio 9.54 Note

PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note

C24 H16 N2 O2

PLAT906_ALERT_3_C Large K value in the Analysis of Variance 2.088 Check

PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density 0 Note

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu not performed for this radiation type.

RADNT01_ALERT_1_G Extra text has been found in the _diffrn_radiation_type field.

Radiation given as synchrotron, Si(111)

Radiation identified as synchrotron

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3 Note

PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report

PLAT302_ALERT_4_G Anion/Solvent Disorder Percentage = 100 Note

PLAT304_ALERT_4_G Non-Integer Number of Atoms (1.26) in Resd. # 2 Check

PLAT860_ALERT_3_G Number of Least-Squares Restraints 1 Note

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 70 Note

PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ 2 Units

PLAT956_ALERT_1_G Calculated (ThMax) and Actual (FCF) Hmax Differ 2 Units

1 **ALERT level A** = Most likely a serious problem - resolve or explain

1 **ALERT level B** = A potentially serious problem, consider carefully

9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

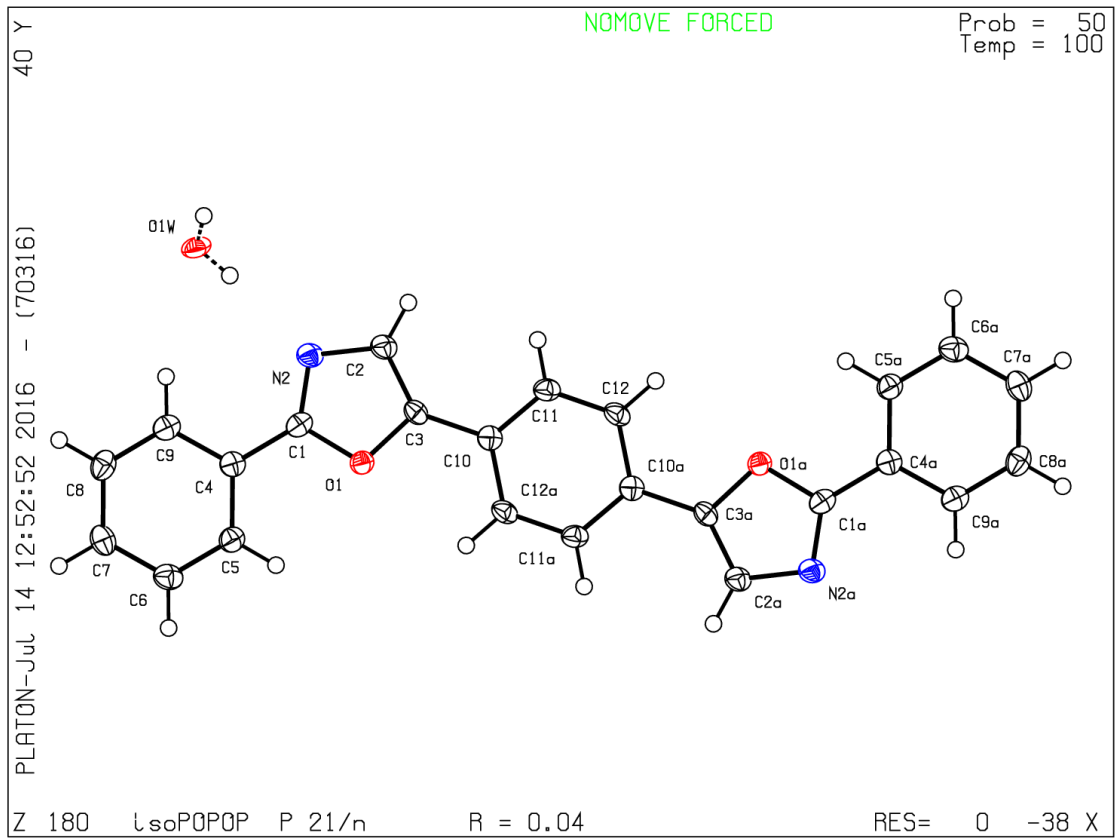
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 08/07/2016; check.def file version of 05/07/2016



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) TMS-POPOP-TMS

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: TMS-POPOP-TMS

Bond precision: C-C = 0.0035 A Wavelength=0.70171

Cell: a=6.4565(2) b=8.2768(2) c=25.2570(5)
 alpha=90 beta=94.960(2) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	1344.66(6)	1344.66(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C30 H32 N2 O2 Si2	C30 H32 N2 O2 Si2
Sum formula	C30 H32 N2 O2 Si2	C30 H32 N2 O2 Si2
Mr	508.76	508.75
Dx,g cm-3	1.257	1.257
Z	2	2
Mu (mm-1)	0.155	0.155
F000	540.0	540.0
F000'	540.49	
h,k,lmax	7,9,30	7,9,30
Nref	2381	2251
Tmin,Tmax	0.983,1.000	0.458,1.000
Tmin'	0.956	

Correction method= # Reported T Limits: Tmin=0.458 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.945 Theta(max)= 24.687

R(reflections)= 0.0570(2127) wR2(reflections)= 0.1607(2251)

S = 1.117 Npar= 166

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.945 Note

Author Response: Measurement was performed by a 360 degree phi-scan on an one-axis goniometer.

Alert level C

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

colourless,

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

strongly

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.

birefringent

CRYSC01_ALERT_1_C No recognised colour has been given for crystal colour.

PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note

C30 H32 N2 O2 Si2

PLAT906_ALERT_3_C Large K value in the Analysis of Variance 2.988 Check

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.595 130 Report

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu not performed for this radiation type.

RADNT01_ALERT_1_G Extra text has been found in the _diffrn_radiation_type field.

Radiation given as synchrotron, Si(111)

Radiation identified as synchrotron

PLAT804_ALERT_5_G Number of ARU-Code Packing Problem(s) in PLATON 8 Info

PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still 95 %

PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF 1 Note

PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density 6 Note

-
- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
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-

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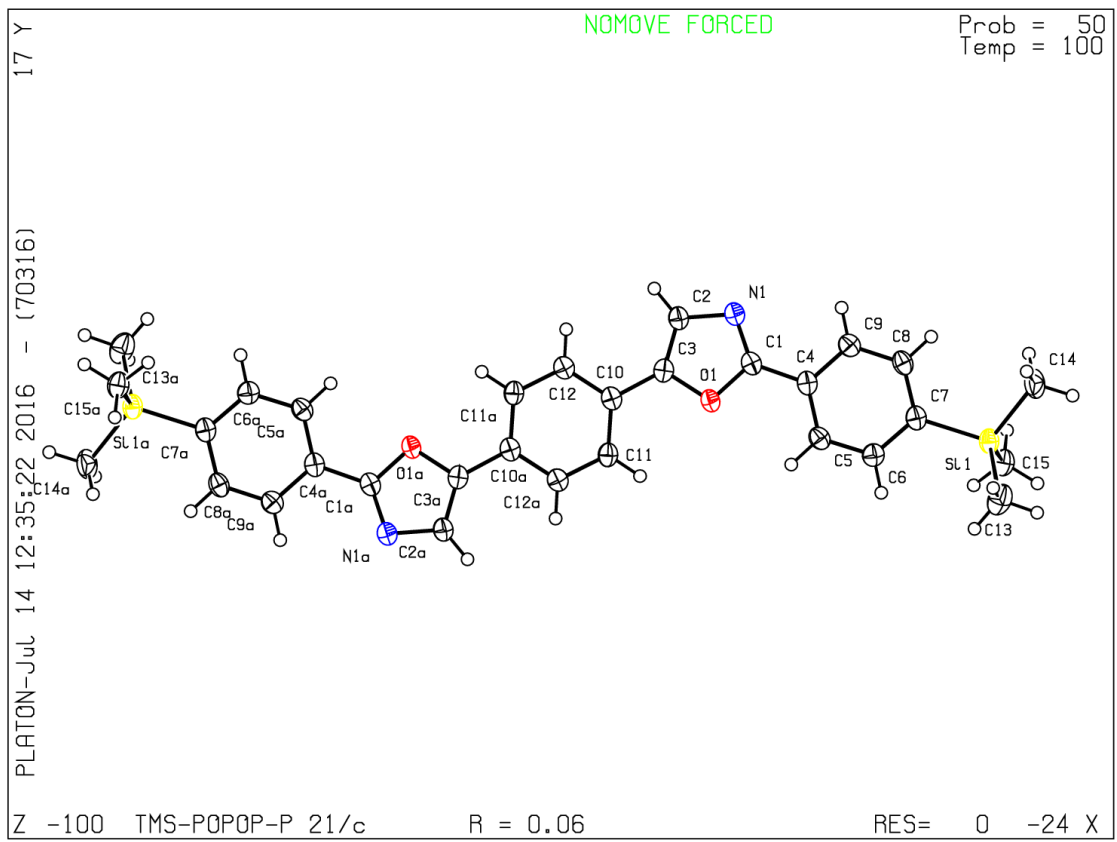
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A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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PLATON version of 08/07/2016; check.def file version of 05/07/2016



Synthesis and photostability of 1,4-*bis*(5-phenyloxazol-2-yl)benzene (POPOP) structural isomers and their trimethylsilyl derivatives

Maxim S. Skorotetcky, Oleg V. Borshchev, Nikolay M. Surin, Yaroslav Odarchenko, Sergey A. Pisarev,
Svetlana M. Peregudova, Karl W. Törnroos, Dmitry Chernyshov, Dimitri A. Ivanov, Sergey A. Ponomarenko

CONTENTS

1. ¹ H, ¹³ C NMR spectra.....	2
2. Mass-spectra (MALDI MS) data.....	10
3. Gel permeation chromatography (GPC) analysis data.....	13
4. Cyclic voltammetry (CV) curves.....	14
5. Thermogravimetric analysis (TGA) data.....	15
6. The frontier molecular orbitals for luminophores calculated by DFT using the B3LYP/6-31G[d] level of theory.....	16
7. Microphotographs of the crystals.....	20

1. ¹H, ¹³C NMR spectra

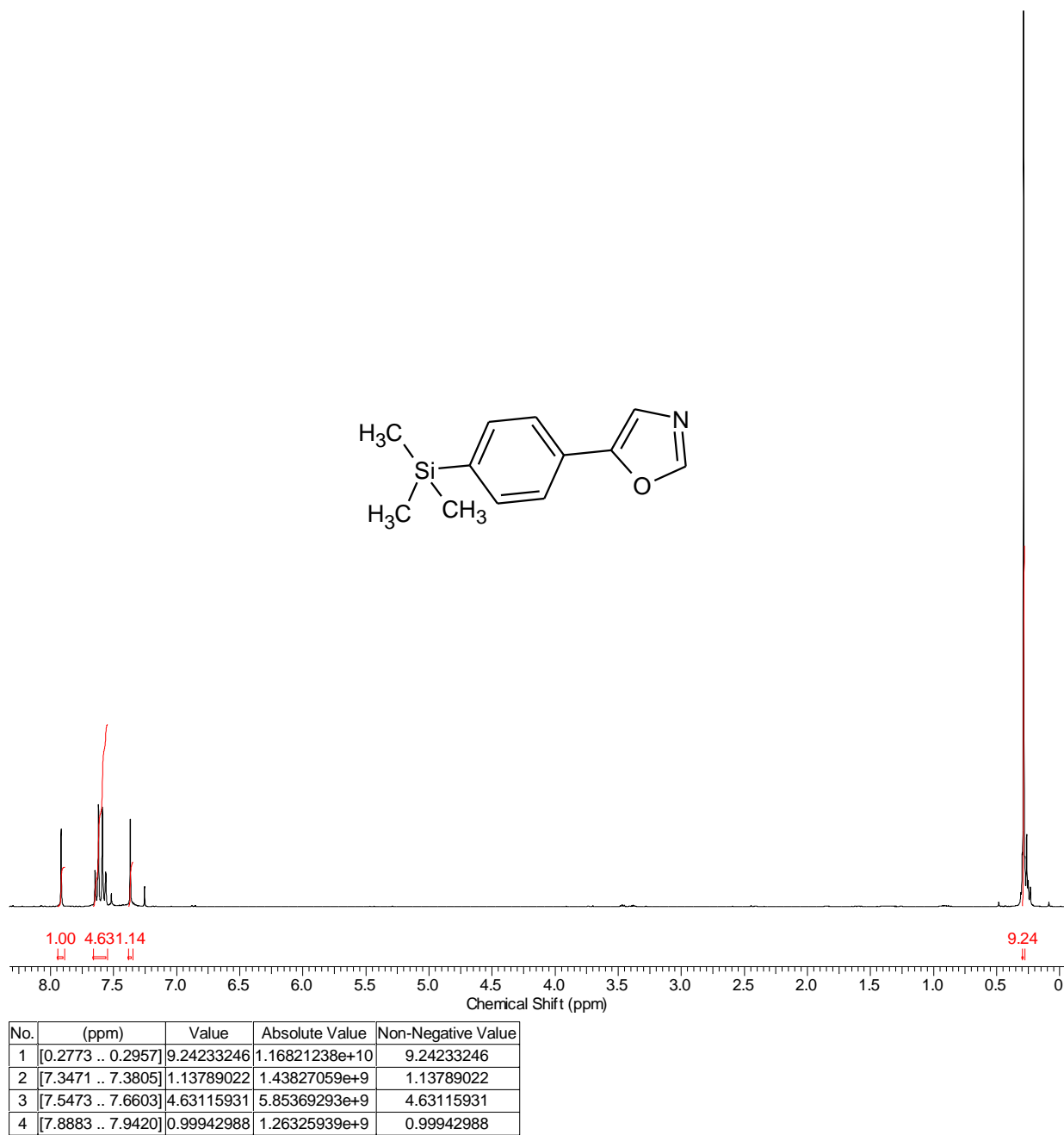


Figure S1. 1 H NMR spectrum of 5-(4-trimethylsilylphenyl)-1,3-oxazole (5)

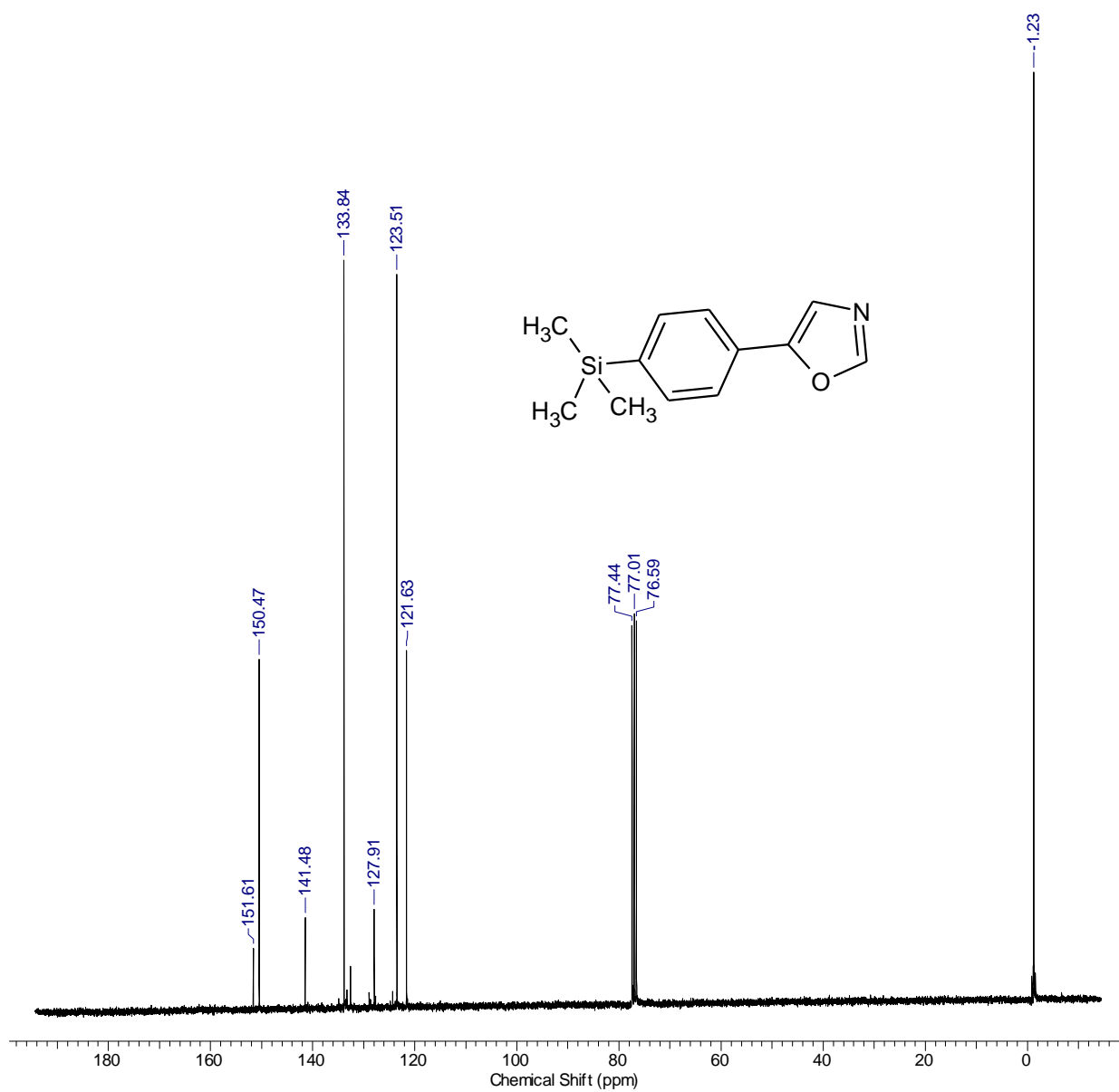
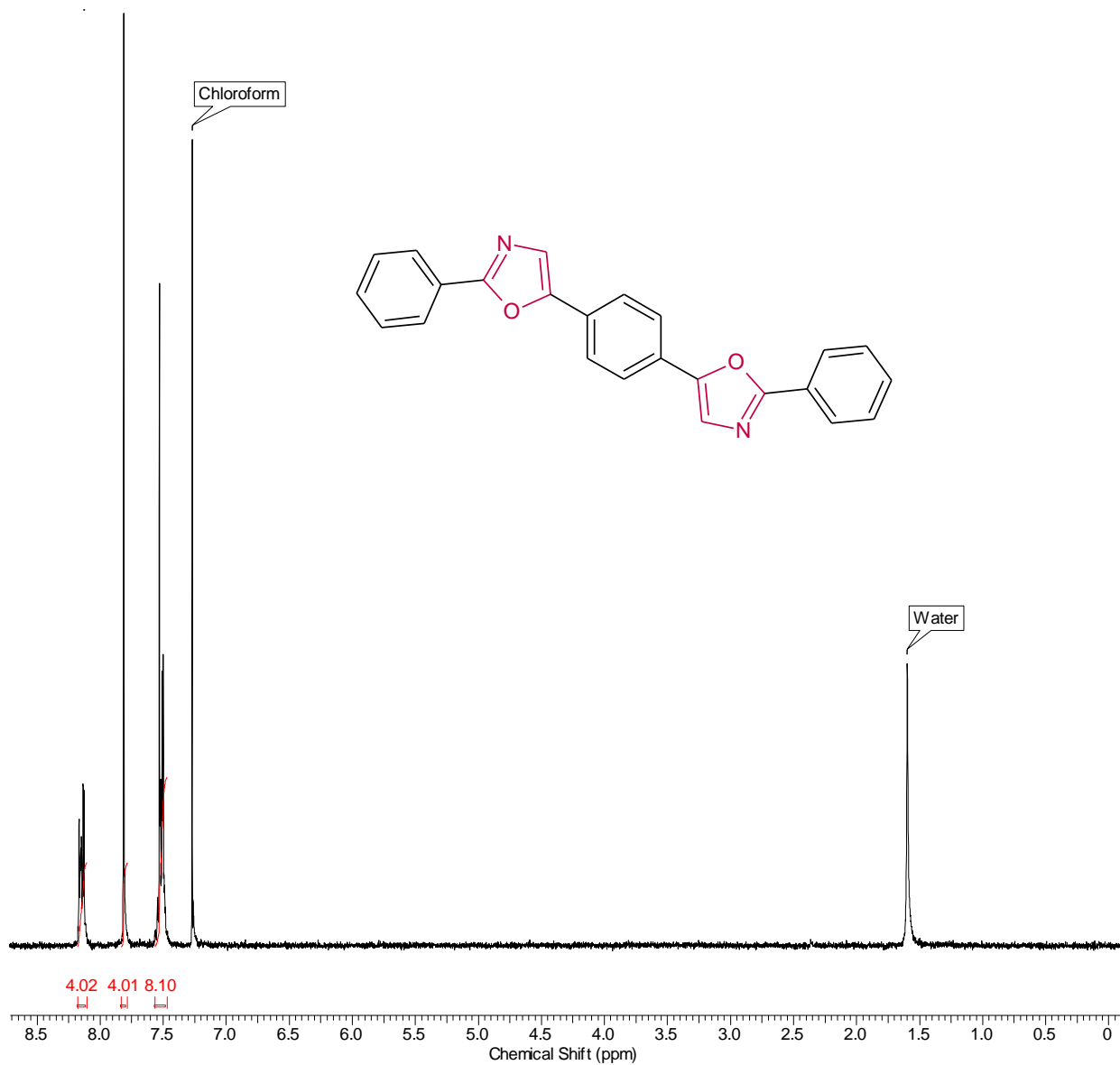


Figure S2. ¹³C NMR spectrum of 5-(4-trimethylsilylphenyl)-1,3-oxazole (5)



No.	(ppm)	Annotation	Layer No.	Created By	Created At
1	1.60	Water	1	Skorotekiy	Пн 19.10.2015 19:54:14
2	7.27	Chloroform	1	Skorotekiy	Пн 19.10.2015 19:54:30

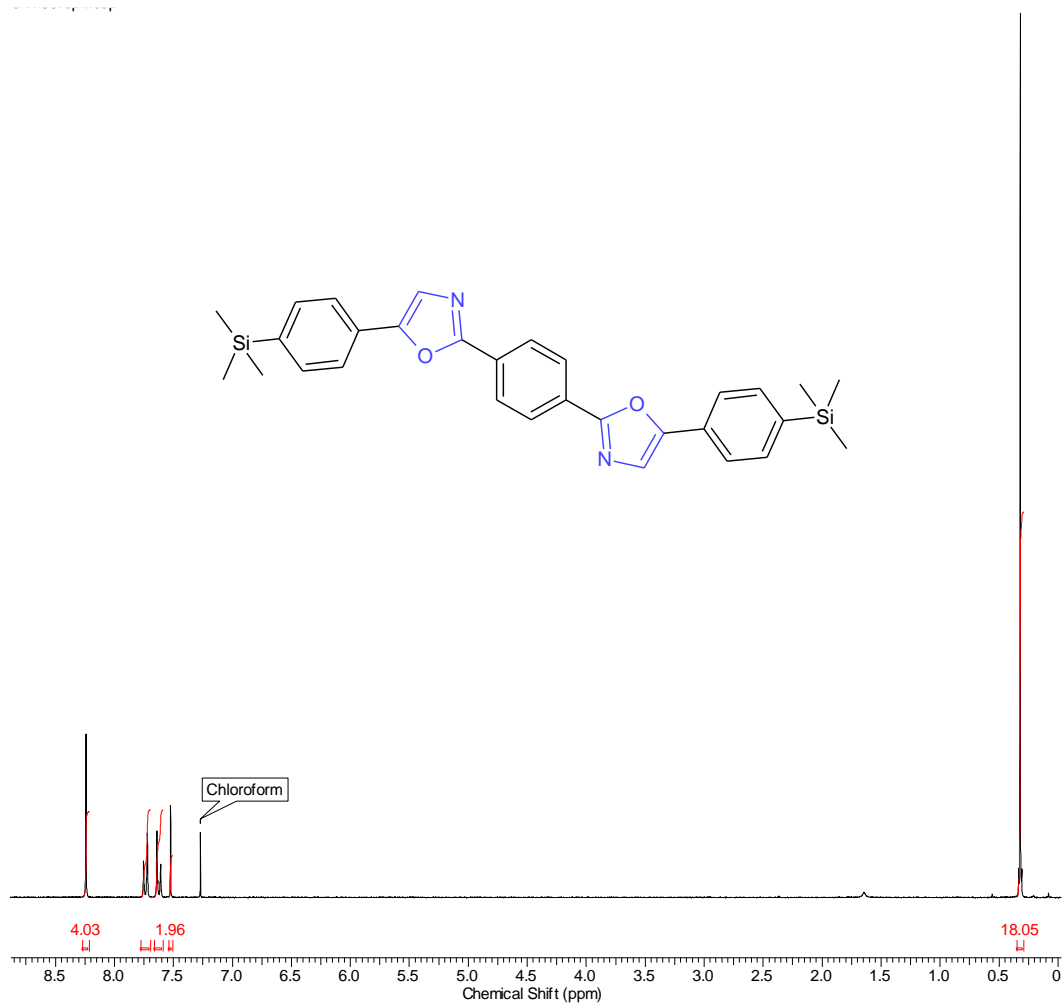
No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[7.4676 .. 7.5643]	8.09863091	2.79531460e+7	8.09863091
2	[7.7832 .. 7.8315]	4.01005507	1.38410620e+7	4.01005507
3	[8.1055 .. 8.1793]	4.02407265	1.38894450e+7	4.02407265

Figure S3. ^1H NMR spectrum of 1,4-bis(2-phenyloxazol-5-yl)benzene (isoPOPOP)



No.	(ppm)	(Hz)	Height
1	76.71	7717.8	0.9941
2	77.03	7750.1	1.0000
3	77.34	7781.6	0.9807
4	124.12	12487.6	0.0807
5	124.65	12541.2	0.1537
6	126.38	12715.1	0.1517
7	127.29	12807.5	0.0477
8	127.78	12855.9	0.0522
9	128.89	12968.2	0.1544
10	130.53	13133.2	0.0740
11	150.69	15161.6	0.0476
12	161.45	16244.4	0.0395

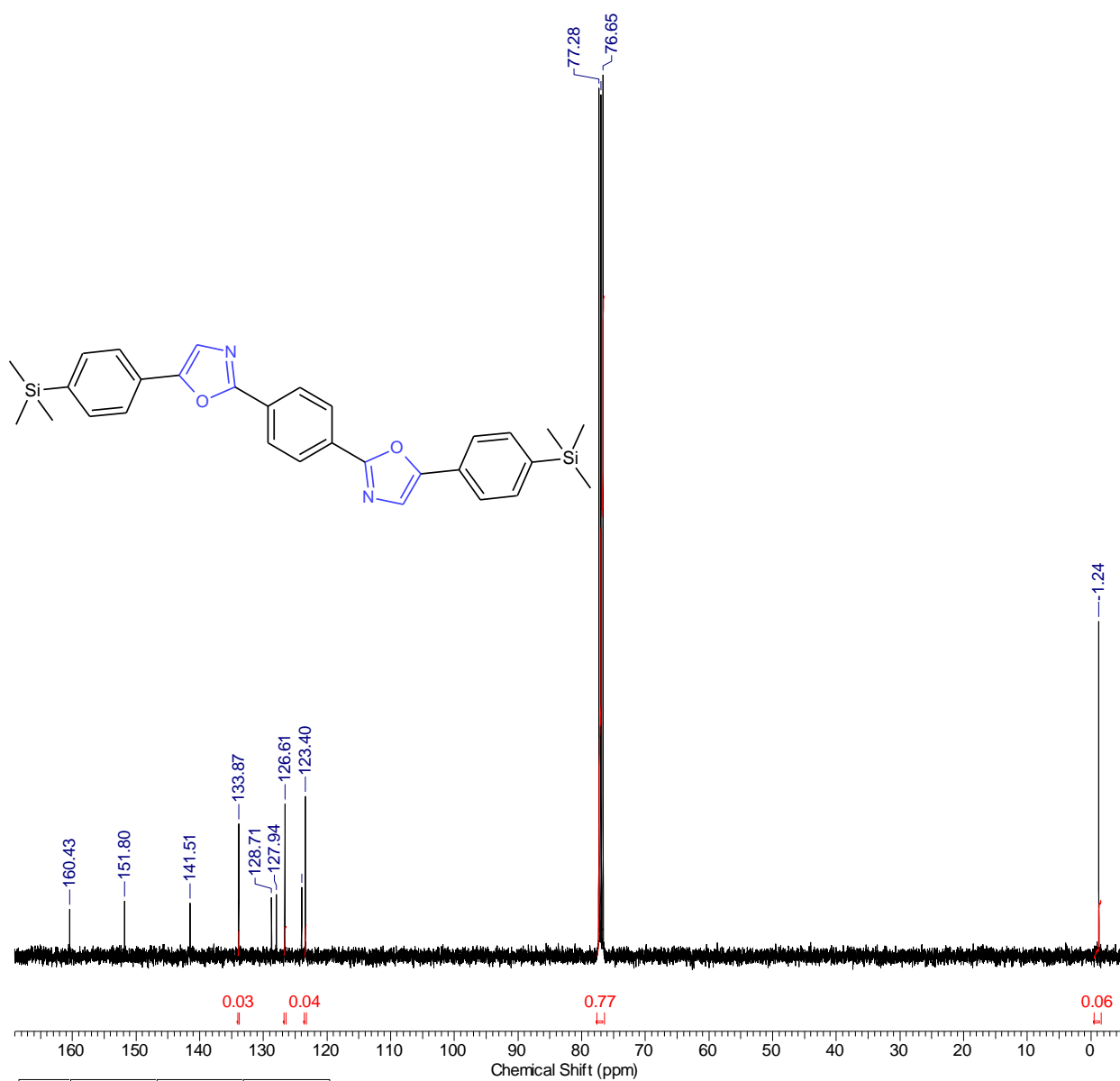
Figure S4. ¹³C NMR spectrum of 1,4-bis(2-phenyloxazol-5-yl)benzene (isoPOPOP)



No.	(ppm)	Annotation	Layer No.	Created By	Created At	Modified By	Modified At
1	7.27	Chloroform	1	Skorotckiy	Cp 21.10.2015 18:37:16		

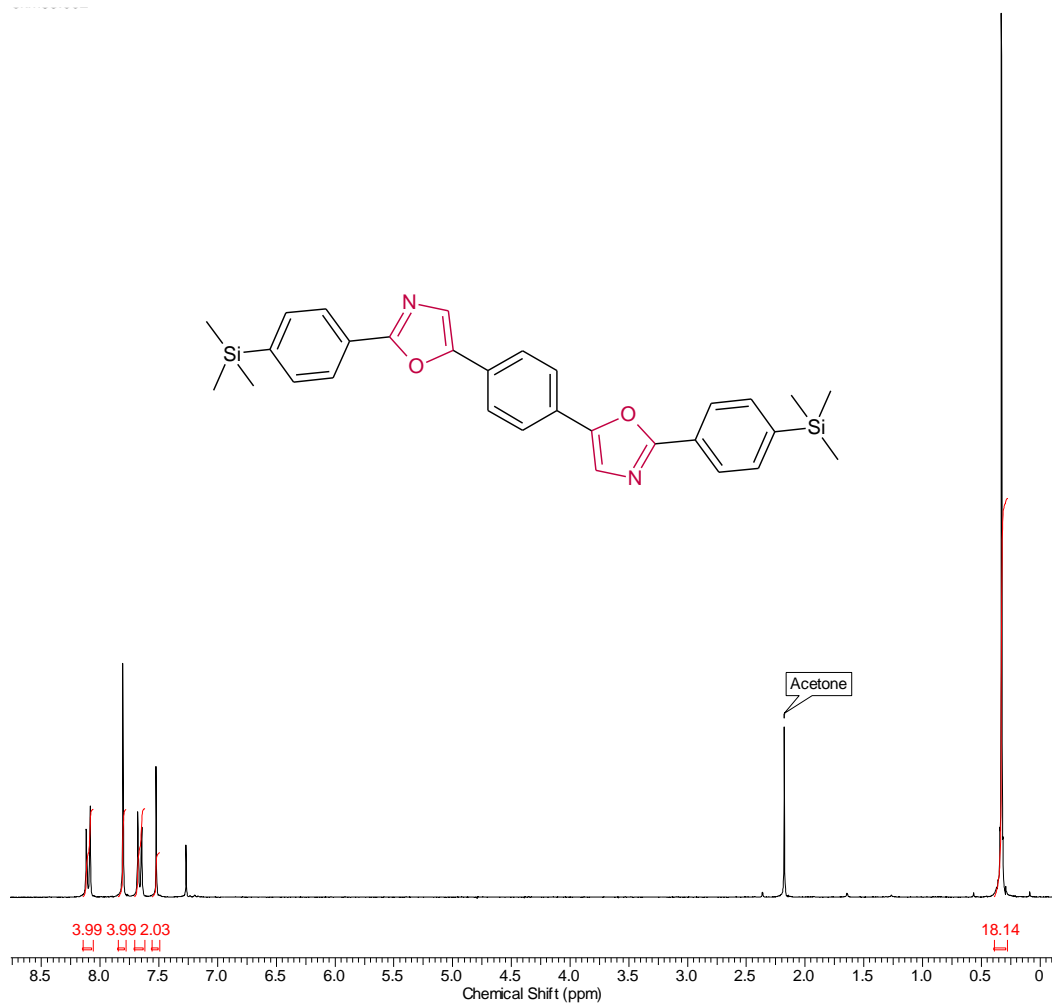
No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.2903 .. 0.3466]	18.05231857	1.46348920e+7	18.05231857
2	[7.5063 .. 7.5393]	1.96029842	1.58920050e+6	1.96029842
3	[7.5860 .. 7.6618]	4.09930468	3.32327825e+6	4.09930468
4	[7.6949 .. 7.7746]	4.10297823	3.32625650e+6	4.10297823
5	[8.2121 .. 8.2685]	4.03025723	3.26730200e+6	4.03025723

Figure S5. ^1H NMR spectrum of 1,4-bis[5-[4-(trimethylsilyl)phenyl]-1,3-oxazolyl-2]benzene (TMS-POPOP-TMS)



No.	(ppm)	(Hz)	Height
1	-1.24	-124.3	0.3798
2	76.65	7712.0	1.0000
3	76.97	7744.3	0.9775
4	77.28	7775.8	0.9852
5	123.40	12415.8	0.1813
6	123.99	12474.5	0.0778
7	126.61	12738.6	0.1722
8	127.94	12872.1	0.0699
9	128.71	12949.8	0.0661
10	133.87	13469.2	0.1502
11	141.51	14238.0	0.0598
12	151.80	15273.1	0.0622
13	160.43	16141.7	0.0532

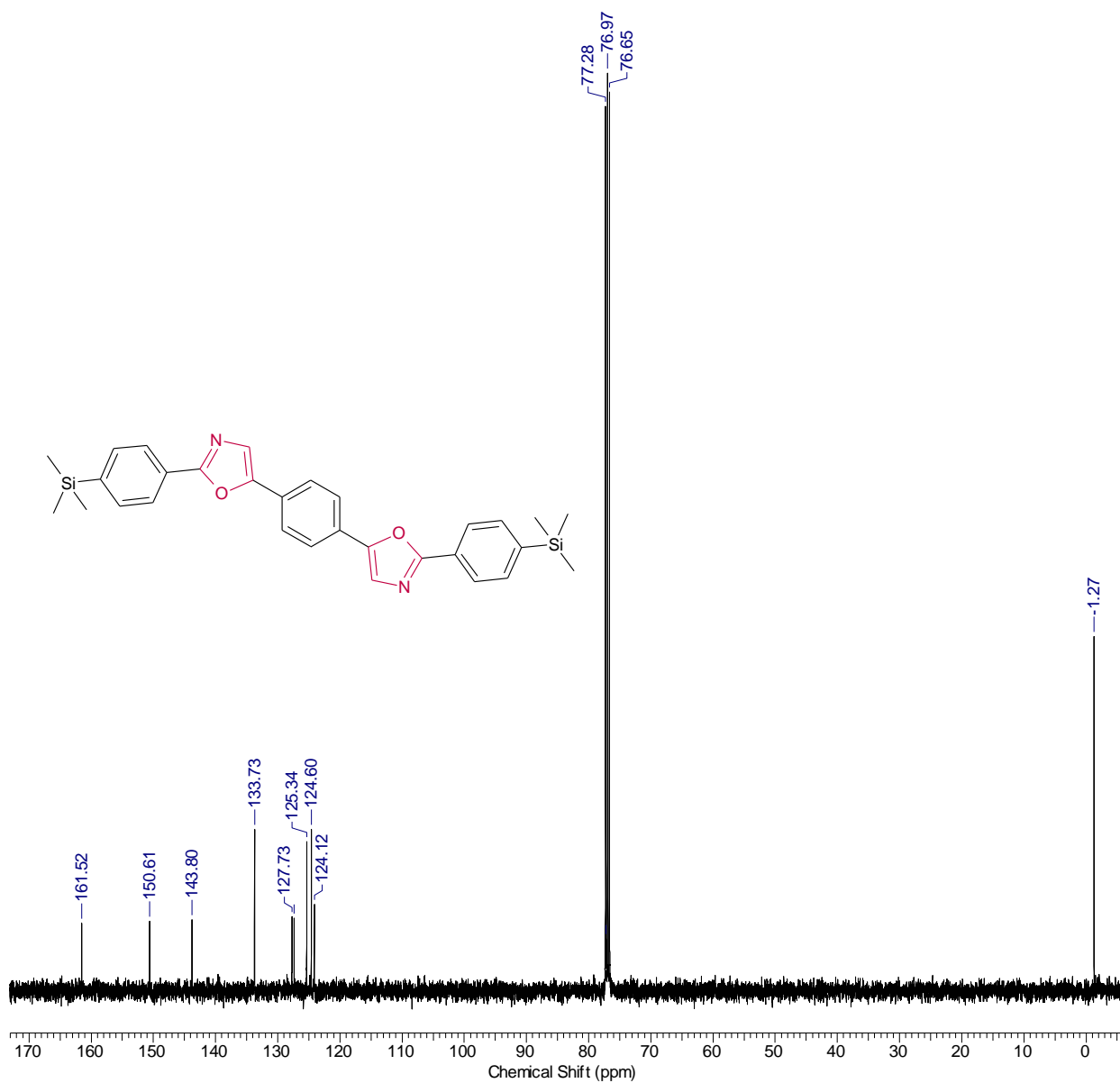
Figure S6. ^{13}C NMR spectrum of 1,4-*bis*{5-[4-(trimethylsilyl)phenyl]-1,3-oxazolyl-2}benzene (TMS-POPOP-TMS)



No.	(ppm)	Annotation	Layer No.	Created By	Created At	Modified By	Modified At
1	2.18	Acetone	1	Skorotckiy	Пн 19.10.2015 20:15:53		

No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.2762 .. 0.3887]	18.13693810	1.25670460e+7	18.13693810
2	[7.4918 .. 7.5560]	2.02916503	1.40600413e+6	2.02916503
3	[7.6193 .. 7.7060]	4.03010321	2.79245000e+6	4.03010321
4	[7.7810 .. 7.8443]	3.98699355	2.76257950e+6	3.98699355
5	[8.0602 .. 8.1451]	3.98618698	2.76202050e+6	3.98618698

Figure S7. ^1H NMR spectrum of 1,4-bis{2-[4-(trimethylsilyl)phenyl]-1,3-oxazolyl-5}benzene (TMS-isoPOPOP-TMS)



No.	(ppm)	(Hz)	Height
1	-1.27	-128.0	0.3860
2	76.65	7712.0	0.9791
3	76.97	7744.3	1.0000
4	77.18	7764.8	0.0566
5	77.28	7775.8	0.9638
6	124.12	12487.7	0.0941
7	124.60	12536.1	0.1758
8	125.34	12610.9	0.1625
9	127.35	12813.4	0.0793
10	127.73	12850.8	0.0806
11	133.73	13455.3	0.1759
12	143.80	14467.7	0.0774
13	150.61	15152.8	0.0760
14	161.52	16251.0	0.0737

Figure S8. ^{13}C NMR spectrum of 1,4-bis{2-[4-(trimethylsilyl)phenyl]-1,3-oxazolyl-5}benzene (TMS-isoPOPOP-TMS)

2. Mass-spectra (MALDI MS) data

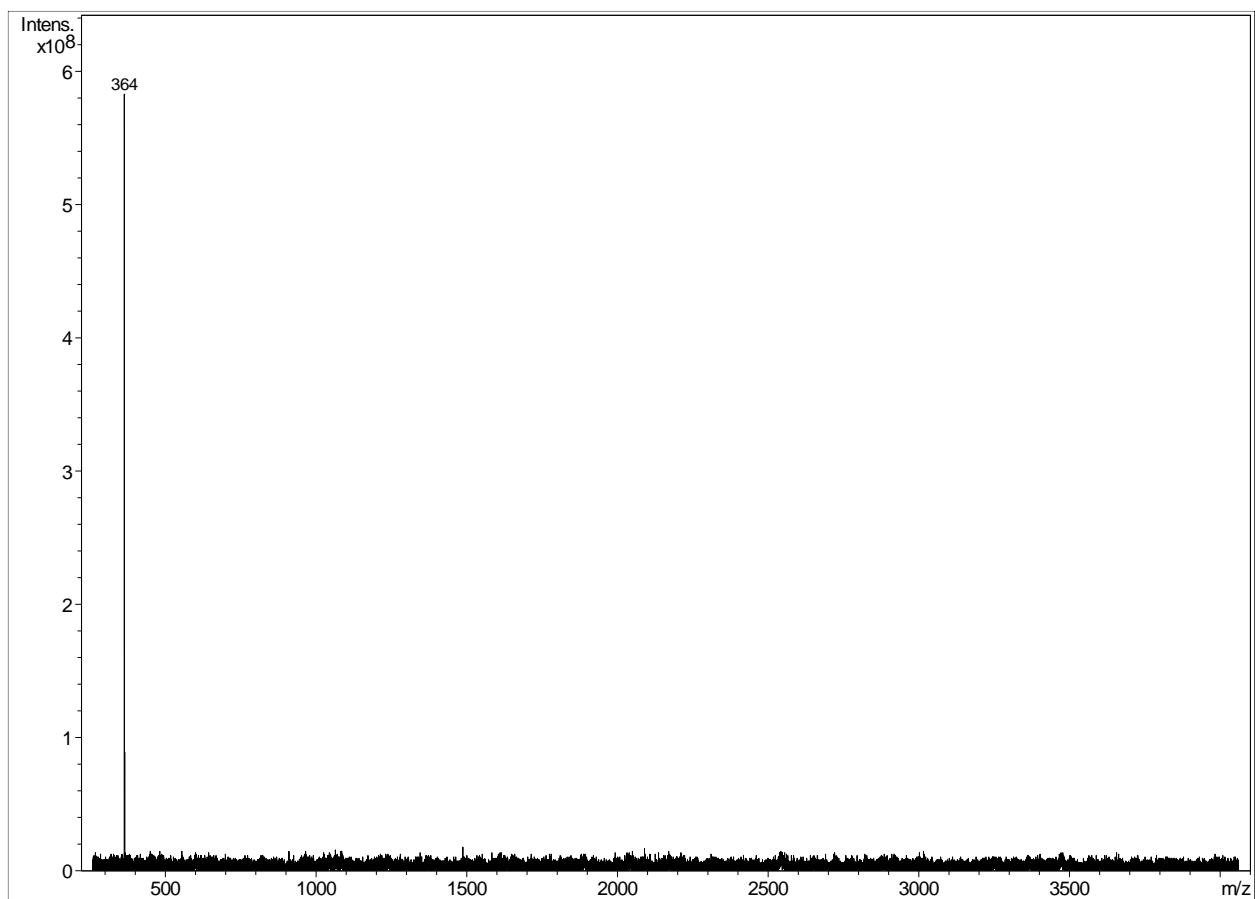
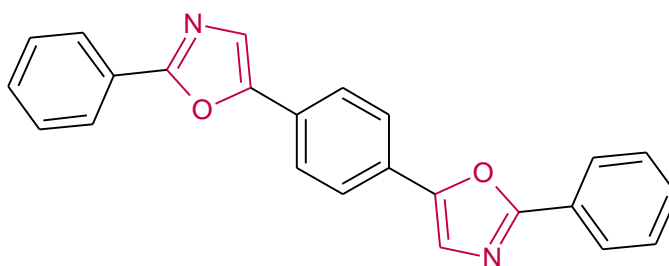


Figure S9. MALDI MS data of isoPOPOP

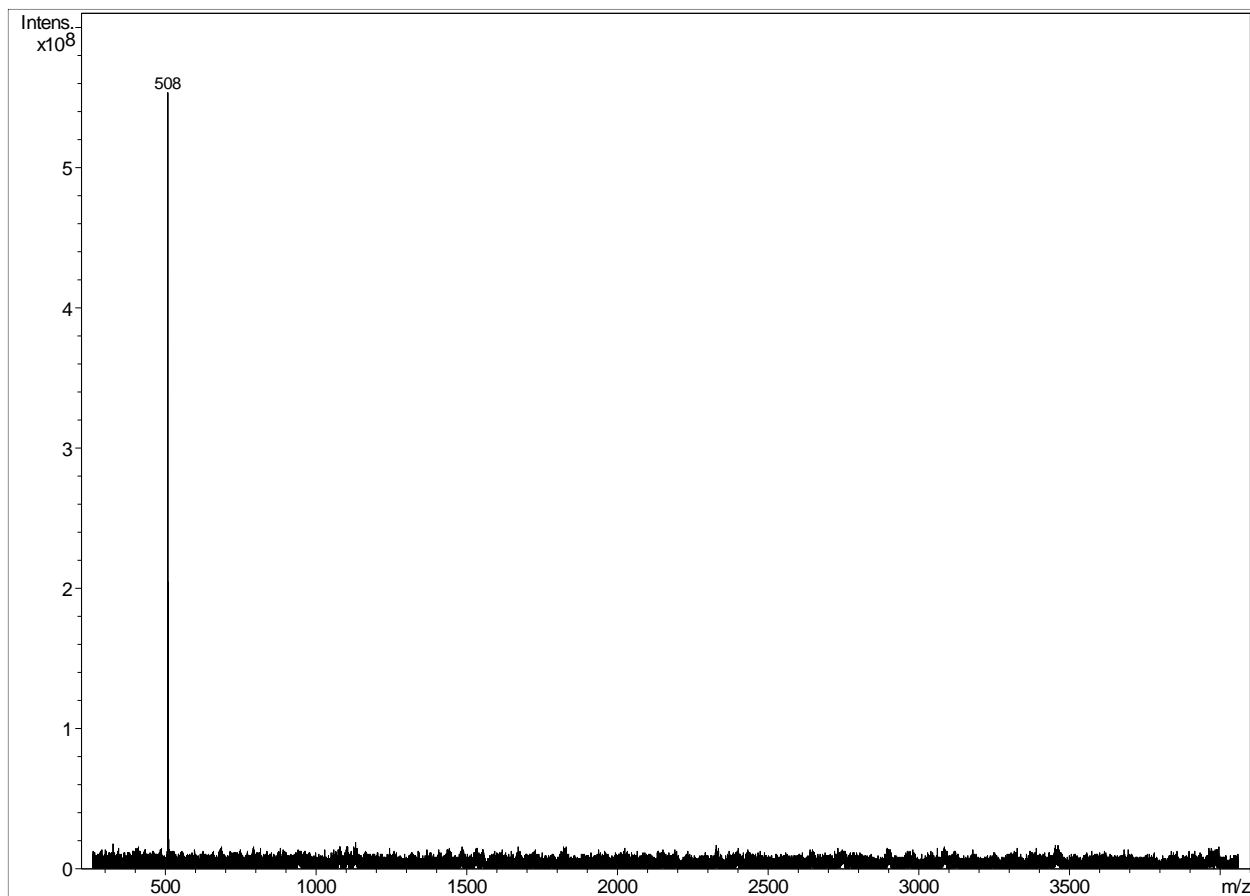
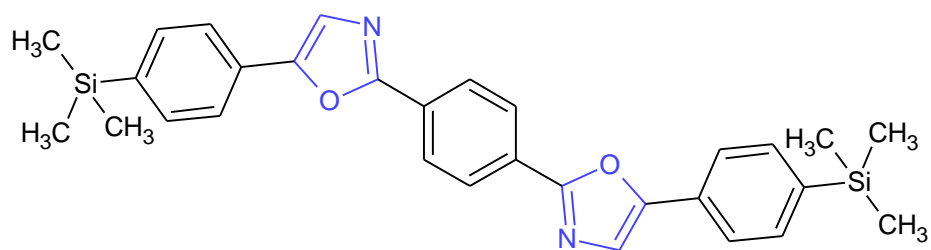


Figure S10. MALDI MS data of TMS-POPOP-TMS

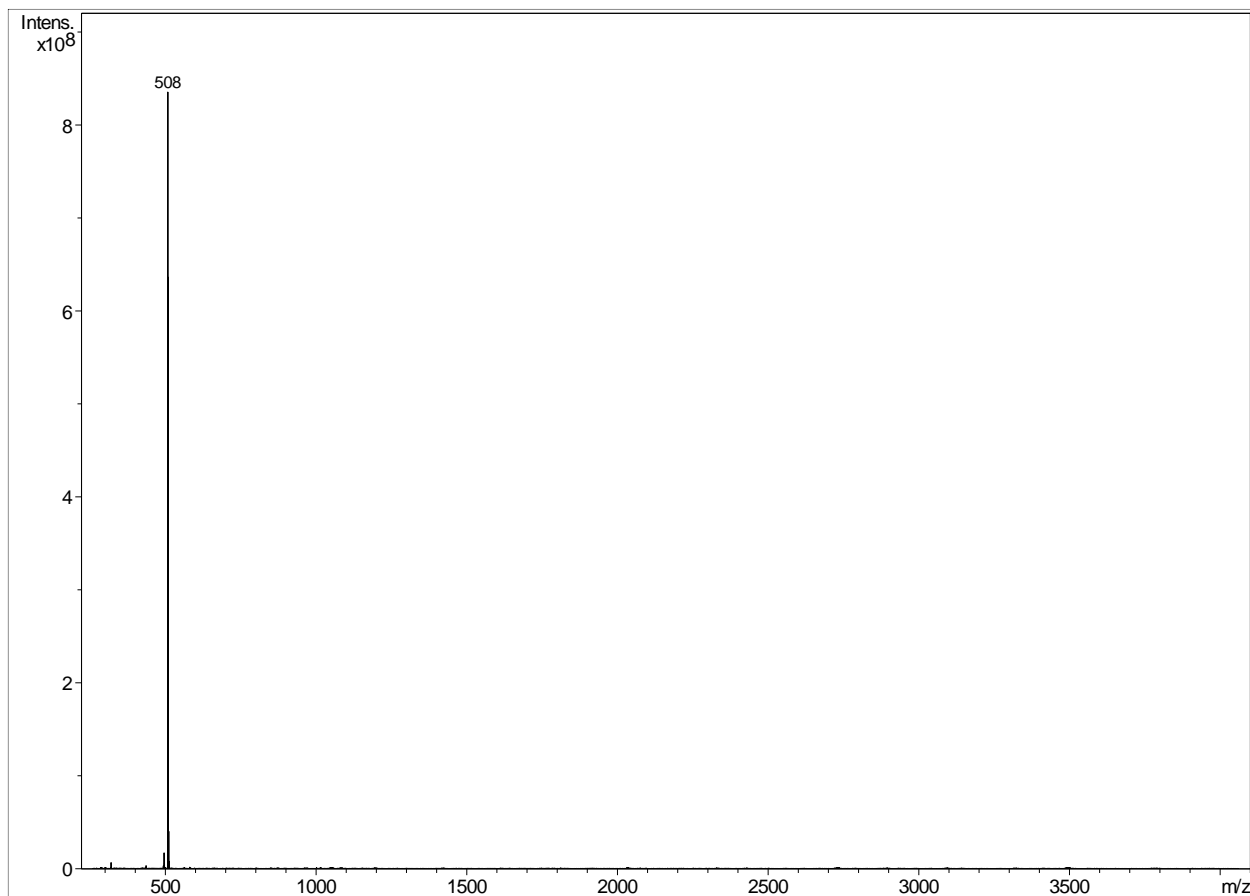
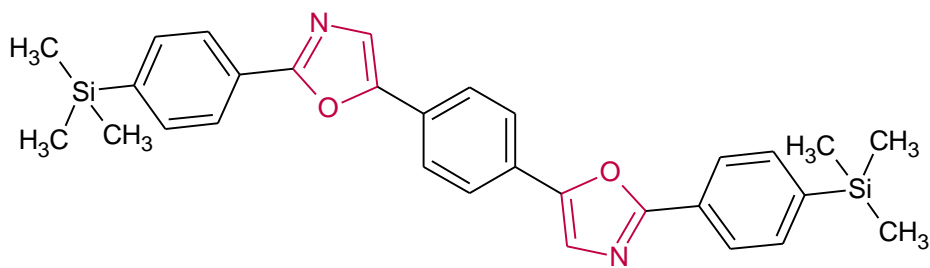


Figure S11. MALDI MS data of TMS-isoPOPOP-TMS

3. Gel permeation chromatography analysis (GPC) data

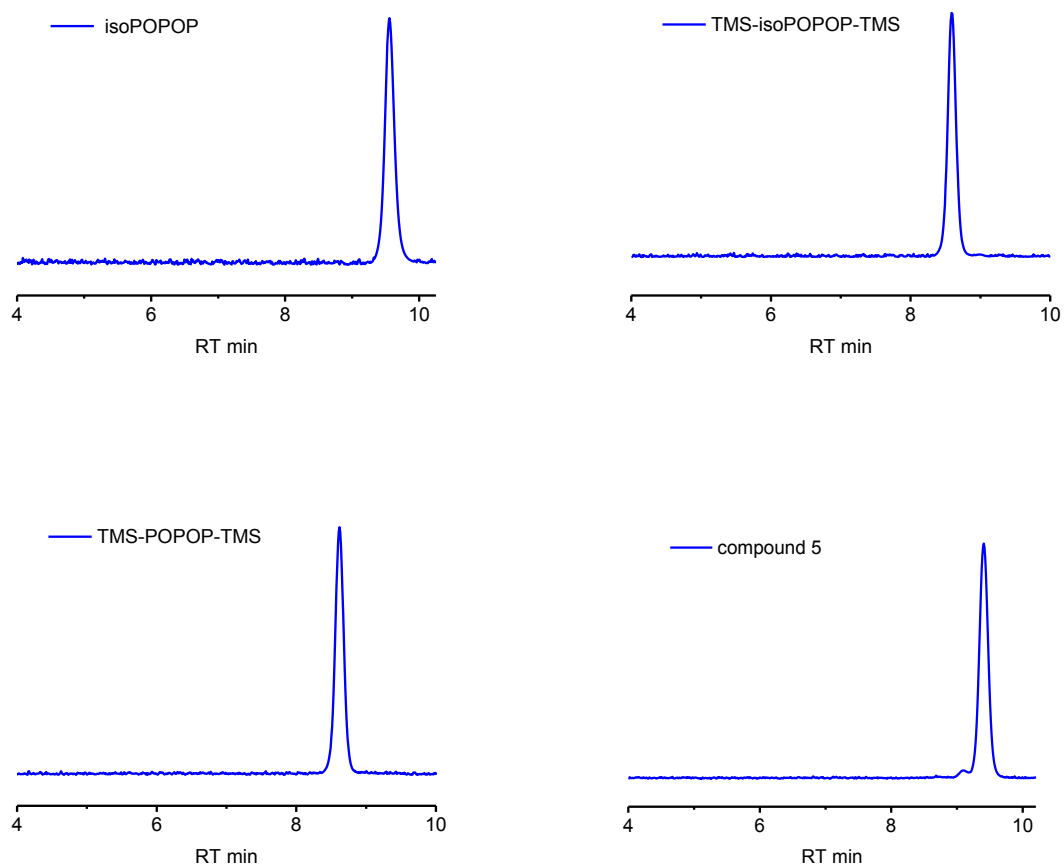


Figure S12. GPC-curves of pure luminophores **isoPOPOP**, **TMS-POPOP-TMS**, **TMS-isoPOPOP-TMS** and 5-(4-trimethylsilylphenyl)-1,3-oxazole (**5**)

4. Thermogravimetric analysis (TGA) data

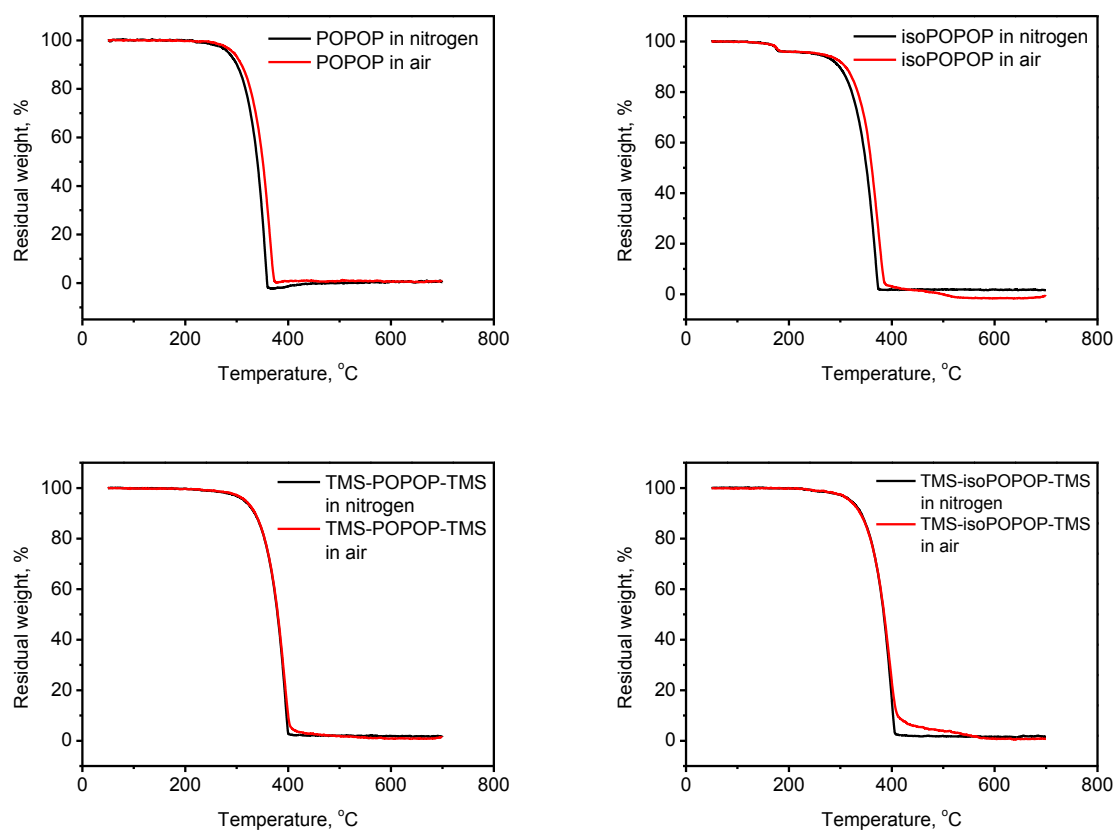


Figure S13. Thermogravimetric analysis (TGA) curves of **POPOP**, **isoPOPOP**, **TMS-POPOP-TMS**, **TMS-isoPOPOP-TMS** compounds

5. Cyclic voltammetry (CV) curves

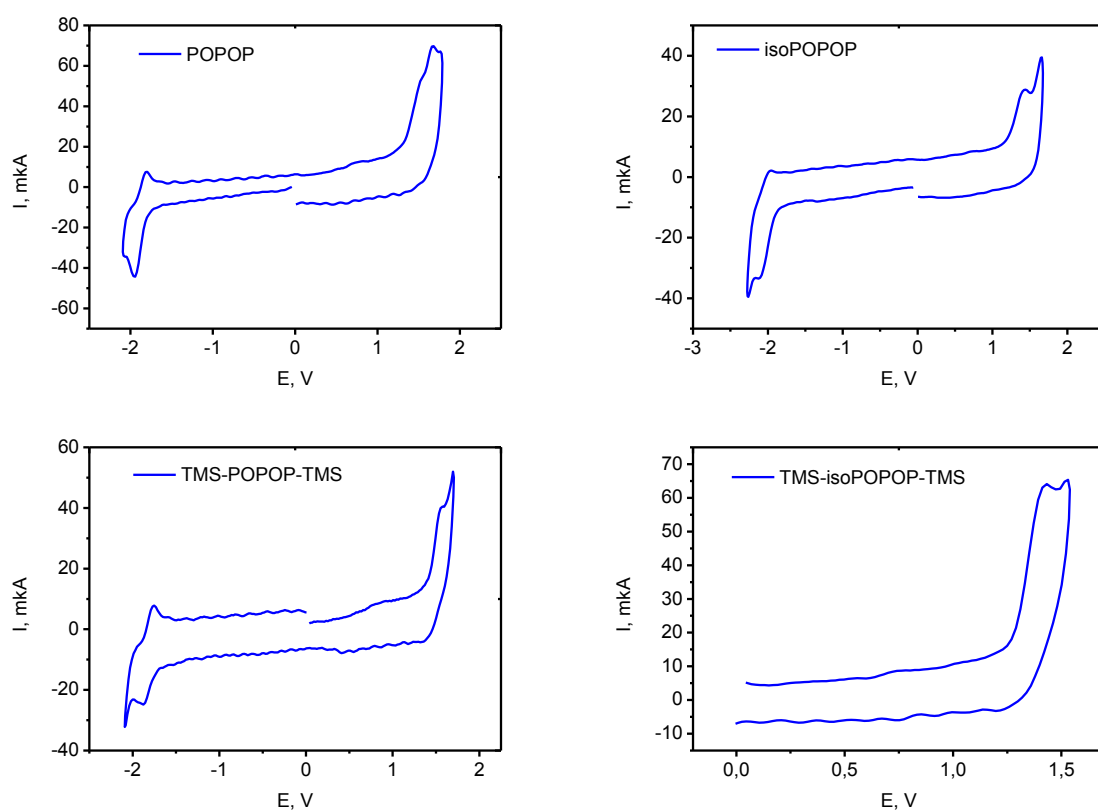


Figure S14. Electrochemical oxidation and reduction curves of **POPOP**, **isoPOPOP**, **TMS-POPOP-TMS**, **TMS-isoPOPOP-TMS** compounds

6. The frontier molecular orbitals for luminophores calculated by DFT using the B3LYP/6-31G[d] level of theory

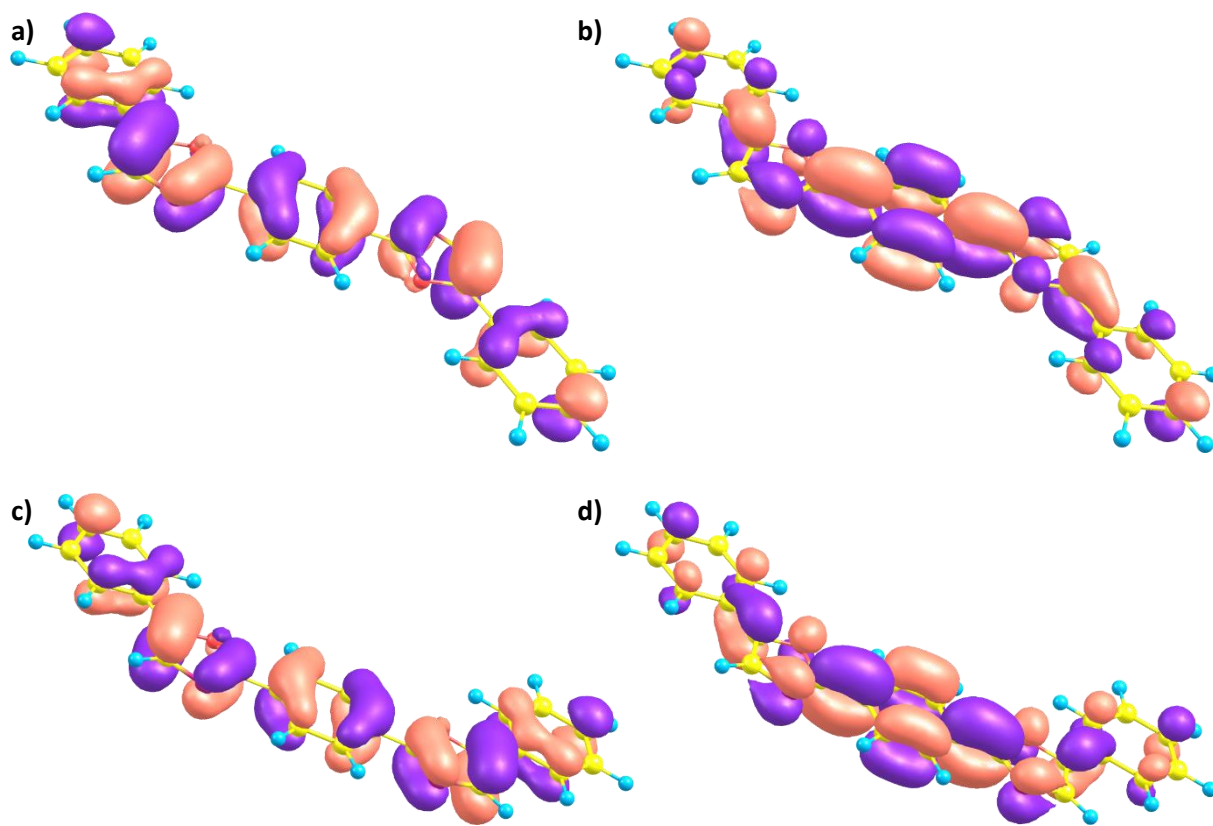


Figure S15. The frontier HOMO (a, c) and LUMO (b, d) molecular orbitals for **POPOP** with C_{2h} (a, b) and C_{2v} (c, d) symmetry

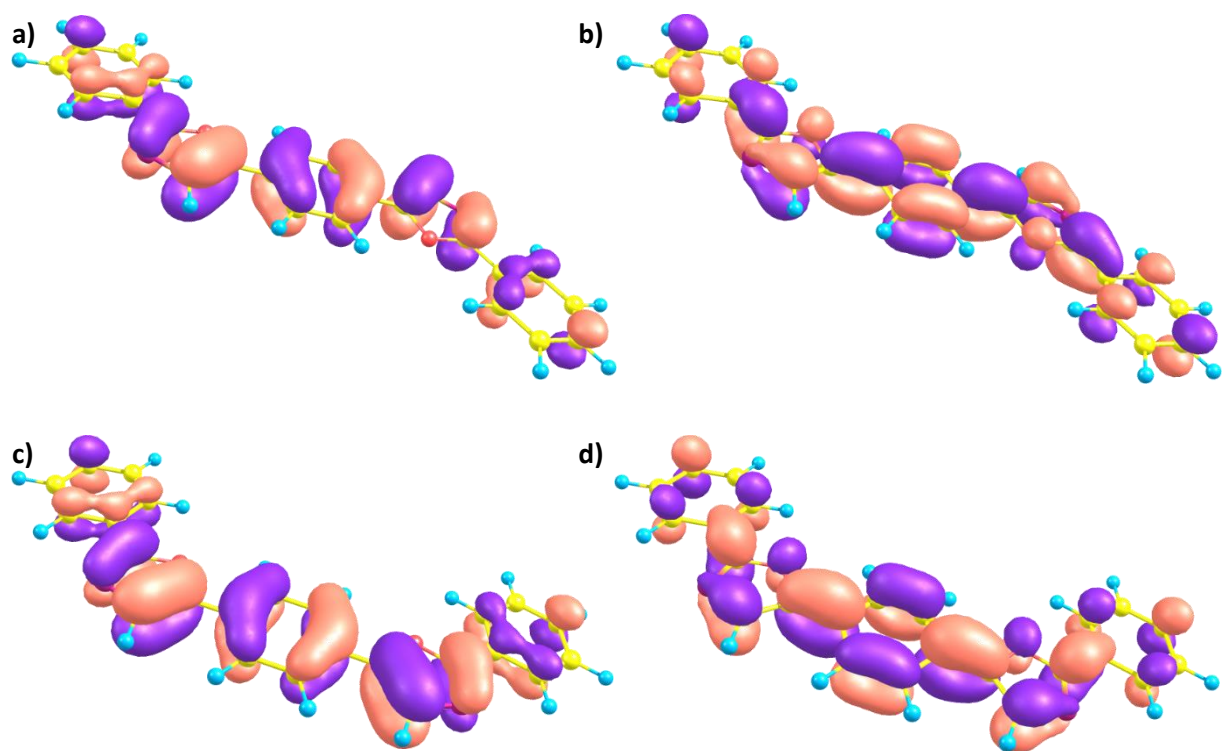


Figure S16. The frontier HOMO (a, c) and LUMO (b, d) molecular orbitals for isoPOPOP with C_{2h} (a, b) and C_{2v} (c, d) symmetry

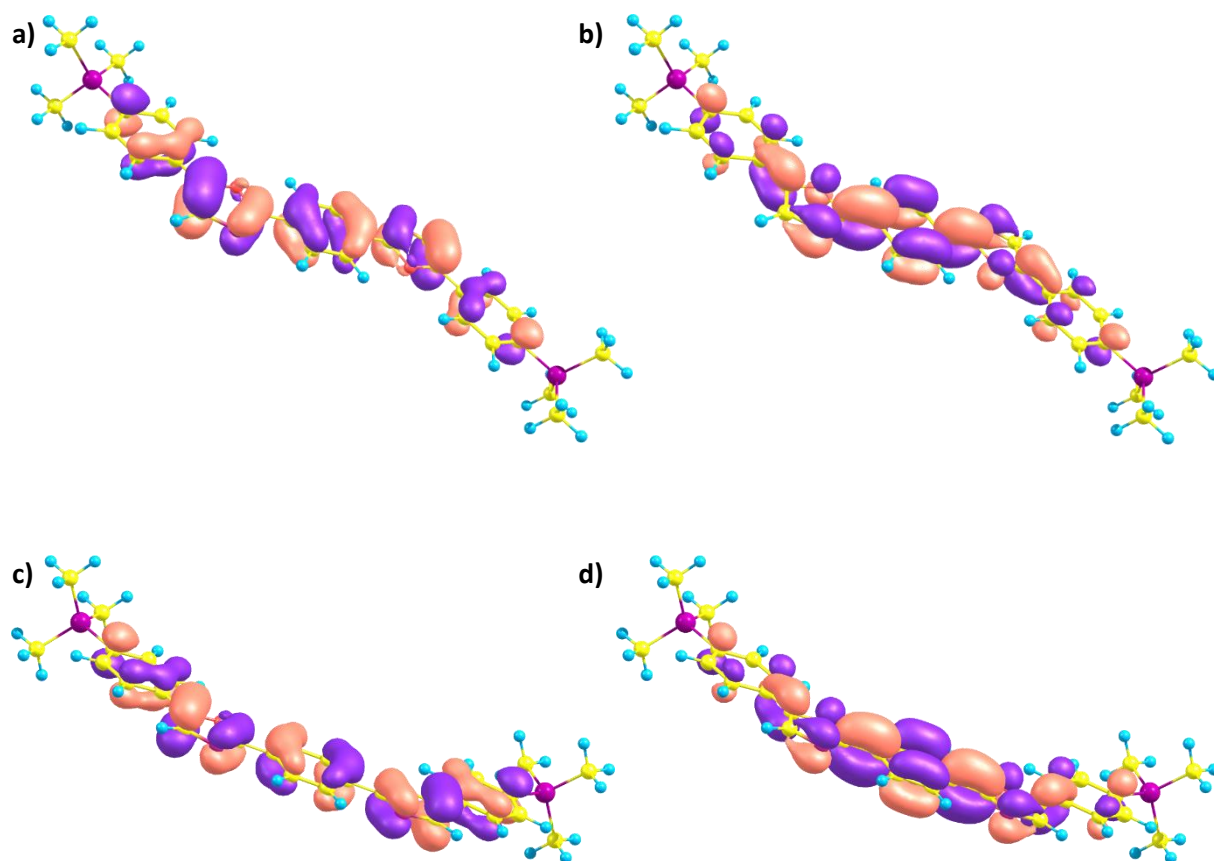


Figure S17. The frontier HOMO (a, c) and LUMO (b, d) molecular orbitals for **TMS-POPOP-TMS** with C_{2h} (a, b) and C_{2v} (c, d) symmetry

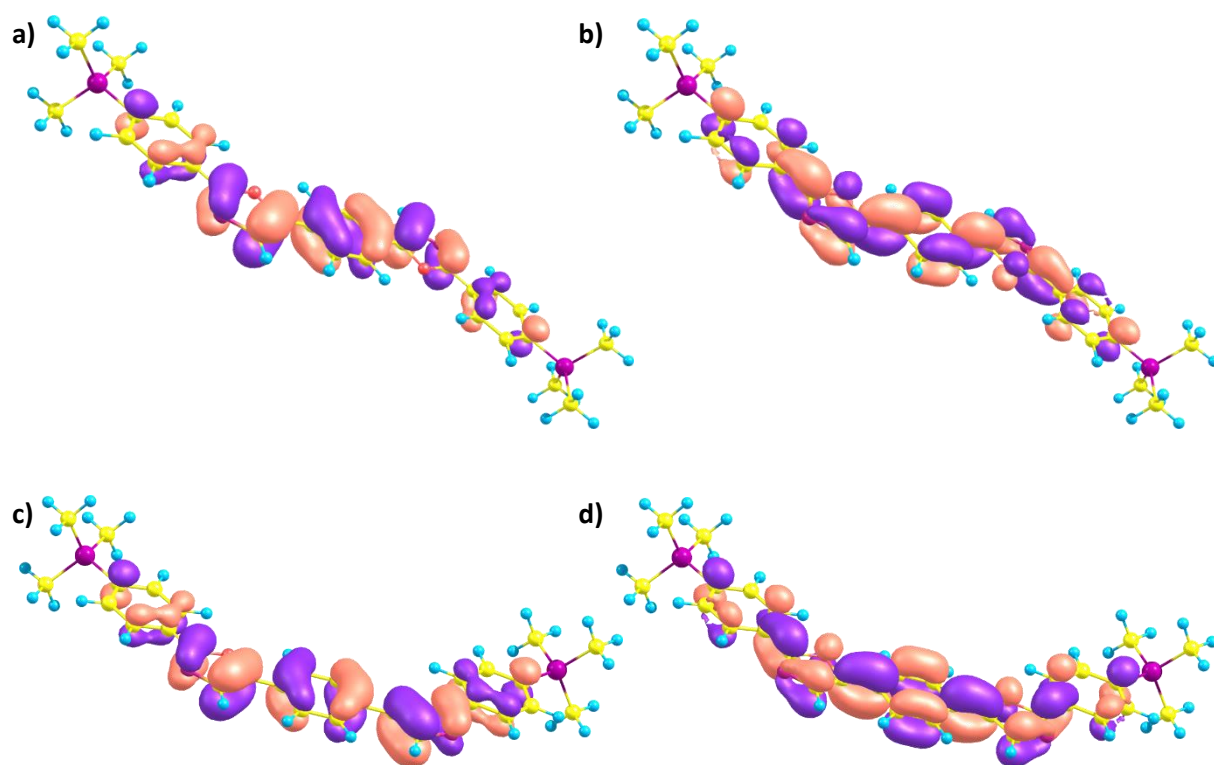


Figure S18. The frontier HOMO (a, c) and LUMO (b, d) molecular orbitals for TMS-isoPOPOP-TMS with C_{2h} (a, b) and C_{2v} (c, d) symmetry

7. Microphotographs of the crystals

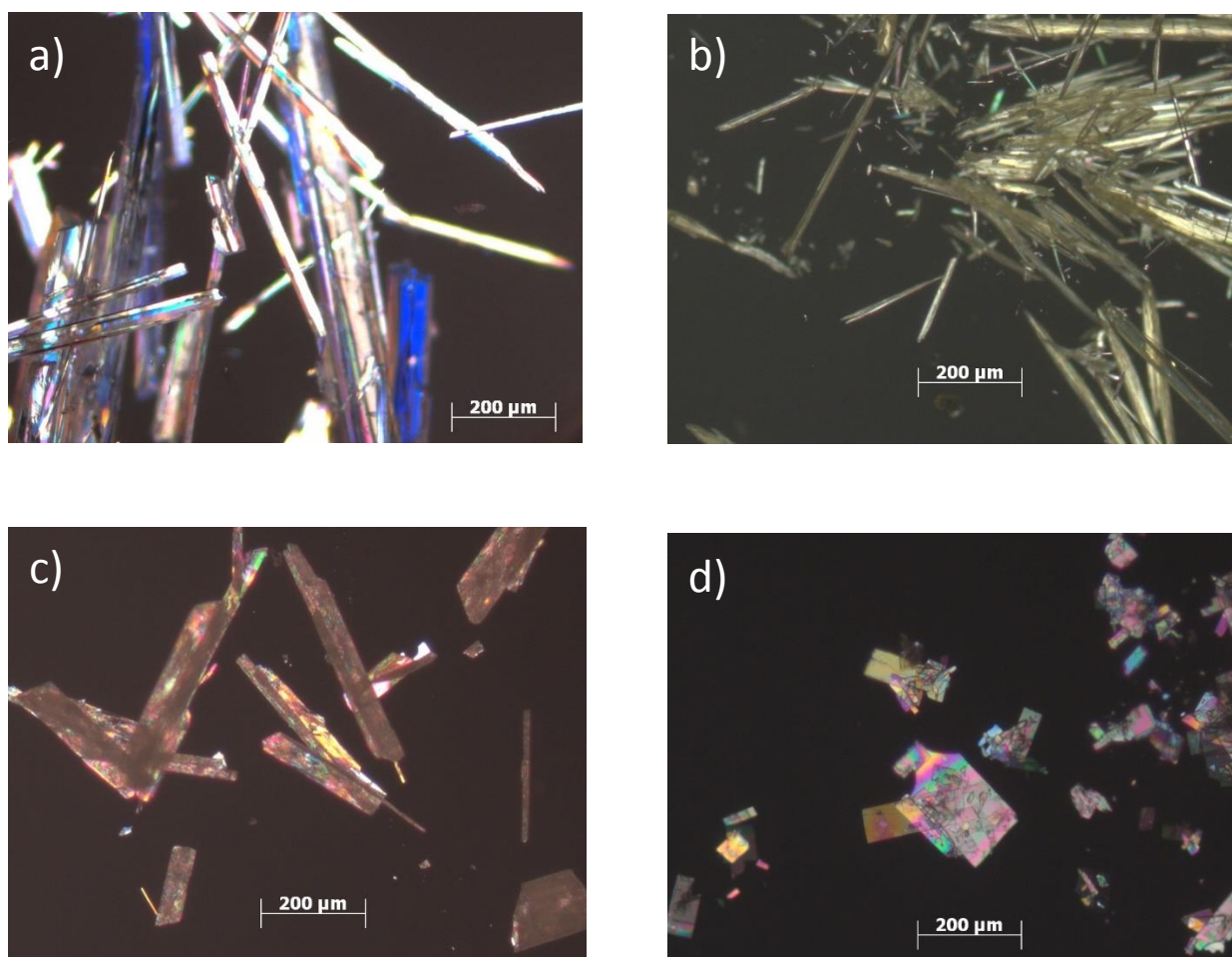


Figure S19. Microphotoes of the crystals made in optical microscope in cross-polarizers: **POPOP** (a), **iso-POPOP** (b), **TMS-POPOP-TMS** (c), **TMS-isoPOPOP-TMS** (d)

- A mild synthesis of phenyloxazoles and their trimethylsilyl derivatives is reported
- All phenyloxazoles synthesized have high PLQYs and molar extinction coefficients
- **POPOP**-type compounds are more stable than their structural isomers
- X-ray diffraction revealed important structural differences between the lattices