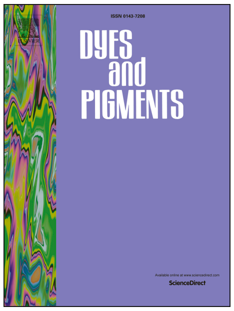

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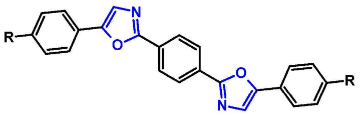
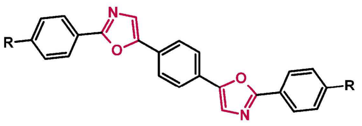
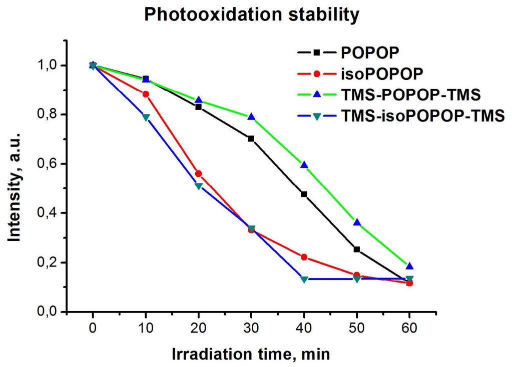


POPOP, R=H
TMS-POPOP-TMS, R=SiMe$_3$



isoPOPOP, R=H
TMS-isoPOPOP-TMS, R=SiMe$_3$



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

Maxim S. Skorotetcky [a], Oleg V. Borshchev [a], Nikolay M. Surin [a], Yaroslav Odarchenko [b]ᵻ, Sergey A. Pisarev [a,c], Svetlana M. Peregudova [d], Karl W. Törnroos [e], Dmitry Chernyshov [f], Dimitri A. Ivanov [b, g], Sergey A. Ponomarenko [a, h] *

[a] *Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences, Profsoyuznaya St. 70, Moscow 117393, Russia*

[b] *Institut de Sciences des Matériaux de Mulhouse-IS2M, CNRS UMR 7361, 15 rue Jean Starcky, 68057 Mulhouse, France*

[c] *Institute of Physiologically Active Compounds of Russian Academy of Sciences, Severny Pr. 1, Chernogolovka 142432, Russia*

[d] *Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova St. 28, Moscow 119991, Russia*

[e] *Department of Chemistry, University of Bergen, Norway*

[f] *Swiss−Norwegian Beam Lines, ESRF BP-220, 38043 Grenoble, France*

[g] *Faculty of Fundamental Physical and Chemical Engineering, Moscow State University, GSP-1, Leninskie Gory 1, 119991, Moscow, Russia*

[h] *Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia*

**e-mail: ponomarenko@ispm.ru*

ᵻ*Current address: Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK*

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

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

1. Introduction

Organic molecules emitting light in various spectral regions are widely used in many fields of science and technology. Among them are aryl-substituted oxazoles, which are highly efficient violet or blue emitting luminophores [1,2]. A burst of interest towards this class of materials was triggered by their applicability as activators and spectral shifters in liquid and plastic scintillators detecting elementary particles and ionizing radiation [3,4]. Moreover, they are widely used as dyes for organic lasers [5,6] and spectral shifters in photonics [7]. Synthetic approaches for preparation of phenyloxazoles are well known: after E. Fisher had synthesized 2,5-diphenyloxazole in 1896, a wide variety of techniques for the preparation of this compound and its derivatives were reported [8]. Additional interest of researchers is drawn to biological activity of oxazole as a structural moiety of various alkaloids as well [9].

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

2. Experimental section

2.1. Materials

Hexane solutions of 2.5 M *n*-butyllithium, toluenesulfonylmethyl isocyanide (TosMIC), terephthaloyl aldehyde, anhydrous potassium carbonate, bromobenzene and 1,4-dibromobenzene were obtained from Acros organics; *tetrakis*(triphenylphosphine)palladium (0) $Pd(PPh_3)_4$, lithium *tert*-butoxide, 1,4-*bis*(5-phenyloxazol-2-yl)benzene (**POPOP**) scintillation grade were obtained from Sigma-Aldrich and used as received. 1-Bromo-4-(trimethylsilyl)benzene (**3**) was obtained by the method described previously [19]. Synthesis of 1,4-*bis*(1,3-oxazol-5-yl)benzene (**2**), 1-bromo-4-(trimethylsilyl)benzene (**3**) and 4-(trimethylsilyl) benzaldehyde (**4**) is described in the results and discussion section. THF, 1,4-dioxane and methanol were dried and purified according to the well-known techniques and then used as the solvents.

2.2. Characterization

The ^{1}H NMR spectra were recorded on a Bruker WP250 SY spectrometer (250.13 MHz) using the residual signal of $CDCl_3$ (δ 7.27 ppm) as the internal standard. The ^{13}C NMR spectra were recorded on a Bruker Avance II 300 spectrometer at 75 MHz. In the case of ^{1}H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in $CDCl_3$. In the case of ^{13}C NMR spectroscopy, the compounds to be analyzed were taken in the form of

3-5% solutions in $CDCl_3$. The spectra were then processed on the computer using the ACD Labs software. Mass-spectra (MALDI) were registered on the Autoflex II Bruker (resolution FWHM 18000), equipped with nitrogen laser (work wavelength 337 nm) and time-of-flight mass-detector working in the reflections mode. The resulting spectrum was the sum of 300 spectra obtained at different points of the sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and α-cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as the matrices.

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

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

GPC analysis was performed on a Shimadzu instrument with a RID10A^{VP} refractometer and a SPD-M10A^{VP} diode matrix as detectors using 7.8 × 300 mm^2 Phenomenex columns (USA) filled with the Phenogel sorbent with pore size of 500 Å and THF as the eluent. In the case of column chromatography, silica gel 60 (“Merck”) was taken. For thin layer chromatography (TLC), “Sorbfil” (Russia) plates were used. The solvents were removed under vacuum (1 mBar) at 40 °C. All reactions, unless stated otherwise, were carried out in an inert atmosphere using anhydrous solvents.

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

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

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

2.3. Structure studies and molecular modeling

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

Single-crystal X-ray diffraction was measured at the Swiss−Norwegian Beamlines of the ESRF. The crystals for all compounds were formed during the recrystallization from toluene solutions. The X-ray patterns were collected with a PILATUS2M pixel area detector. A monochromatic beam at a wavelength of λ = 0.69411 Å was slit-collimated down to 100 × 100 μm^2. The sample-to-detector distance and parameters of the detector were calibrated using a LaB6 NIST standard. The detector images were recorded by phi-scans in shutter-free mode with a 0.1 deg angular step. The data were preprocessed by SNBL Tool Box [24] and then by CrysAlis Pro [25]. The crystal structures were solved with SHELXS and refined with SHELX [26]. CCDC1493771 and CCDC1493772 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

2.4. Synthesis of the phenyloxazoles

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

1,4-*bis*(2-phenyloxazol-5-yl)benzene (**isoPOPOP**). Solutions of lithium *tert*-butoxide (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.), bromobenzene (0.89 g, 5.6 mmol, 2.3 equiv.) and Pd(PPh_3)$_4$ (54 mg, 0.047 mmol, 2%) in 1,4-dioxane (60 mL) was heated to boiling. The reaction mixture was refluxed for 1 h. Progress of the reaction was monitored by GPC analysis. After completeness of the reaction, the reaction mixture was cooled to room temperature (23 °C) and poured into water (200 mL), filtered off and thoroughly washed with water and acetone. The crude product was passed over a short column of silica gel in toluene: ethyl acetate 10:1 mixture to remove the rest of the catalyst. The product was purified by recrystallization from toluene to give a pure compound (686 mg, yield 80%) as yellowish needle crystals, mp. 238-240 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 7.53 (8H, overlapping peaks), 7.82 (s, 4H), 8.15 (4H, overlapping peaks). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 124.12, 124.65, 126.38, 127.29, 127.78, 128.89, 130.53, 150.69, 161.45. Calcd (%) for $C_{24}H_{16}N_2O_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 78.93; H, 4.53; N, 7.53. MALDI MS: found *m/z* 364.39; calculated for $[M]^+$ 364.396.

1,4-*bis*{2-[4-(trimethylsilyl)phenyl]-1,3-oxazol-5-yl}benzene (**TMS-isoPOPOP-TMS**). This compound was obtained by the method described above for **isoPOPOP** using lithium *tert*-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 equiv.), 1-bromo-4-(trimethylsilyl)benzene (**3**) (1.3 g, 5.6 mmol, 3 equiv.) and Pd(PPh_3)$_4$ (43 mg, 0.04 mmol, 2 %) in 1,4-dioxane (50 mL). The product was purified by recrystallization from toluene to give pure compound (709 mg, yield 74%) as yellowish plate-like crystals, mp. 267-269 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 0.33 (s, 18H), 7.52 (s, 2H), 7.66 (d, 4H, J = 8.55 Hz), 7.81 (s, 4H), 8.10 (d, 4H, J = 8.55 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] -1.27, 124.12, 124.60, 125.34, 127.35, 127.73, 133.73, 143.80, 150.61, 161.52. Calcd (%) for $C_{30}H_{32}N_2O_2Si_2$: C, 70.82; H, 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* 508.75; calculated for $[M]^+$ 508.758.

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

butoxide (1.7 g, 21 mmol, 5 equiv.), 1,4-dibrombenzene (1 g, 4.2 mmol, 1 equiv.), 5-(4-trimethylsilylphenyl)-1,3-oxazole (**5**) (2.21 g, 10 mmol, 2.4 equiv.) and $Pd(PPh_3)_4$ (98 mg, 0.085 mmol, 2 %) in 1,4-dioxane (100 mL). The product was purified by recrystallization from toluene to give pure compound (1.78 g, yield 83%) as yellowish plate-like crystals, mp. 269-271 °C. ^1H NMR (250 MHz, $CDCl_3$): δ [ppm] 0.32 (s, 18H), 7.52 (s, 2H), 7.62 (d, 4H, J = 7.94), 7.73 (d, 4H, J = 7.94), 8.24 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] -1.24, 123.40, 123.99, 126.61, 127.94, 128.71, 133.87, 141.51, 151.80, 160.43. Calcd (%) for $C_{30}H_{32}N_2O_2Si_2$: C, 70.82; H, 6.34; N, 5.51; Si, 11.04. Found: C, 70.56; H, 6.24; N, 5.51; Si, 10.84. MALDI MS: found *m/z* 508.75; calculated for $[M]^+$ 508.758.

3. Results and discussion

3.1. Synthesis

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

Two synthetic schemes were suggested based on the methods described above (Fig.1). It was found that preparation of the **POPOP** isomer – 1,4-*bis*(2-phenyloxazol-5-yl)benzene (**iso-POPOP**), which differs from the **POPOP** solely by the position of oxazole rings relative to the central 1,4-phenylene unit, comprises fewer reaction steps (**method 1**) as compared to the synthesis of the exact **POPOP** structure (**method 2**). At the same time, **method 1** is preferable for further development of corresponding NOL preparation approach, since it allows direct using of already available 4-bromophenylsilyl functional luminophore precursors [10]. However, we were surprised to find out that almost no data is available in the literature regarding to this **iso-POPOP** structure. The only description of this **POPOP** isomer preparation was reported in 1979 [31]. In this case 1,4-*bis*(2-phenyloxazol-5-yl)benzene was obtained via Lewis acid (boron fluoride) catalyzed decomposition of the corresponding α-diazoketophenone in excess of benzonitrile in 80% yield. However, this method is not applicable for the synthesis of organosilicon derivatives due to sophisticated procedures of the starting materials preparation and high affinity of silicon to fluoride ion.

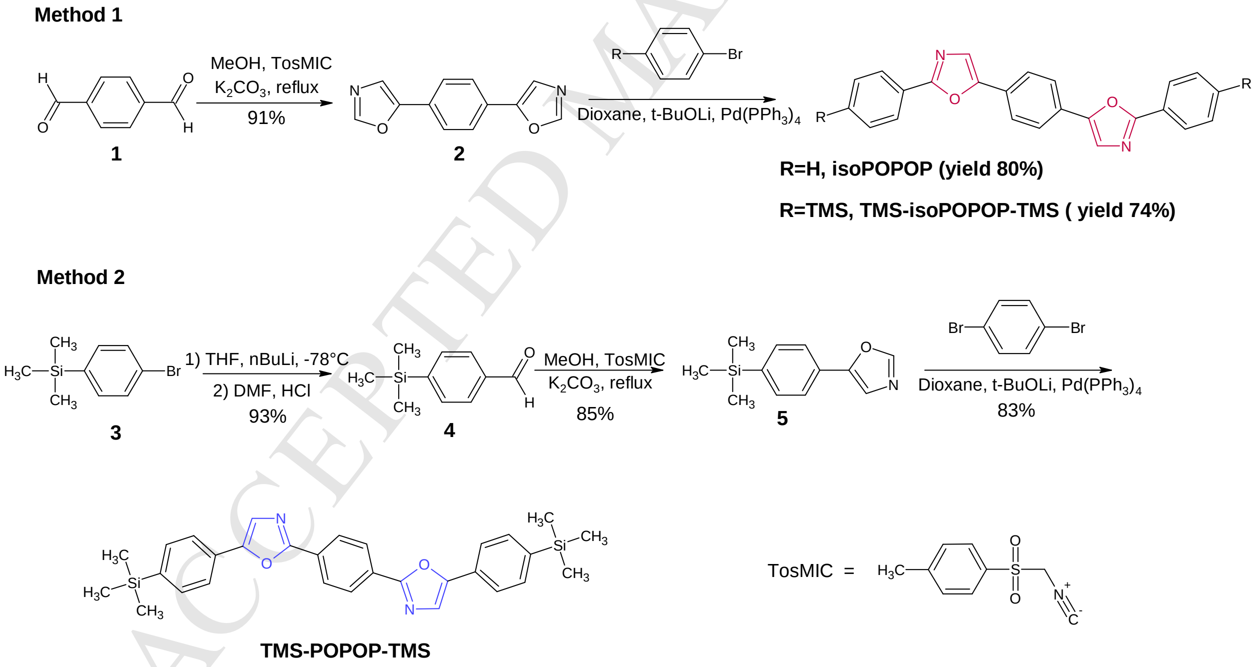


Fig. 1. Scheme of the synthesis of 1,4-*bis*(2-phenyloxazol-5-yl)benzene (**isoPOPOP**), 1,4-*bis*{2-[4-(trimethylsilyl)phenyl]-1,3-oxazol-5yl}benzene (**TMS-isoPOPOP-TMS**) and 1,4-*bis*{5-[4-(trimethylsilyl)phenyl]-1,3-oxazol-2-yl}benzene (**TMS-POPOP-TMS**).

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

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

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

3.2. Thermal behaviour

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

3.2. X-ray measurements

To analyze the structure of the POPOP isomers and their TMS derivatives, single-crystal X-ray diffraction experiments were carried out. Table 1 compares the unit cell parameters found for **isoPOPOP** and **TMS-isoPOPOP-TMS** with the cell parameters of the known **POPOP** luminophore [34].

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

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 between layers[c] (deg)	Interplane distance[d] (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

[a] Literature data [34]

[b] number of molecules per unit cell

[c] dihedral angle measured between the mean planes in the adjacent molecular layers

[d] distance measured between the mean planes in the adjacent molecular layers

Figure 2 allows appreciating important structural differences in the molecular packing. Table 1 summarizes the values of the angles and distances between the adjacent molecular planes in the layers. First of all, the molecular planes in the unit cell of **POPOP** are running almost orthogonal to each other in the successive layers. The angle between the molecular planes is approx. 82 deg (see Table 1). By contrast, in the unit cell of **iso-POPOP**, the molecules are inclined to each other less strongly, with the angle between the molecular planes being only of about 52 deg. Surprisingly, the introduction of bulky TMS side groups almost does not affect this angle. For **TMS-isoPOPOP-TMS** it equals ca. 46 deg. The distance between mean planes in the adjacent molecular layers decreases with the angle from 3.41 to 3.22 Å. Also, an important difference between the crystals consists in the positions of the nitrogen atoms. Thus, in the **POPOP** crystals, all nitrogen atoms are located within one plane, which is 200. In the case of **isoPOPOP**, the nitrogen atoms are split about the ***bc*** plane, being offset at a distance of 1.453 Å. For the lattice of **TMS-isoPOPOP-TMS**, this distance is increased to 2.957 Å, which could explain different thermal stability of these materials.

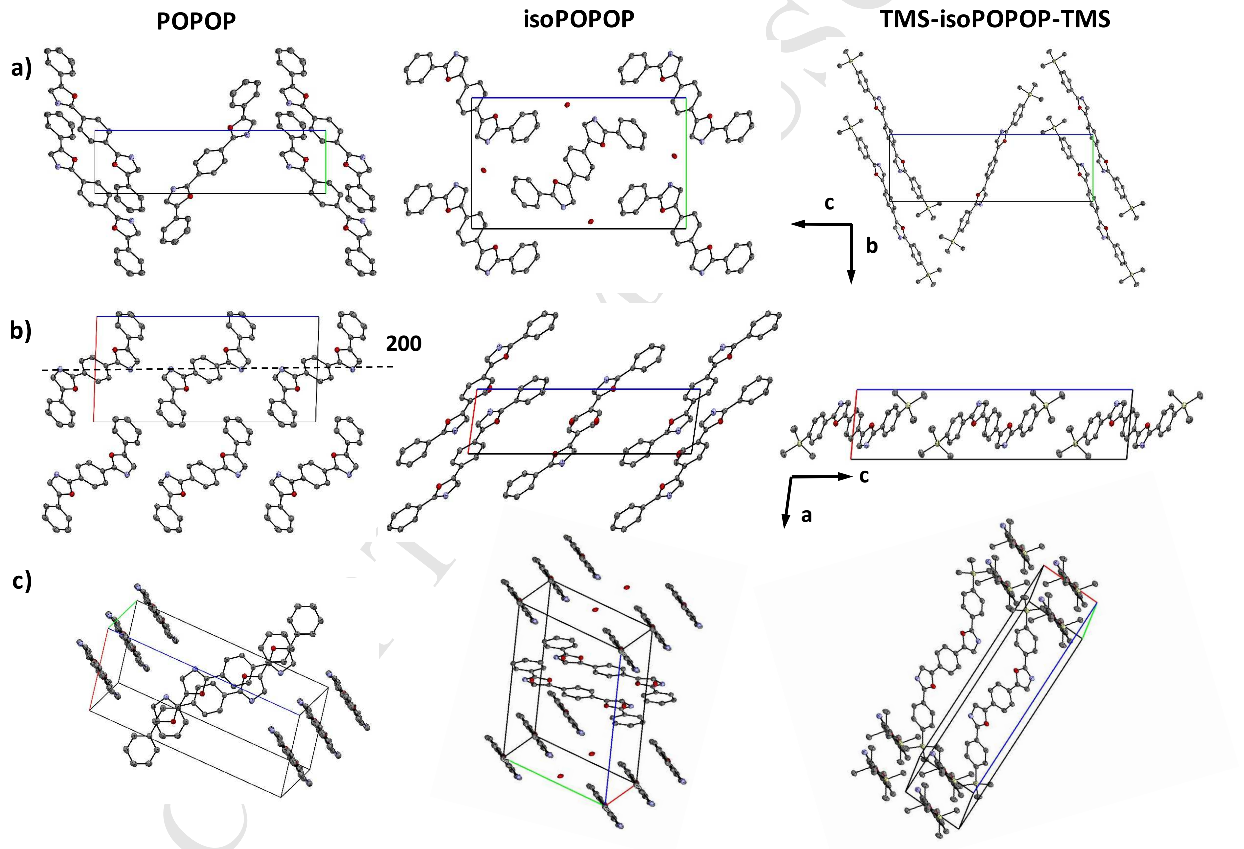


Fig. 2. (a-b) ORTEP views along ***a*** (top) and ***b*** (middle) axis of the **POPOP**, **isoPOPOP** and **TMS-isoPOPOP-TMS** unit cells. For **POPOP** all the nitrogen atoms (given in blue) are positioned within (200) plane. (c) Projection showing the stacks of the molecular planes with angle between the molecular planes in the successive layers reducing from 82.12 to 45.86 deg and interplane distance decreasing from 3.41 to 3.22 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 (E) corresponding to the absorption maxima.

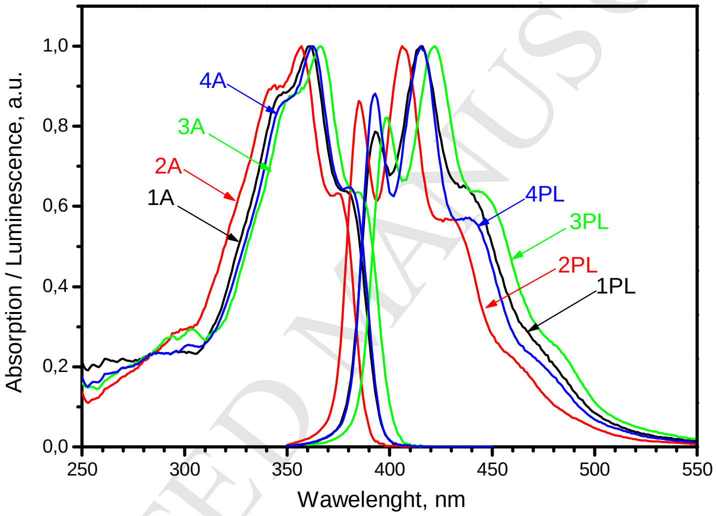


Fig. 3. Absorption (**A**) and photoluminescence (**PL**) spectra of the compounds investigated in diluted THF solutions: 1A, 1PL – **POPOP**; 2A, 2PL – **isoPOPOP**; 3A, 3PL – **TMS-POPOP-TMS**; 4A, 4PL – **TMS-isoPOPOP-TMS**.

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 also worth to note that molar extinction coefficients of

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

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

	Abs	PL	E_g^{opt},	PLQY,	ε,	CV		
	λ_{max}, nm	λ_{max}, nm	eV	%	10^3*M^{-1}*cm^{-1}	φ_{ox}(HOMO) (V)/(eV)	φ_{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.

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

3.4. Photooxidaiton stability

In order to estimate photooxidation stability of the dyes in THF solution, accelerated photostability tests with a help of 150W xenon lamp having a maximum emission at 300-400 nm wavelength range was performed. Fig. 4 shows plots of changes in the absorption spectra of the dyes as a function of irradiation time. As can be seen from the data presented, under continuous UV irradiation the long-wavelength absorption peaks at 300-400 nm dramatically decrease, while absorption in the short-wavelength region (below 300 nm) simultaneously increases. Such results indicate on destruction of the conjugated system of the phenyloxazoles investigated. Moreover, it was found that the compounds containing **POPOP**-like fragment are more resistant to degradation than the corresponding **isoPOPOP** derivatives (Fig. 5). The estimated half-life time of **TMS-isoPOPOP-TMS** and **isoPOPOP** dyes was found to be 19+/-4 and 21+/-4 min respectively. Whereas the half-life time of **POPOP** and **TMS-POPOP-TMS** dyes was twice longer and reached 37+/-4 and 39+/-4 min, respectively. Thus, introduction of organosilicon substituents does not have any significant influence on the photooxidation stability, which is mainly defined by the conjugated core structure (**POPOP** or **isoPOPOP**). THF was chosen as a solvent as one of the most aggressive for photooxidation stability investigations that allows to reach the maximal photo bleaching of the dyes for a minimum time.

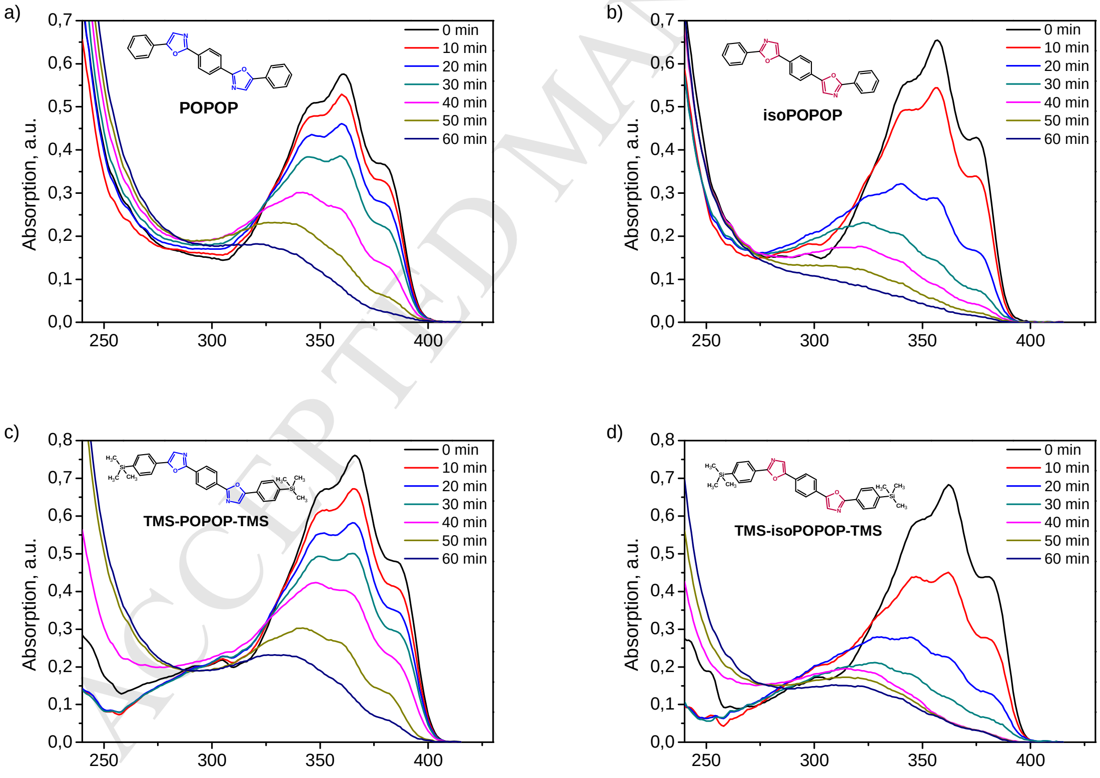


Fig. 4. UV–vis absorption spectral changes of the dyes investigated in THF at 296 K as a function of irradiation time upon exposure to light from 150 W xenon lamp in the presence of air.

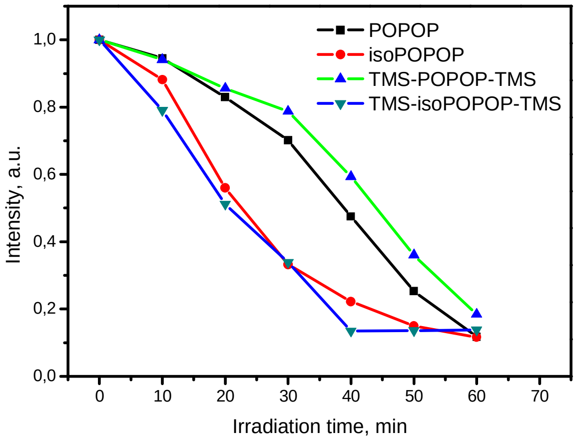


Fig. 5. Changes in absorption (at their peak values) of the phenyloxazoles over irradiation time.

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]:

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

$$E(LUMO)=-e(\varphi_{red}+4.40)\ (eV) \qquad (2)$$

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**	**Eg^{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

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

4. Conclusions

In this work two novel organosilicon derivatives of phenyloxazole luminophores were synthesized under mild conditions using Van Leusen reactions and palladium complexes catalyzed regioselective direct C-H arylation. All the reactions used were highly selective and led to excellent yields. Moreover, they allow preparation of **POPOP** and its isomer **iso-POPOP** derivatives, which are unstable under acidic conditions. Investigation of their spectral luminescent properties revealed that all of them possess high PLQYs and high molar extinction coefficients up to 70.2×10^3 $M^{-1}*cm^{-1}$, while their absorption and emission maxima vary within 357-366 nm and 406-422 nm, respectively. Cyclic voltammetry showed that the molecules with the **POPOP** structure are more stable to oxidation as compared to their isomers, while presence of the TMS substituents does not affect the values of the oxidation or reduction potentials. Single-crystal X-ray diffraction experiments revealed important structural differences between the lattices of the isomers: the angle between the molecular planes and positions of the nitrogen atoms is different for **POPOP** and **isoPOPOP** structures. Quantum mechanical parameters of these oligomers calculated via TD DFT method (HOMO and LUMO energy values, energy gap and oscillator strength) correspond well to the optical spectroscopy and cyclic voltammetry experimental data. The novel trimethylsilyl derivatives of phenyloxazoles reported in this work may find applications in organic photonics due to their high PLQY, large molar extinction coefficients as well as high photo- and thermo- stability.

Acknowledgments

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Supplementary material

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

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- 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