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Materials for optical, magnetic and electronic devices

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#### Abstract

In this work, the synthesis of oligomers having rigid conjugated 4.4'-bis(2-thienyl)biphenyl fragment end-capped with various types of solubilizing groups (SGs), such as either alkyl or alkylsilyl or alkyl-oligodimethylsiloxane are reported. The comprehensive study of their thermal and optical properties as well as rheology in comparison to model highly crystalline oligomers with simple either hexyl or trimethylsilyl SGs allowed us to elucidate structure-properties correlations and find the most powerful type of SG in terms of liquefaction for them. It was revealed that oligomers with long and branched alkyl SGs still remain high crystallinity, whereas oligomers with alkyl-oligodimethylsiloxane SGs combine very low glass transition temperatures (up to  $-111 \,^{\circ}$ C) with a residual crystallinity. The alkylsilyl SGs were found to be the most efficient, since the oligomers end-capped with trihexyl- and tri(2-butyloctyl)silyl SGs are liquid and have low values of both the glass transition temperature (up to -48 °C) and viscosity (up to 1.98 Pa s). All the oligomers prepared have similar optical absorption/luminescence spectra and high values of photoluminescence quantum yield in solution (up to 90%) without a significant impact of the SG type on that. In the neat films, the type of SG has a huge impact on the shape and maxima of absorption and luminescence spectra as well as the photoluminescence efficiency. Among this series of molecules, oligomers with alkylsilyl SGs demonstrate the highest values of photoluminescence quantum yield in the neat form (24% - 61%) and close to the solution optical characteristics, which indicate their strong capability to suppress aggregation of molecules in the bulk. Thus, for the first time liquid luminescent thiophene/phenylene co-oligomers were reported and a solubilizing capability of some of the most perspective types of SG was comprehensively investigated and compared to each other. The results obtained can be used as a guideline for design of functional materials based on conjugated oligomers with a tunable and controllable phase behaviour, solubility and optical properties in the neat state.

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#### 1. Introduction

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Solvent-free nonvolatile room temperature molecular liquids based on luminescent organic  $\pi$ -conjugated molecules represent a new generation of luminescent soft matter with unique properties [1,2]. Molecules of liquid organic chromophores (LOCs) consist of a  $\pi$ -conjugated fragment and an efficient solubilizing group (SG), which allows them to be fluid at room temperature. LOCs have a number of outstanding features over the traditional chromophores such as an easy and ecologically friendly processability at room temperature, unlimited deformability with no impact in their photophysical properties, isotropy of optical and electrical properties, etc. Moreover, LOCs can serve as a fluorescent matrix the properties of which can be easily changed and tuned by addition of functional organic or inorganic dopants [2-6]. LOCs have been actively investigated over the last decade and used as functional materials for various applications [2]. Examples of LOCs applications include luminescent inks[7], liquid semiconductors[8-10], sensors[11-13], organic lasers[10-15], organic light-emitting devices[16-20], memory devices[24], etc.

Although some examples of LOCs have been reported many years ago, a real interest to their investigation and application has been appeared recently, due to a fast development of novel generation of optoelectronic devices based on organic materials. Nowadays, various organic both luminescent and non-luminescent LOCs such as porphyrins,[25,26] phthalocyanines,[27], carbazoles[16, 28], fluorenes[10], pyrelenes[29], arylamines[9,] oligo(p-phenylenevinylene)s[7], coumarines[30], azo compounds[31], etc. have been reported. A number of approaches to suppress crystallinity and decrease inter- and intramolecular interactions of LOCs have been applied [2, 29]. The most often used approaches include change of SG position, its length or branching degree.

Alkyl fragments can be considered as the simplest and the most often used SG to design LOCs[1,2]. Besides them, several examples of LOCs with short oligodimethylsiloxane [9,10,27] and oligo(ethylene oxide)[32,33] SGs have been also reported. Although alkylsilyl groups are known for a long time, we were able to find only a single example of their utilization for the design of LOCs [34]. We believe that alkylsilyl groups are a promising and powerful tool to design LOCs especially for those having extended and rigid conjugated backbone. Indeed, one can expect that the solubilizing ability of the alkylsilyl group may be up to three times more efficient as compared to the alkyl group, since the silicon atom possess three alkyls instead of one.

In this work, in order to investigate and compare a liquefaction power of alkylsilyl group in the design of LOCs we synthesized a series of molecules based on rigid conjugated 4,4'-bis(2thienyl)biphenyl (TPPT) [35,36] backbone with various types of terminal SGs attached to 5,5'positions of thiophene rings (Figure 1), such as alkyl (Alk), alkyl-oligodimethylsiloxane (Alk-SiO)

and alkylsilyl (Alk-Si). To the best of our knowledge, this work is the first example, in which various and the most efficient types of SGs are investigated and compared to each other of the other of



Figure 1. Chemical structures of the oligomers based on TPPT fragment with terminal alkyl, alkyl-oligodimethylsiloxane and alkylsilyl SGs.

# 2. Results and discussion

#### 2.1 Synthesis

The synthesis of the molecules based on TPPT fragment with different SGs can be divided into three main stages (Fig. 2).



Figure 2. Scheme of TPPT-based oligomers synthesis.

The first stage includes preparation of various monofunctionalized SGs precursors (Fig. 2, I). Synthesis of monofunctional alkylchlorosilanes (**3a-c**) includes two steps. First, Grignard reagents were prepared from commercially available alkyl bromides (**1a-c**) followed by their reacting with freshly distilled trichlorosilane to give alkylhydrosilanes (**2a-c**) in the yields of 91-96%. Alkylchlorosilanes (**3a-c**) were obtained by refluxing of **2a-c** in anhydrous carbon tetrachloride at the presence of PdCl<sub>2</sub> as a catalyst[37,38]. Synthesis of 1,1,1,3,3,5,5,7,7,9,9,11,11-tridecamethylhexasiloxane (**6**) was carried out by condensation of 1,1,3,3,5,5,7,7,9,9,11,11-tridecamethyltetrasiloxan-1-ol[39] (**4**) with chloropentamethyldisiloxane[40] (**5**) in 68% yield (Figure 2, I).

The second stage consists of attachment of SGs or their parts to thiophene followed by preparation of organoboron precursors (Fig. 2, II). Synthesis of thiophene precursors with SGs (7a-g) was carried out by coupling reaction between a thiophene lithium derivative and either

Finally, oligomers with alkyl (**TPPT-Hex**, **TPPT-Dodec**, **TPPT-BuOct**) and alkylsilyl SGs (**TPPT-Si-Me**, **TPPT-Si-Hex**, **TPPT-Si-MeHex**, **TPPT-Si-BuOct**, were obtained by Suzuki cross-coupling reaction between boronic esters (**8a-g**) and 4,4'-dibromobiphenyl (Figure 2, III). It should be noted that the synthesis of **TPPTSi--Me** *via* palladium-catalyzed direct arylation has been reported previously [41].

The synthesis of **TPPT-Bu-3SiO** and **TPPT-Bu-6SiO** having alkyl-oligodimethylsiloxane groups included two sequential reaction steps. First, Suzuki cross-coupling reaction between **10** and 4,4'-dibromobiphenyl gave 4,4'-(5-but-3-en-1-yl-thiophene-2-yl)biphenyl (**11**) in 72 % yield. Second, the hydrosilylation reaction of **11** with commercially available 1,1,1,3,5,5,5-heptamethylsiloxane or its longer linear analogue, 1,1,1,3,3,5,5,7,7,9,9,11,11-tridecamethylhexasiloxane (**6**), gave rise to **TPPT-Bu-3SiO** or **TPPT-Bu-6SiO**, respectively. All the target oligomers were purified and their chemical structure and high purity were proved by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy, MALDI–TOF mass spectrometry and elemental analysis (see Electronic supporting information (ESI), Fig. S1 – Fig. S67).

### 2.2 Thermal properties and rheology.

Methods of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were applied in order to reveal the effect of SG on the thermal stability and phase behaviour of the novel luminophores and the data obtained are summarized in Table 1. TGA data showed that all the materials have high thermal and thermal-oxidative stability, since their values of the destruction temperature ( $T_d$ ), measured as 5% weight loss of samples, exceed 275°C in air and under inert atmosphere (Figure 3, Table 1). Comparing the effect of SG on the thermal-oxidative stability one can see that  $T_d$  values in air for all the materials are quite similar. In the inert atmosphere the difference between the molecules stability is a more pronounced. In general, thermal stability of the molecules with Alk-Si groups was found to be slightly higher as compared to those of their analogs with Alk and Alk-SiO groups. The exception only is the molecule with trimethylsilyl groups (**TPPT-Si-Me**) having the lowest  $T_d$  value among this series of molecules, which can be explained by its lower molecular weight allowing sublimation of the material before the thermal destruction begins.



Figure 3. TGA curves of TPPT-based oligomers in air (a) and under inert atmosphere (b).

	$T_{\rm d}air/T_{\rm d}N^2$	$T_{\alpha}$	$T_{I}$ °C	$T_2$ °C	<i>T</i> <sub>i</sub> °C	State	n	E
Compounds	°C	°C	$(\Delta H, J/g)$	$(\Delta H, J/g)$	$(\Delta H, J/g)$	at r.t.	Pa·s	kJ·mol⁻
TPPT-Hex	286/290	_	69(19)	261(38)	270(26)	solid	—	
<b>TPPT-Dodec</b>	276/327	_	99(73)	221(25)	228(41)	solid	_	_
<b>TPPT-BuOct</b>	288/315	-41	-	42(44)	60(14)	solid	—	_
<b>TPPT-Si-Me</b>	283/280	_	75	202	240(70)	solid	_	_
<b>TPPT-Si-Hex</b>	309/356	-54	_	_	_	liquid	1.94	45
TPPT-Si-MeHex	289/379	-22	_	_	53(27)	solid	_	_
<b>TPPT-Si-BuOct</b>	283/376	-60	_	_	_	liquid	5.84	48
TPPT-Bu-3SiO	285/315	-64	-	-	95(6)	solid	—	_
TPPT- Bu-6SiO	283/333	-111	-	-	85(3)	solid	—	_

Table 1. Thermal and rheology properties of TPPT-based oligomers

Notes:  $T_d$  is the decomposition temperature calculated for 5% weight-loss;  $T_g$  is a glass transition temperature;  $T_1$  is a temperature of the first endothermic transition (suggested as alkyl melting);  $T_2$  is a temperature of the second endothermic transition;  $T_i$  is an isotropization peak temperature; In parentheses the corresponding value of transition enthalpy  $(\Delta H, J \cdot g^{-1})$  is given;  $\eta$  is a dynamic viscosity;  $E_a$  is an activation energy of viscous flow.

Comparison of DSC data for the series of molecules allowed us evaluating the efficiency degree of SGs for reducing crystallinity of TPPT fragment. The first and second heating DSC scans are shown in Fig. 4 and in Fig S68a (see ESI), respectively. As can be seen from these data some molecules demonstrate several endothermic transitions and some of them have relatively low values of enthalpy ( $\Delta$ H), which indicate on a liquid crystalline behaviour and was confirmed by polarizing optical microscopy (Fig. S69).

As expected, **TPPT-Hex** having the shortest aliphatic fragment within the series of molecules with alkyl SGs was found to be a material with high values of both temperature and enthalpy of phase transitions (Table 2). Moreover, the DSC heating scan of **TPPT-Hex** shows several endothermic peaks, where the first (T<sub>1</sub>) at 69°C with  $\Delta H$  of 19 J/g could be attributed to the melting of alkyl chains, the second one (T<sub>2</sub>) at 261°C with  $\Delta H$  of 38 J/g – to the transition from a liquid crystalline smectic phase (Sm1) to the other smectic phase (Sm2) (Fig. S69) followed by

the final isotropization (T<sub>i</sub>) at 270°C. **TPPT-Dodec** has similar to **TPPT-Hex** phase behaviour. However the doubling of alkyl chain length in the SGs from hexyl to dodecyl leads to an increase of the temperature for the first endothermic transition responsible for alkyl chain melting and to decrease for the subsequent Sm1 to Sm2 transition and final isotropization. The similar trend of further temperature decreasing of the liquid crystal phase transitions was found to be also for **TPPT-BuOct**. However the change of the linear dodecyl group at TPPT fragment by 2-butyl-octyl one being the alkyl with the same number of carbon atoms but having a branched architecture, leads to the appearance of a glass transition at -41°C (Fig S68b) instead of the alkyls melting observed previously for **TPPT-Dodec** and **TPPT-Hex** molecules.



Figure 4. The first heating DSC scans of TPPT-based oligomers.

The usage of alkylsilyl groups leads to a change in the phase behaviour of the TPPT molecules. While the model **TPPT-Si-Me** being the first representative from the series of molecules with Alk-Si groups is a crystalline material with a relatively high  $T_m$  at 240°C and  $\Delta H_m$  of 70 J/g, the subsequent analogue with longer hexyl groups (**TPPT-Si-Hex**) is a liquid material with a low glass transition temperature ( $T_g$ ) of -54 °C. This is also in a sharp contrast to **TPPT-Hex** analogue being a solid material with high-temperature phase transitions. Surprisingly, the replacement of hexyl chains by 3,5,5-trimethylhexyl ones at the silicon atom leads to a solid aggregate state for **TPPT-MeHex** with increased  $T_g$  value of -22° and melting peak at 53°C ( $\Delta H_m = 27$  J/g). This fact may be explained by a branched character of 3,5,5-trimethylhexyl groups capable to form an interpenetrating network in the bulk state and thus increase intermolecular interactions. However, the absence of an endothermic peak on the second heating DSC scans indicates that the crystalline phase does not recover from a melt (Fig. S68), which often happens

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for branched molecules [42]. The phase behaviour of **TPPT-Si-BuOct** was found to be quite similar to that of **TPPT-Si-Hex**, since this material is also a liquid with a glass transition at coose and no melting peaks on the DSC scan.

The molecules with Alk-SiO groups, namely **TPPT-Bu-3SiO** and **TPPT-Bu-6SiO**, demonstrate the lowest  $T_g$  values in this series of molecules, -64°C and -111 °C, respectively, which is originated from a flexible oligodimethylsiloxane fragments nature [40]. Although these data indicate that the solubilizing ability of the latter is much better than that of alkyl SGs, it was found to be slightly insufficient to suppress completely  $\pi$ - $\pi$  interactions of TPPT fragments in the neat state. One can see an endothermic phase transition on the DSC scan at 95°C for **TPPT-Bu-3SiO** and at 85°C for **TPPT-Bu-6SiO** with rather low enthalpy melting values of 6 and 3 J/g, respectively with the typical for hexagonal columnar mesophase textures [43-45]. Similar to **TPPT-Si-BuOct** the **TPPT-Bu-3SiO** and **TPPT-Bu-6SiO** molecules showed only a glass transition process on the second DCS heating scan (Fig S68).

Thus, among the series of molecules investigated only **TPPT-Si-Hex** and **TPPT-Si-BuOct** were found to be in liquid aggregate state at room temperature (Fig. 5).



Figure 5. Photographs of TPPT-based oligomers on glass substrates under (a) day light and (b) 365 nm UV light; Photograph of TPPT-Si-Hex under (c) day light and (d) 365 nm UV light; (e) dependence of viscosity on shear rate (flow curves) at various temperatures for TPPT-Si-Hex and TPPT-Si-BuOct.

The fluid behaviour of **TPPT-Si-Hex** and **TPPT-Si-BuOct** were studied by the rotational viscometry technique. The dependence of the luminophores flow curves for various temperatures

in coordinates shear rate – viscosity ( $\eta$ ) are presented in Figure 5e. One can see that both materials are Newtonian liquids, since the viscosity is independent of the shear rate. The viscosity of **TPPT Si-BuOct** at all temperatures was found to be 5.84 Pa·s which is almost three times higher as compared to that of **TPPT-Si-Hex** (1.94 Pa·s) due to a longer and branched alkyls of the former. Moreover, using the temperature-viscosity plots for the molecules (Fig. S70) and Arrhenius equation, the activation energy of viscous flow ( $E_a$ ) was evaluated (Table 1). The fact of slightly higher  $E_a$  value for **TPPT-Si-BuOct** (48 kJ·mol<sup>-1</sup>) as compared to **TPPT-Si-Hex** (45 kJ·mol<sup>-1</sup>) confirms the abovementioned conclusion about the influence of branched alkyls on the viscosity increase.

Therefore by introducing various end groups the intermolecular interactions for oligo(phenylene-thiophene)s can be finely tuned thus regulating their aggregate state, thermal stability, phase behaviour and viscosity.

## 2.3 Optical properties.

The optical properties of novel luminophores were studied by absorption and luminescent spectroscopy in both the diluted THF solutions and in the neat state (Table 2, Fig. 6). For a more detailed comparison, average values were calculated for all main optical parameters in solution (see **TPPT-SG**<sub>mean</sub>).

Deviations between values of absorption and photoluminescent parameters of the molecules with different substituents in their diluted THF solutions are within the measurement error (Fig. 6a, Table 2). The absorption and luminescence spectra contour for THF solutions remains almost unchanged when replacing one terminal substituent with the other one having different architecture or type. The photoluminescence quantum yield (PLQY) in solution is very high (up to 95%) and similar for all the molecules. Thus, the type of SG does not have any noticeable effect on the optical and photophysical properties of their solutions.

		sol	lution i	n THF		neat state				
Compound	$\lambda_{abs},$	ε <sub>max</sub> ,	$v_{1/2},$	$\lambda_{lum}$ ,	PLQY,	λ <sub>abs</sub> ,	$v_{1/2}$ ,	$\lambda_{lum}$ ,	PLQY,	÷
	nm	$L(mol \cdot cm)^{-1}$	cm <sup>-1</sup>	nm	%	nm	cm <sup>-1</sup>	nm	%	C
TPPT-Si-Me	340	55000	4600	386/407	95	-	-	404/424	63	5
<b>TPPT-Si-Hex</b>	342	68000	4550	389/409	94	344	4600	395/416	37	C
<b>TPPT-Si-MeHex</b>	342	59000	4600	388/409	91	339	5500	398/419	61	U
<b>TPPT-Si-BuOct</b>	344	65000	4650	391/411	94	344	4600	394/414	24	
<b>TPPT-Hex</b>	341	54300	4600	387/406	90	_	>10000	431/455	11	S
<b>TPPT-Dodec</b>	341	66000	4700	388/408	93	_	>10000	431/457	13	ŋ
<b>TPPT-BuOct</b>	342	66000	4650	389/409	91	335	10000	430/453	11	5
TPPT-Bu-3SiO	341	59000	4500	388/408	90	342	7600	419/440	3	
TPPT-Bu-6SiO	342	61000	4700	388/408	95	334	5900	422/443	5	ζ
average values of the measured parameters										
TPPT-SG <sub>mean</sub> *	342	61500	4600	389/409	93				,	C
	$\pm 2$	$\pm 6500$	$\pm 100$	$\pm 2$	$\pm 2$	—	_	_	_	

 Table 2. Optical and photophysical properties of TTPT-based oligomers with various SGs in

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Notes: \* **TPPT-SG** acronym is used to illustrate average values of optical parameters in THF solution;  $\lambda_{abs}$  is an absorption maximum;  $\varepsilon_{max}$  is a molar extinction coefficient;  $\lambda_{abs}$  is a photoluminescence spectrum maximum;  $v_{1/2}$  is a half-width of the absorption spectrum; PLQY is a photoluminescence quantum yield.

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**Figure 6**. Normalized absorption and photoluminescence spectra of TPPT-based compounds with various SGs in THF solutions (a) and in neat state of molecules with alkylsilyl (b), alkyl (c) and oligodimethylsiloxane (d) SGs in comparison to **TPPT-SG**<sub>mean</sub> (average optical spectrum in THF solution).

View Article Online However, optical properties in the neat state of TPPT-based molecules significantly depend on the type of SG (Table 2, Fig.6b-d).

Considering molecules with long alkylsilyl SGs (TPPT-Si-Hex, TPPT-Si-MeHex, **TPPT-Si-BuOc**) one can see that both their absorption ( $\lambda_{abs}$ ) and photoluminescence ( $\lambda_{lum}$ ) maximum as well as the half-width of the absorption spectrum ( $\Delta v_{1/2}$ ) are very similar to those of the average spectrum and characteristics in solution (compare to TPPT-SGmean) (Fig. 6b). Since according to DSC the longer alkylsilyl substituents prevent the formation of a crystalline phase, it leads to an increased amount of molecules in the amorphous phase. As a result, the absorption and luminescence spectra in the neat state of TPPT-Si-Hex, TPPT-Si-MeHex and TPPT-Si-BuOct almost coincide with the spectra of their solutions. The slight bathochromic shift of their luminescence spectrum in the neat state compared to the solution can be explained by changing of the environment field. The slightly red-shifted and broadened absorption and luminescence spectra of **TPPT-Si-MeHex** indicate a stronger  $\pi$ - $\pi$  interaction between molecules as compared to **TPPT**-Si-Hex and TPPT-Si-BuOct, which is in a good agreement with the DSC data described above. It was not possible to obtain an absorption spectrum for TPPT-Si-Me in the neat state, due to a strong reflection and scattering from its polycrystalline film. Besides the fact that luminescence spectrum of the most crystalline TPPT-Si-Me material is pronouncedly red-shifted, the above described patterns in the luminescence spectrum are typical for this molecule as well (Figure 6).

PLQY values for all neat oligomers with alkylsilyl groups were found to be relatively high and ranged from 24% to 63%. The PLQY decrease in the neat state as compared to solution and the difference of photoluminescence efficiency for the series of molecules with Alk-Si SGs can be explained by both a different environment field and an incomplete correspondence of the molecule conformation in the bulk to that in the solution. The latter means that molecules in the neat state can have different torsion angles between adjacent units in TPPT backbone as compared to the solution, which in turn leads to some changes in the structure of electronic transitions and affects the luminescence efficiency. It is also known that bulky substituents affect the torsion angles in TPPT molecules [46], thus one can expect that the torsion angles in the neat state can be slightly varied within the series of molecules with Alk-Si SGs having different bulkiness of terminal substituents.

In contrast, optical properties in the neat state of the molecules with either alkyl or alkylsiloxane SGs differ significantly from those in the solution (Fig.6c and Fig.6d). Comparing to solution, their absorption spectra were found to be broadened and even unstructured in the case of molecules with alkyl SGs, whereas their photoluminescence spectra remained relatively structured but red shifted by 2000 - 2600 cm<sup>-1</sup>. Among the molecules with alkyl SGs, a more 11

defined spectrum structure appeared in the absorption of **TPPT-BuOct**, which indicates a better shielding ability of branched 2-butyl-octyl groups from  $\pi$ - $\pi$  interactions in the **Dulk** as **Compared** to linear hexyl and dodecyl ones. In addition, both a more defined absorption spectrum structure and slight hypochromic shift of the luminescence spectra for **TPPT-Bu-3SiO** and **TPPT-Bu-6SiO** molecules with alkyl-oligodimethylsiloxane SGs indicate a higher solubilizing ability of these groups as compared to the alkyl one, which is also in a good agreement with the DSC data. PLQY for TPPT molecules with alkyl and alkylsiloxane SGs in the neat state was found to be quite low: 11-13% and 3-5%, respectively.

One can see that the highest photoluminescence efficiency in the neat state is observed for the series of molecules with alkylsilyl groups. It is known that in the TPPT fragment the torsion angle between the thiophene and phenyl rings affects the optical properties [46]. Thus, as a possible reason to explain higher PLQY of molecules with alkylsilyl SGs can be assumed that these compounds during the transition from the solution to a solid state may maintain the conformation of molecules close to that in solution. This assumption needs further confirmation by X-ray analysis, which is however quite challenging due to the predominantly amorphous character of these materials.

#### Conclusions

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To conclude, a series of luminescent oligomers based on 4,4'-bis(2-thienyl) biphenyl  $\pi$ -conjugated fragment with various type of SGs have been synthesized. The influence of the type, length and branching degree of SGs on thermal stability, aggregate state, phase behaviour, rheology and optical properties of the oligomers were comprehensively studied. It was revealed that the ability to suppress intermolecular interactions in the neat state increases in the row Alk <Alk-SiO < Alk-Si. As a result, while molecules with alkyl SGs (TPPT-Hex, TPPT-Dodec, TPPT-BuOct) remain a pronounced crystallinity, molecules with alkyl-oligodimethylsiloxane SGs (**TPPT-Bu-3SiO**, TPPT-Bu-6SiO) demonstrate low glass transition temperatures (up to -110 °C) and lower temperature and enthalpy of mesophase transitions. The most interesting results were found for the series of oligomers with alkylsilyl SGs (TPPT-Si-Me, TPPT-Si-Hex, TPPT-Si-Dodec, TPPT-Si-BuOct) since they not only have similar to their solutions absorption and luminescent spectra and much higher PLQY (up to  $\approx 60\%$ ) in the neat state, but also some of them (TPPT-Si-Hex and TPPT-Si-BuOct) are liquids with a low viscosity (up to 1.98 Pa·s). One more benefit of alkylsilyl solubilizing groups is that they slightly increase the thermal stability of the oligomers. Thus, the results obtained clearly indicate that alkylsilyl groups are a powerful tool for liquefaction of chromophores with a highly crystalline and rigid conjugated core. In this work, for the first time liquid luminescent oligo(phenylene-thiophene)s were reported and solubilizing capability of some

of the most perspective types of SG was comprehensively investigated and compared to each other. The results can be used as a guideline for researchers to choose appropriate SG or or der to design luminescent materials based on conjugated oligomers with a desirable and controllable phase behaviour, solubility and optical properties in the neat state.

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