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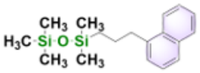
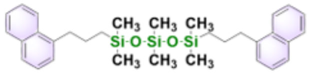
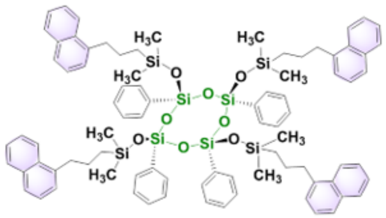


Mono-Naph



Di-Naph



Tetra-Naph

Monomer emission in ***CyH, DCM, EtOH, DMSO***

Monomer **+** **Excimer** emission in ***DMSO:H_2O*** mixtures

Solvent-Controlled Intramolecular Excimer Emission from Organosilicon Derivatives of Naphthalene

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Abstract

New mono-, bis- and tetra-fluorophoric organosilicon naphthalene derivatives, that are able to form intramolecular excimers have been synthesized and characterized. The synthesized compounds show only monomeric fluorescence in dilute solutions of common organic solvents, but exhibit relatively strong excimer-like emission in DMSO-water and THF-water mixtures. In all cases, the intensity of excimer fluorescence increases with increasing water content and decreases with increasing temperature. Fully and partially overlapping excimer conformations have been modeled by DFT-based calculations. Properties of different intramolecular excimers in an ensemble of four naphthalene molecules linked to a cyclotetrasiloxane ring in an all-*cis* arrangement are considered.

Keywords: excimer, fluorescence, naphthalene, siloxane.

1. Introduction

Excimers are excited dimers formed as a result of interaction of one molecule in an excited state and another in the ground state. They have attracted great research interest in terms of their fundamental and applied value since the seventies of the last century.[1–3] Typically, molecular excimers are formed when there is a small intermolecular distance between two interacting molecules, which facilitates the formation of excimers due to π-π interaction. As a rule, this is achieved in crystals, amorphous films and concentrated solutions of aromatic hydrocarbons such as benzene, naphthalene, anthracene, pyrene, perylene, etc., and their derivatives.[4–6]

Excimer-based fluorescent probes can be widely used in various fields of science and technology. In particular, they may be used as selective fluorescent sensors for the detection of metal ions,[7–9] in biosensing processes as fluorescent probes for the detection of DNA,[10] amino acids,[11] enzymes,[12] ribonucleases[13] and bioimaging of living cells, bacteria, etc.[14] Another area of application for excimer-forming compounds is organic electronics, where such compounds are used to develop new materials for OLED applications.[15–17]

At present, naphthalene and its derivatives are one of the most studied classes of organic compounds capable of forming fluorescent excimers. Excimers of these compounds were observed in the crystalline[18–22] and liquid states.[23,24] Naphthalene derivatives are particularly attractive fluorescent compounds because their excimers are sensitive to local environmental properties and temperature, that leads to a redistribution of the monomer/excimer emission intensity.[25,26] As a consequence, these phenomena can find many applications, for example, in the development of fluorescent molecular thermometers[27] or sensors for detecting metal ions.[27–37]

In concentrated solutions, naphthalene derivatives exhibit strong excimer emission as a result of the interaction of neighboring molecules. An alternative effective approach to increasing the probability of excimer formation is to increase the local concentration of chromophores by fixing two or more molecules at close distances, usually using alkyl spacers. In a series of studies, it was shown that the nature and conformation of the alkyl spacer play a crucial role in the formation of an intramolecular excimer, and a stable excimer configuration takes place only in the case of a symmetric sandwich arrangement.[38–40] The literature describes many examples of grafting several naphthalene molecules to matrices with different architectures, such as propane,[41–43] cyclodextrines,[29,44–54] dendrimers,[55] cyclotriphosphazenes,[56,57] thiacalix[4]arene,[58] polymers,[59–62] silanes,[63] siloxanes,[64] POSSs (polyhedral oligomeric silsesquioxanes)[65] and others.[66,67]

There are several examples of a combination of naphthalene derivatives and a siloxane matrix in the literature. Interesting examples include siloxane-bridged cyclic dimers with naphthalene fragments,[64] and naphthalene-containing POSS,[65] which exhibit excimer fluorescence. Siloxanes of different structures are convenient matrices for grafting chromophores, since they make it easy to obtain multichromophore systems with a controlled architecture.[68–72] In addition, rigidity/flexibility of the corresponding spacer can be adjusted by using silane or siloxane bonds in the spacers. This approach can be effective for the preparation of intramolecular excimers.[73] Stereoregular cyclic organosiloxanes are of particular interest among a wide range of organosilicon compounds because they have the advantage of controlled ring size and cis/trans conformation.[74] For example, excimer formation in cyclotetrasiloxane functionalized with four fluorophores based on terthiophene has been shown.[75]

Understanding the excimer formation in organic materials is of fundamental importance for optimizing their performance for a given application. Using femtosecond spectroscopy, Iyer and co-authors have recently shown that formation of benzene excimers in neat liquid benzene at room temperature follows the mechanism involving UV electronic excitation of two nearby benzenes in a nearly parallel arrangement that are already in a configuration facilitating sharing the excitation.[76] As soon as the excitation selects such a pre-formed excimer, the interaction between the two molecules is instantaneously switched to a more stronger attraction and the entities become locked. The authors noted that the proposed mechanism of excimer formation can be applied to other aromatic systems with short-range stacked configurations.

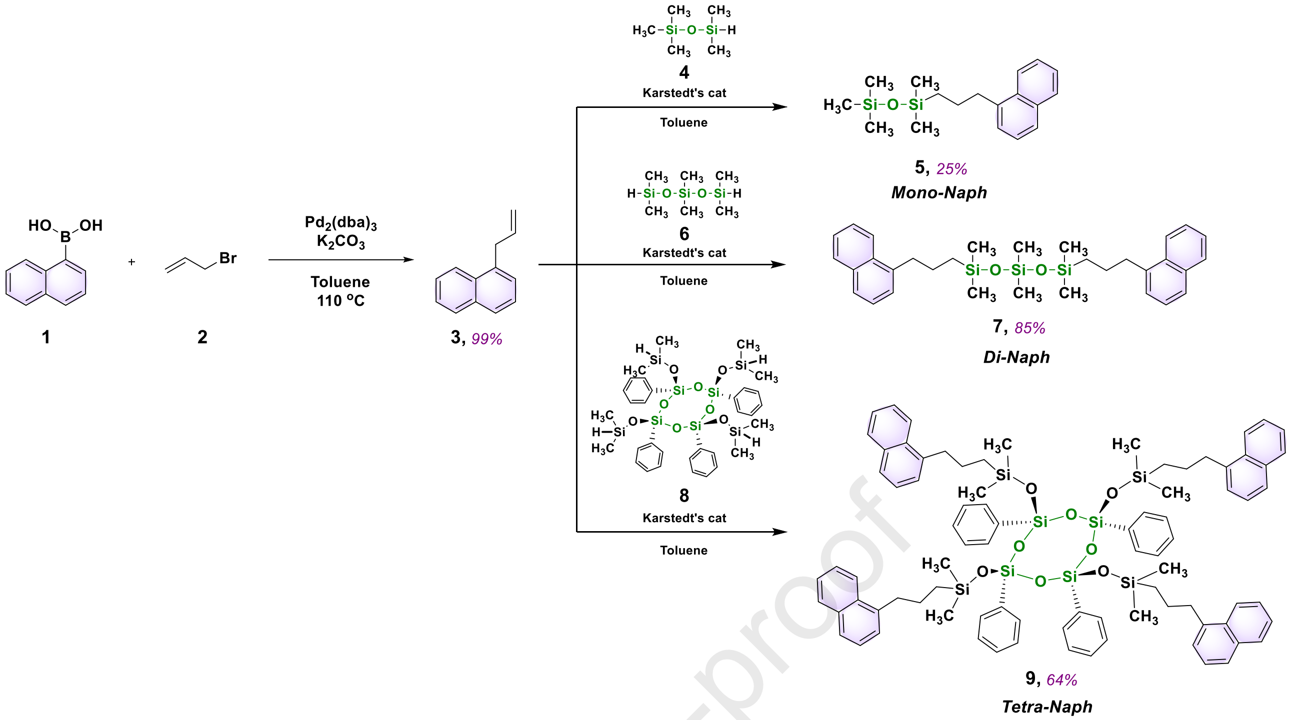
In particular, molecular clusters can be considered as an example of such systems. Saigusa and co-authors reported that the efficiency of excimer formation in van der Waals naphthalene clusters isolated in the supersonic state and consisting of two, three or four naphthalene molecules strongly depends on the size and geometry of the clusters.[77]

The use of a cyclotetrasiloxane framework seems to make it possible to construct similar systems for research in solution and solid state. In this paper, we present the observation of intramolecular excimers in a bis-naphthalene system as well as in an ensemble of four naphthalene molecules linked to a cyclotetrasiloxane ring in an all-*cis* arrangement with respect to the siloxane cycle. To allow the fluorophores to approach neighboring molecules, they were tethered with flexible spacers. In order to induce the formation of intramolecular excimers in this system, binary DMSO–water and THF-water mixtures were used.

2. Results and discussion

2.1. Synthesis of organosilicon derivatives of naphthalene

Mono-naphthyl (***Mono-Naph***) **5**, bis-naphthyl (***Di-Naph***) **7** and tetra-naphthyl (***Tetra-Naph***) **9**, organosilicon derivatives were synthesized in two stages according to Scheme 1. It is noteworthy that ***Tetra-Naph*** contains all naphthalene moieties in the same plane of the cyclotetrasiloxane ring. It can be occurring by using functional cyclotetrasiloxane **8** described by us earlier.[74] At the first stage, 1-allylnaphthalene derivative **3** was prepared in almost quantitative yield by the reaction of naphthalene-1-boronic acid **1** with allylbromide **2** through refluxing the reaction mixture in dry toluene in an argon atmosphere in the presence of $Pd_2(dba)_3$ as a catalyst and K_2CO_3 as a base. Then, 1-allylnaphthalene **3** was involved into the reaction with 1,1,1,3,3-pentamethyldisiloxane (mono-silylhydride **4**), 1,1,3,3,5,5-hexamethyltrisiloxane (di-silylhydride **6**) and *cis*-tetra[(phenyl)(dimethylsiloxy)] cyclotetrasiloxane[74] (tetra-silylhydride **8**) in dry toluene using Karstedt's catalyst. After isolation and purification by column chromatography on silica using hexane and hexane–toluene mixture as an eluent, the corresponding ***Mono-Naph*** **5**, ***Di-Naph*** **7** and ***Tetra-Naph*** **9** were obtained as viscous oils. All compounds were fully characterized by NMR- and IR-spectroscopy (Supporting Information).



Scheme 1. Synthesis of **Mono-Naph**, **Di-Naph** and **Tetra-Naph**.

2.2. Photophysical properties

The photophysical characteristics of the synthesized organosilicon naphthalene derivatives were studied in various solvents. The results obtained are summarized in Table 1. Figure 1 shows the normalized electronic absorption and emission spectra of **Mono-**, **Di-** and **Tetra-Naph** in various solvents at room temperature. The absorption spectra of the compounds have an almost identical vibration structure up to 320 nm which is typical for naphthalene derivatives (Figure 1). The absorption maxima of solutions of all studied compounds in cyclohexane, dichloromethane, ethanol and DMSO vary in the range of 283-285 nm (Table 1), which indicates that the solvent polarity does not have a strong effect on the absorption spectra. There are no spectral shifts for **Di-Naph** and **Tetra-Naph** in comparison with **Mono-Naph** that indicates the absence of intramolecular electronic interactions between the naphthalene chromophores in the ground state. The molar extinction coefficient ε for **Mono-Naph** is about 7 000 M^{-1} cm^{-1} which corresponds to the data for unsubstituted naphthalene. In the case of **Di-** and **Tetra-Naph** the molar extinction coefficient ε is about 13 000 $M^{-1}cm^{-1}$ and 28 000 $M^{-1}cm^{-1}$, respectively. The data indicate that an increase in the amount of naphthalene entities in these molecules leads to an almost proportional increase in the molar extinction coefficient (Table 1). The solvent polarity does not affect the value of the molar extinction coefficient.

Compound	**Solvent**	**λ_{abs} (nm)**	**ε (M^{-1} cm^{-1}) *in S0→S2 maximum***	**λ_{em} (nm)**	**Φ_f [b] (air)**	**Φ_f [b] (argon)**	**$\Delta\nu_{St}$ (cm^{-1})**
Mono-Naph	Cyclohexane	315 (S0→S1) 283 (S0→S2)	7 300	328 (340)	0.10	0.24	1258
	Dichloromethane	314 (S0→S1) 285 (S0→S2)	7 170	336 (328)	-	-	2085
	Ethanol	314 (S0→S1) 283 (S0→S2)	7 370	327 (336)	-	-	1266
	DMSO	315 (S0→S1) 285 (S0→S2)	7 530	337 (328)	-	-	2072
Di-Naph	Cyclohexane	315 (S0→S1) 284 (S0→S2)	12 800	328 (340)	0.12	0.25	1258
	Dichloromethane	315 (S0→S1) 285 (S0→S2)	12 700	338 (328)	-	-	2160
	Ethanol	314 (S0→S1) 283 (S0→S2)	12 600	338 (328)	-	-	2261
	DMSO	315 (S0→S1) 285 (S0→S2)	13 100	337 (328)	-	-	2072
Tetra-Naph	Cyclohexane	315 (S0→S1) 284 (S0→S2)	28 300	328 (340)	0.13	0.27	1258
	Dichloromethane	315 (S0→S1) 285 (S0→S2)	27 700	338 (328)	-	-	2160
	Ethanol	314 (S0→S1) 283 (S0→S2)	20 630[a]	328 (338)	-	-	1359
	DMSO	315 (S0→S1) 285 (S0→S2)	28 000	337 (328)	-	-	2072

Table 1. Optical properties of ***Mono-Naph***, ***Di-Naph*** and ***Tetra-Naph*** in various solvents.

λ_{abs} – Absorption wavelength; λ_{em} – emission wavelength; ε – extinction coefficient at the maximum; Φ_f – fluorescence quantum yield; $\Delta\nu_{St}$ – Stokes shift. The wavelength of the second fluorescence peaks are given in parentheses. [a] Low extinction coefficient most likely is due to error obtained through solution preparation because the compound is poorly soluble in ethanol. [b] Naphthalene was used as a standard for calculating the quantum yield (Φ_f =0.23; argon-purged solution in cyclohexane).[78]

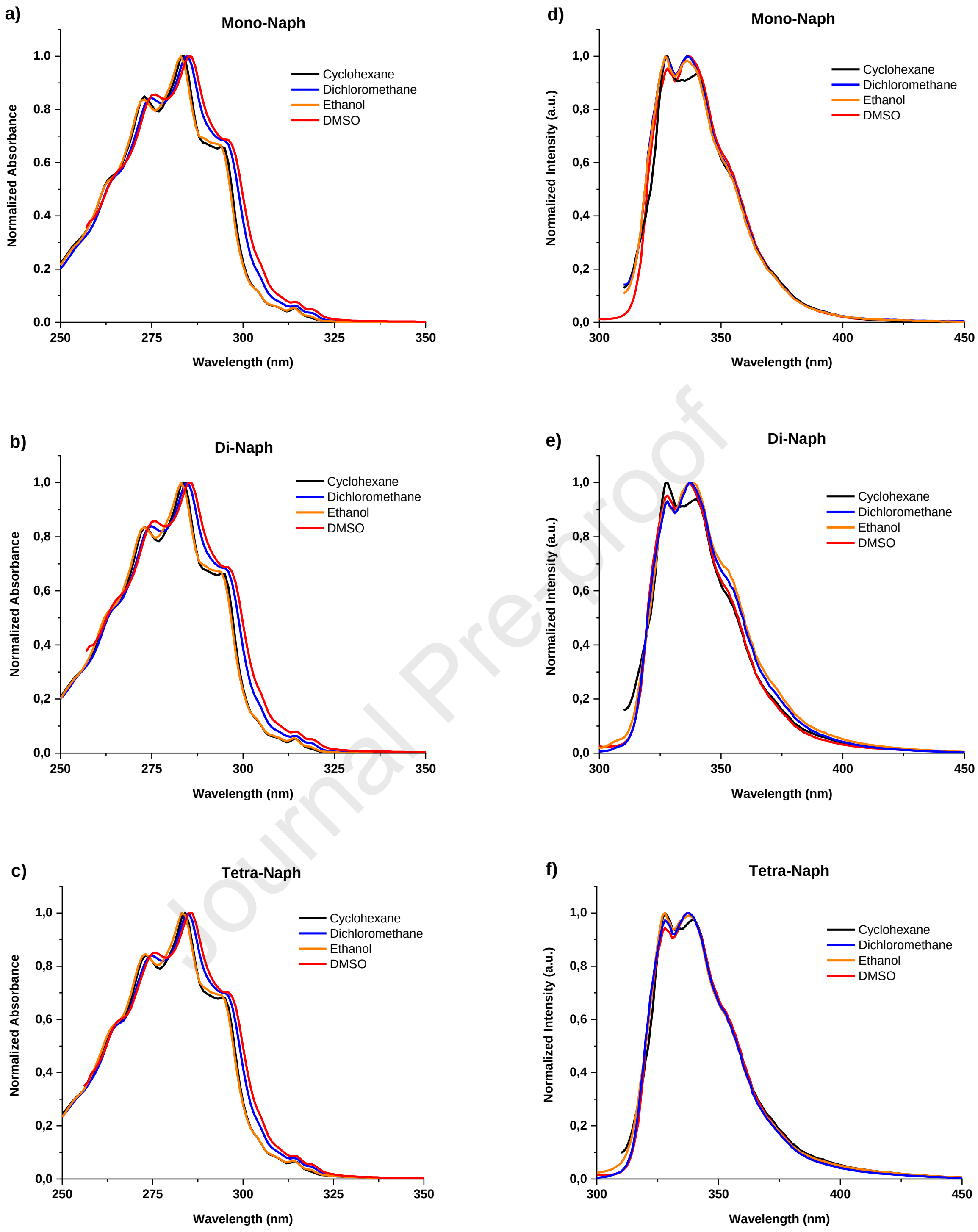


Figure 1. Normalized electronic absorption spectra of **Mono-Naph** (c = 13 × 10^{-5} M) (a), **Di-Naph** (c = 6.5 × 10^{-5} M) (b), **Tetra-Naph** (c = 3.3 × 10^{-5} M) (c) and fluorescence spectra of **Mono-Naph** (c ≈ 1.3 × 10^{-5} M) (d), **Di-Naph** (c ≈ 6.5 × 10^{-6} M) (e), **Tetra-Naph** (c ≈ 3.3 × 10^{-6} M) (f) in different solvents at room temperature (λ_{ex} = 270 nm for all compounds).

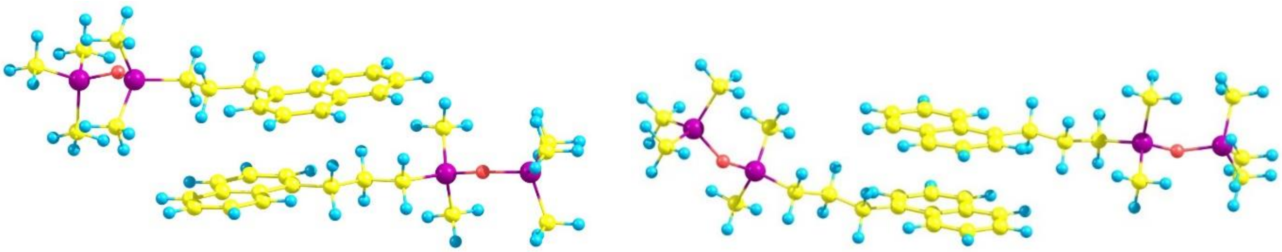
Figure 1 shows the normalized fluorescence spectra of **Mono**-, **Di**- and **Tetra-Naph** that were measured in solvents with different polarity (cyclohexane, dichloromethane, ethanol, dimethylsulfoxide) at room temperature. It was found that the solvent polarity does not affect the fluorescence spectra of studied compounds (Figure 1). The obtained fluorescence spectra consist of two well-defined maxima at 327-328 nm and 336-340 nm, respectively, and a shoulder at about 360 nm. These spectra are assigned to fluorescence of the naphthalene monomer. The quantum yields of the fluorescence of studied compounds were measured using deaerated solutions in cyclohexane. Solution of naphthalene in cyclohexane (Φ_f = 0.23) was used as the fluorescence standard. As seen from Table 1 **Mono**-, **Di**- and **Tetra-Naph** exhibit a slightly higher quantum yield than naphthalene, which increases on going from mono-chromophoric to tetra-chromophoric derivatives (0.24 → 0.25 → 0.27). In addition, the fluorescence intensity of **Mono**-, **Di**- and **Tetra-Naph** drops twice in aerated solvents, which is typical for naphthalene derivatives and is associated with their long fluorescence lifetime (120 ns for solution of naphthalene in cyclohexane and 77 ns for solution of 1-methylnaphthalene in n-hexane) and corresponding fluorescence quenching by oxygen.[79]

2.3. Results of modeling

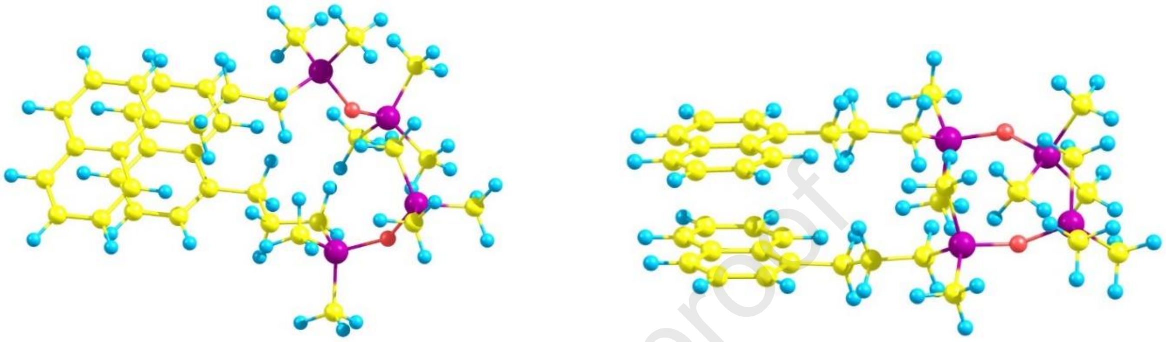
To determine what types of intramolecular complexes are possible for the synthesized compounds, we performed theoretical modeling. Structures of molecules and complexes in the ground electronic states were calculated by the DFT method with the PBE functional and the def2-SVP basis set with the dispersion correction. More complete description of the calculation method is given in the Supplementary Information.

Two structures (**Mono-Naph**-1 and **Mono-Naph**-2) of the dimer were optimized for **Mono-Naph** (Figure 2). In the ground electronic state, naphthalene fragments are shifted, whereas for the excited state the structures exhibit exactly face-to-face arrangement. **Mono-Naph**-2 was found more favorable than structure **Mono-Naph**-1 by 4.9 and 2.3 kcal/mol for the ground and excited states, respectively.

Different structures were obtained for the **Di-Naph** molecule including the open structure (**Di-Naph**-1) and several structures that can be considered as intramolecular complexes (**Di-Naph**-2, **Di-Naph**-3 and **Di-Naph**-4) including the stacked structure **Di-Naph**-4 (Figure 3). In the latter structure, naphthalene fragments are shifted in the ground state and exhibit exact face-to-face arrangement in the excited state (Figure 4). The intramolecular structure is more favorable than the open one by 10–12 kcal/mol for the ground state. For the excited state, the exact face-to face structure **Di-Naph**-ftf-ES is more favorable than the shifted structure **Di-Naph**-sh-ES by 4 kcal/mol.

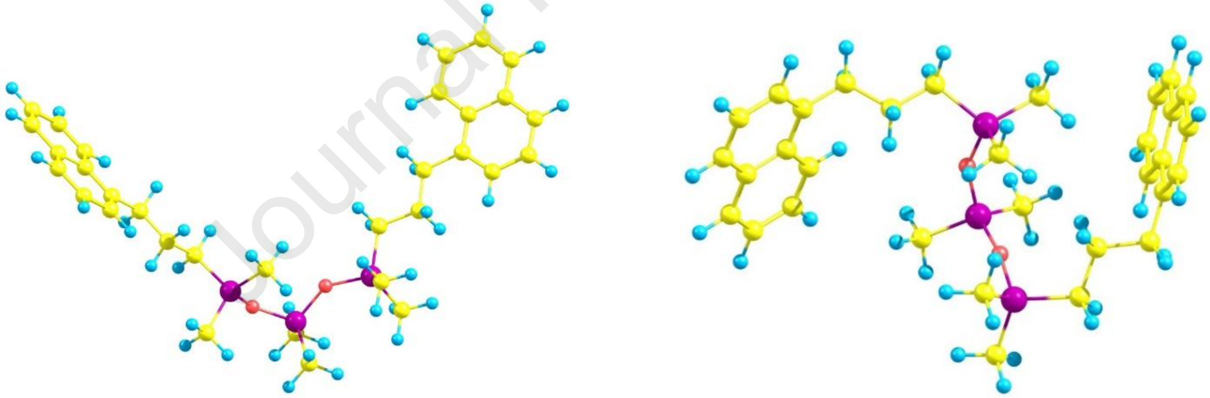


Mono-Naph-1-GS **Mono-Naph**-1-ES

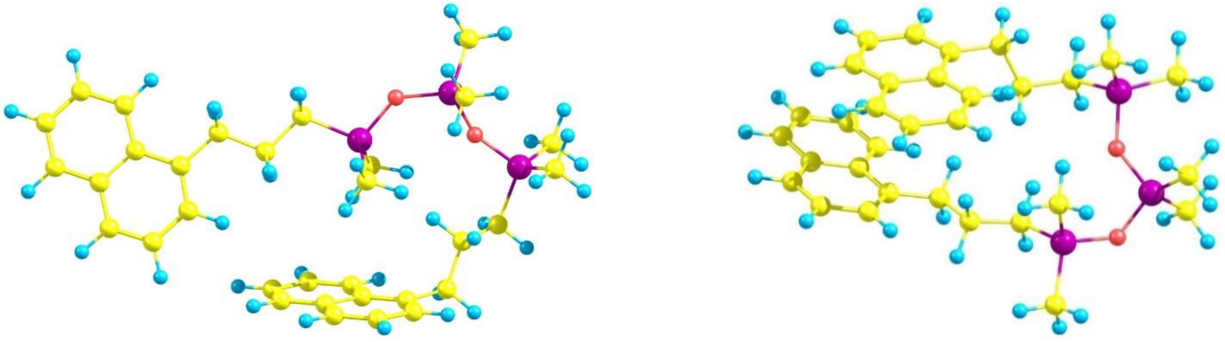


Mono-Naph-2-GS **Mono-Naph**-2-ES

Figure 2. Calculated equilibrium structures of **Mono-Naph** dimers in the ground (GS) and excited (ES) electronic states.

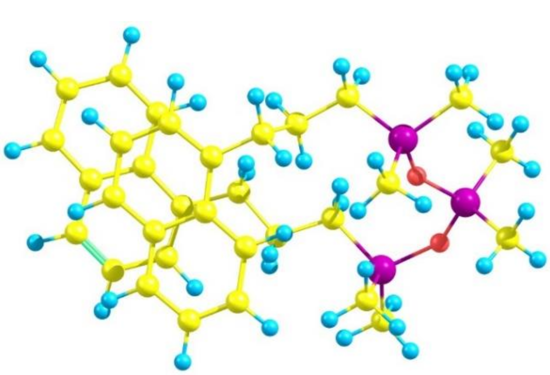


Di-Naph-1-GS **Di-Naph**-2-GS

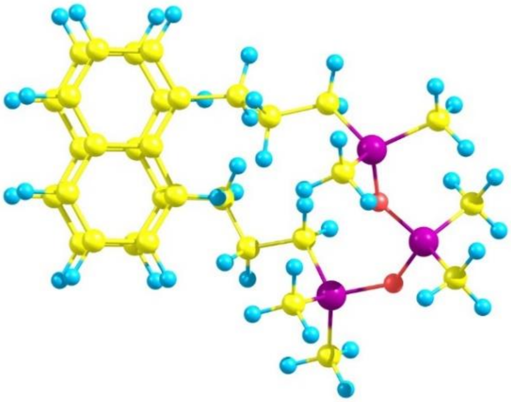


Di-Naph-3-GS **Di-Naph**-4-GS

Figure 3. Calculated equilibrium structures of **Di-Naph** in the ground (GS) electronic state.



Di-Naph-sh-ES

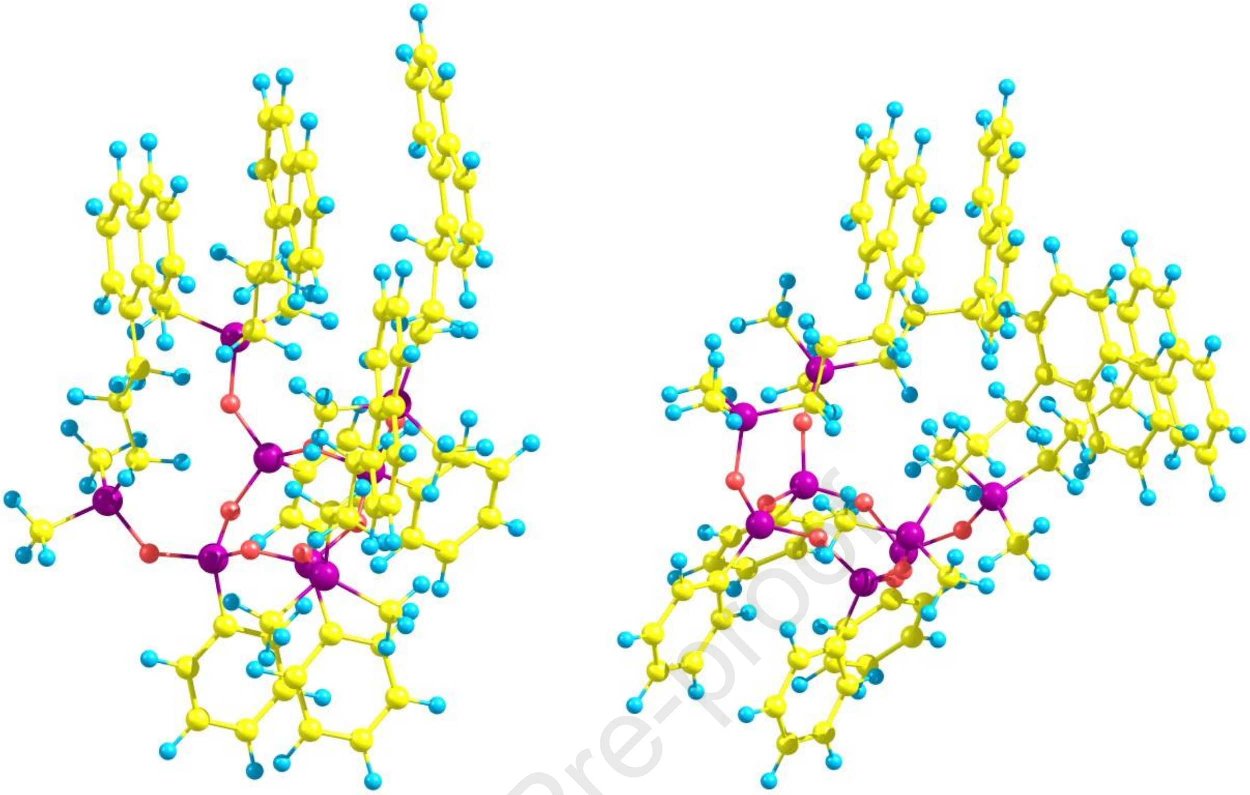


Di-Naph-ftf-ES

Figure 4. Calculated equilibrium structures of **Di-Naph** in the excited (ES) electronic state.

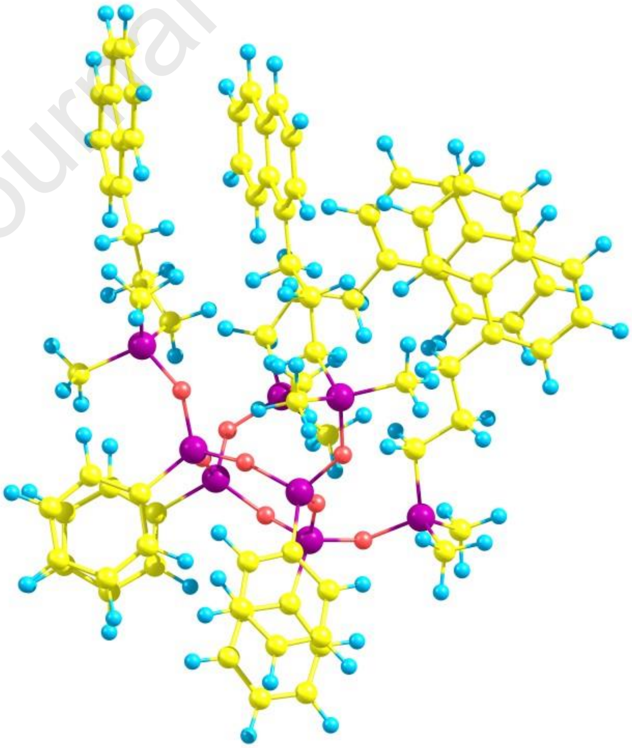
It was failed to obtain an "open" structure for **Tetra-Naph**. The naphthalene fragments stack together in the course of geometry optimization for all of tested initial configuration. Some optimized structures are shown in Figure 5, including structure **Tetra-Naph**-3-GS with two pairs of stacked naphthalene fragments. The stacked structure is the most favorable, structures **Tetra-Naph**-1-GS and **Tetra-Naph**-2-GS are higher in energy by 6.6 and 1.6 kcal/mol. It should be emphasized that a unique feature of **Tetra-Naph** is the possibility of the simultaneous formation of two pairs of dimers or a trimer cluster from naphthalene molecules. Obviously, these preformed face-to-face conformations can promote the formation excimers through π-π-staking interactions, provided that they are sufficiently close to each other. The calculated average equilibrium distance between naphthalene molecules in these ground-state dimer complexes is 3.8-4.0 Å. This distance decreases up to 3.0-3.2 Å after formation of corresponding excimers according to calculations.

To calculate the emission spectrum (position of the emission band), it was necessary to reduce the size of the molecule. Towards this, two of the propylnaphthalene fragments were removed retaining only one stacked pair and all phenyl fragments replacing them with hydrogens. The structures of truncated (**tr**) molecules were optimized for the first excited state (Figure 6). In structure **Tetra-Naph**-3tr-ES, the naphthalene fragments assumed the exact face-to face arrangement, whereas in structure **Tetra-Naph**-2tr-ES, the fragments were shifted with respect to each other. Calculated fluorescence spectra (wavelengths of emission maxima) for all of the considered systems are presented in Table 2. For all of the systems (naphthalene excimer, **Mono-Naph** dimer, **Di-Naph**, and **Tetra-Naph**), where two naphthalene fragments assume face-to face arrangement, the calculated emission wavelength is in the range 425–437 nm.



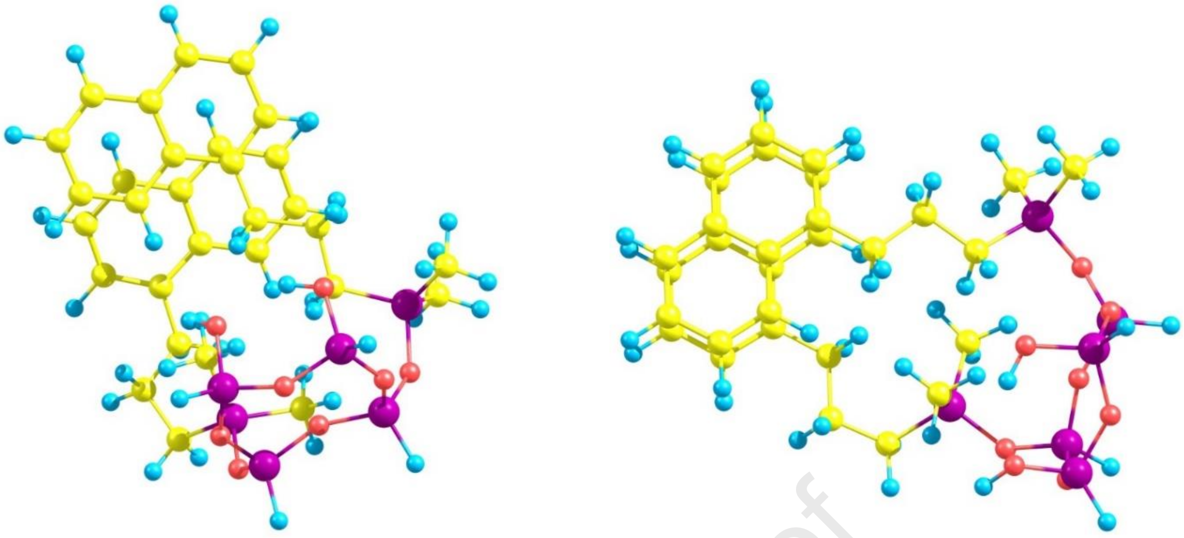
Tetra-Naph-1-GS

Tetra-Naph-2-GS



Tetra-Naph-3-GS

Figure 5. Calculated equilibrium structures of **Tetra-Naph** in the ground (GS) electronic state.



Tetra-Naph-2tr-ES **Tetra-Naph**-3tr-ES

Figure 6. Calculated equilibrium structures of truncated **Tetra-Naph** molecule in the first excited (ES) electronic state.

Table 2. Calculated positions of emission bands for **Mono-**, **Di-** and **Tetra-Naph**.

System	**λ (nm)**	**E (eV)**
Naphthalene	287	4.32
Naphthalene excimer	437	2.84
Mono-Naph	294	4.22
Mono-Naph-1-ES	429	2.89
Mono-Naph-2-ES	425	2.92
Di-Naph-sh-ES	316	3.93
Di-Naph-ftf-ES	437	2.84
Tetra-Naph-2tr-ES	329	3.77
Tetra-Naph-3tr-ES	428	2.90

2.4. Study of excimer formation

To assess the presence of intramolecular excimers in dilute solutions of **Di-** and **Tetra-Naph** in cyclohexane, dichloromethane, ethanol and DMSO, correspond fluorescence spectra were compared with fluorescence spectra of **Mono-Naph** measured in the same solvents (Figure S31). Then, using equation (1), which is as a rule used for this purpose, the ratio excimer/monomer was found.[80]

$$I_{ex}/I_m=(I_{ex400}-I_{Mono\text{-}Naph400})/I_{norm}$$

(1)

where I_{ex} is the intensity of excimer emission; I_m denotes the intensity of monomer emission; I_{ex400} is the intensity at 400 nm in normalized emission spectra of **Di-** and **Tetra-Naph** (400 nm was selected as the wavelength close to the excimer emission maximum); $I_{Mono\text{-}Naph400}$ denotes intensity at 400 nm in normalized emission spectra of **Mono-Naph**; I_{norm} is the intensity used for normalization of emission spectra at the maximum.

Table 3. I_{ex}/I_m ratio in ***Di-Naph*** and ***Tetra-Naph*** in various solvents with c = 3.3-6.5 × 10^{-6} M.

Compound	**Solvent**	I_{ex}/I_m
Di-Naph	Cyclohexane	0.02
	Dichloromethane	0.02
	Ethanol	0.03
	DMSO	0.01
Tetra-Naph	Cyclohexane	0.03
	Dichloromethane	0.02
	Ethanol	0.03
	DMSO	0.03

The spectra were normalized: in cyclohexane at 328 nm, in dichloromethane at 337 nm, in ethanol at 338 nm, in DMSO at 337 nm. Excimer intensity was measured at 400 nm.

The obtained data presented in Figure S31 and Table 3 show that **Di-** and **Tetra-Naph** can form subtle excimers with I_{ex}/I_m ratio in the range of 0.01-0.03 in dilute solutions at room temperature.

It should be noted that these results differ from the data reported by Bravo et al.,[81] for the formation of intramolecular excimers in naphthalene-attached isomeric pure cyclohexane derivatives. The authors also found that the conformation of the compounds plays a crucial role in the formation of intramolecular excimers.

Fluorescence lifetime measurements were performed for **Tetra-Naph** and **Di-Naph** in DMSO at emission maxima wavelength (Supporting information Figures S16-S17 and Tables S1-S3). The fluorescence decay curve obtained for **Di-Naph** is in good agreement with the mono-exponential model with a lifetime of 37.2 ns. Using the bi-exponential model, two lifetimes will be obtained equal to 36 and 80 ns, with a relative contribution of the second component to the total intensity equal to approximately 3%. This value is comparable to the contribution of excimer radiation to the total intensity obtained from the analysis of steady-state fluorescence spectra, and thus a small fraction of excimers can exist in dilute **Di-Naph** solutions.

In the case of **Tetra-Naph**, the fluorescence decay cannot be described by mono-exponential model. Two lifetimes were obtained, 29.1 ns and 45 ns, with a relative contribution of 54% and 46%, respectively. These results clearly indicate the formation of an excimer in the case of **Tetra-**

Naph, although its contribution to the fluorescence spectra seems to be rather small. To test this assumption, ten fluorescence decay curves were measured at different wavelengths. The global fitting procedure shows that the data obtained can be significantly well described by two exponents with lifetimes of 24 ns and 40.9 ns with wavelength-dependent contributions (Supporting Information, Figures S18- S20 and Tables S4-S5). These results are in good agreement with the model of kinetics of excimer formation described by Birks.[82]

Practical absence of excimers in dilute organic solutions of **Tetra-Naph** and **Di-Naph** is not unexpected. The relatively weak dispersion interaction is known to be the primary cause of attraction in the naphthalene dimers.[83] Note that polar DBMBF$_2$ derivative connected by the same spacer as in **Di-Naph** exhibits spectrum characteristic of intramolecular excimer.[73]

Figure 7 shows the fluorescence spectra of **Mono**-, **Di**- and **Tetra-Naph** in films. As seen, their solid-state emission spectra consist of monomeric (minor) and excimeric (main) components. These results are very similar to those obtained for 1-methylnaphthalene.[84]

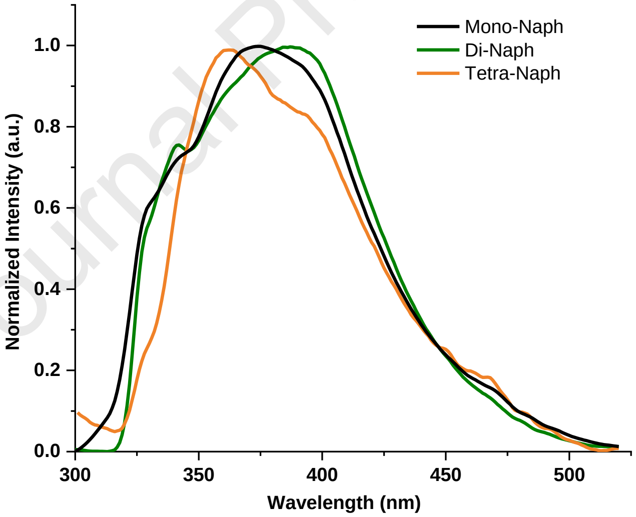


Figure 7. Normalized fluorescence spectra of **Mono-Naph**, **Di-Naph** and **Tetra-Naph** in the solid state (λ_{ex} = 270 nm).

In recent years, binary mixtures containing water and polar organic molecules such as THF and DMSO have been widely used as solvents in many experiments, particularly, in studies of aggregation-induced fluorescence. Such mixtures exhibit composition-dependent properties in bulk which deviate significantly from the ideal behavior as a result of microscopic heterogeneity and liquid–liquid phase separation. The heterogeneity results from a delicate balance of intermolecular interaction between different components. For example, mixing of THF and water leads to formation of nanodroplets, which are highly enriched in THF molecules.[85] Dissolved molecules may be localized in either of the two liquid phases or the interface. Molecular dynamics simulations predict, for instance, that in DMSO-water mixtures, the highly polar formamide should preferably be surrounded by water, while the less polar dimethylformamide is surrounded by DMSO.[86] Cheng et al. reported that the presence of a trace amount of a hydrophobic compound in THF-water mixtures results in the formation of core-shell structures with a core made from the compound and a shell made from THF-rich aqueous mixture.[87]

Thus, it can be assumed that **Mono-**, **Di-** and **Tetra-Naph,** consisting of hydrophobic naphthalene molecules and hydrophobic linkers, will tend to form relatively large solute–THF or solute–DMSO clusters in such solvents. With increasing the water content of the solvent mixtures, THF or DMSO molecules can be gradually displaced by water in the solvation shells of such solutes. As a consequence, this should lead to a compression of the DMSO-rich solvation shells and a closer arrangement of the terminal naphthyl groups, which should facilitate the formation of complexes between them.

To check whether **Tetra-Naph** exhibits solvent-controlled emission properties, the changes in its fluorescence spectrum were recorded using THF-water and DMSO–water mixtures with different water fractions. In both cases, new emission appears in the region of 350-450 nm, which is characteristic of naphthalene excimer (Figure 8). The intensity of the excimer fluorescence increases with increasing water content from 0 to 90 vol. % and this effect is much more pronounced in the case of DMSO.

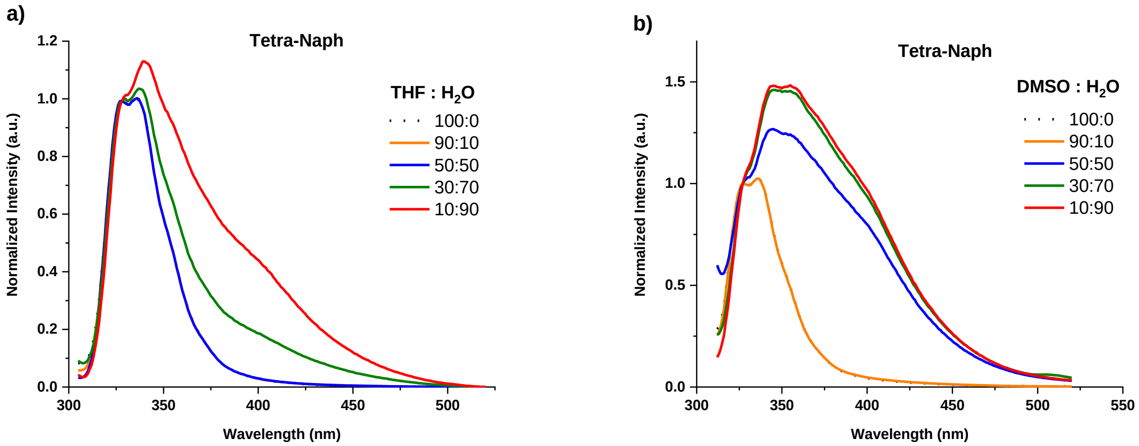


Figure 8. Normalized fluorescence spectra of **Tetra-Naph** in THF-water and DMSO-water mixtures with different water contents ($c \approx 10^{-6}$ M, λ_{ex} = 270 nm).

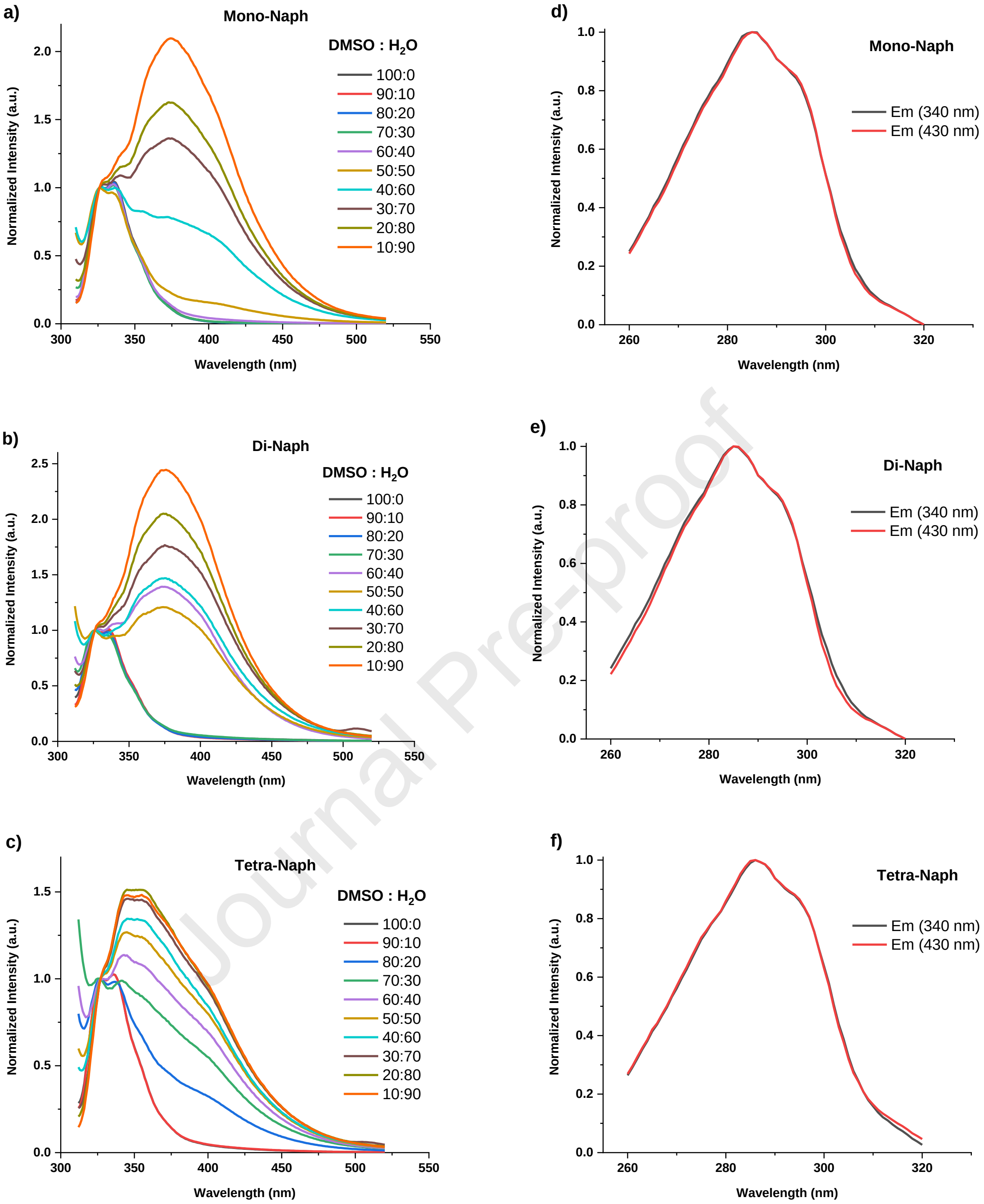


Figure 9. Normalized fluorescence spectra of **Mono-Naph** (a), **Di-Naph** (b) and **Tetra-Naph** (c) in pure DMSO and DMSO:water mixtures with different water contents at room temperature ($c \approx 10^{-6}$ M, λ_{ex} = 270 nm) and corresponding normalized excitation spectra of **Mono-Naph** (d), **Di-Naph** (e) and **Tetra-Naph** (f) recorded at various wavelengths of emission in DMSO:water mixture (10:90 (**Mono-Naph, Di-Naph**) and 20:80 (**Tetra-Naph**). In the case of emission, all spectra were normalized by short-wavelength maximum.

Table 4. I_{ex}/I_m ratio in **Mono-Naph**, **Di-Naph** and **Tetra-Naph** solutions in mixtures DMSO:water with different ratio at room temperature with $c \approx 10^{-6}$ M.

Compound	**DMSO:water mixture**	I_{ex}/I_m
Mono-Naph	100 : 0	0
	90 : 10	0
	80 : 20	0
	70 : 30	0
	60 : 40	0.02
	50 : 50	0.14
	40 : 60	0.64
	30 : 70	1.10
	20 : 80	1.30
	10 : 90	1.67
Di-Naph	100 : 0	0.02
	90 : 10	0.02
	80 : 20	0.02
	70 : 30	0.04
	60 : 40	1.12
	50 : 50	0.99
	40 : 60	1.20
	30 : 70	1.50
	20 : 80	1.70
	10 : 90	1.98
Tetra-Naph	100 : 0	0.03
	90 : 10	0.03
	80 : 20	0.30
	70 : 30	0.53
	60 : 40	0.67
	50 : 50	0.78
	40 : 60	0.82
	30 : 70	0.92
	20 : 80	0.94
	10 : 90	0.95

All spectra were normalized by short-wavelength maximum. Excimer intensity was measured at 400 nm.

Figure 9 shows fluorescence spectra of **Mono-**, **Di-**, and **Tetra-Naph** in the DMSO:water mixture with ratios from 100:0 to 10:90 (λ_{ex} = 270 nm) normalized at short-wavelength maximum. As can be seen from Figure 9, there is notable excimer existence in DMSO:water mixtures already with ratios 50:50 (**Mono-Naph**), 60:40 (**Di-Naph**) and 80:20 (**Tetra-Naph**). Moreover, in the case of **Mono-** and **Di-Naph**, the excimer fluorescence maxima are shifted in the short-wavelength region and are located at 375 nm. It should be noted that fluorescence spectra measured from solutions of **Mono-**, **Di-** and **Tetra-Naph** in DMSO:water mixture with 90 vol% water content are very similar to the fluorescence spectra of these compounds in the solid state (Figure 7). Excitation spectra of of **Mono-**, **Di-** and **Tetra-Naph** obtained by monitoring at various emission wavelengths are almost identical that suggests the dynamic nature of the formation of intramolecular excimers (Figure 9). In addition, a twofold dilution of the **Tetra-Naph** solution only leads to decreasing in the total fluorescence intensity, which confirms the assumption of the intramolecular nature of its excimers (Figure S32). Using formula (1) the ratios I_{ex}/I_m for **Mono-**, **Di-**, and **Tetra-Naph** in the mixture DMSO:water with various proportions of solvents were calculated and summarized in Table 4 and Figure S33.

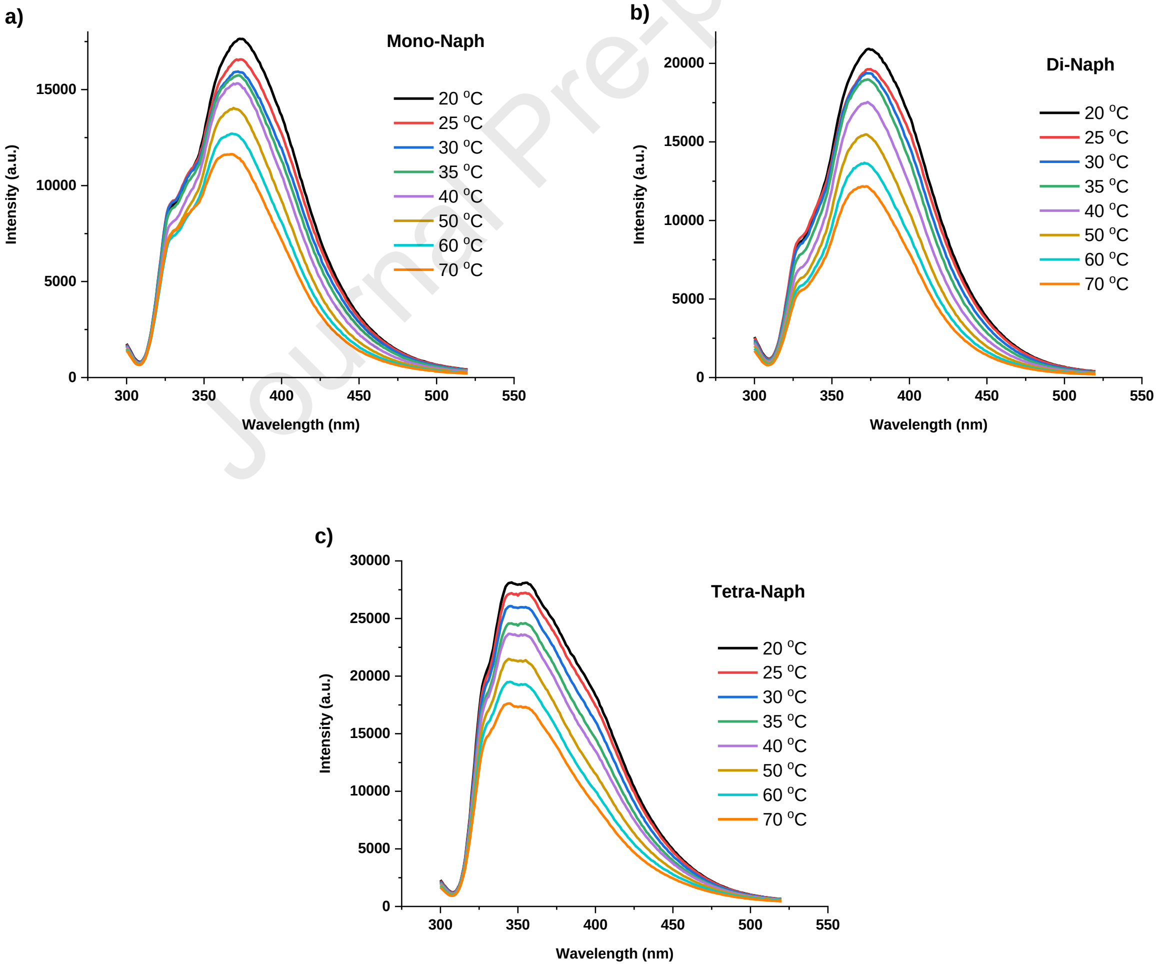


Figure 10. Fluorescence spectra of **Mono-Naph** (a), **Di-Naph** (b) and **Tetra-Naph** (c) in the mixture DMSO:water (10:90) at different temperatures (λ_{ex} = 270 nm) with c= ≈ 10^{-6} M.

Table 5. I_{ex}/I_m ratio in **Mono-Naph**, **Di-Naph** and **Tetra-Naph** solutions in the mixture DMSO:water (10:90) at different temperature with $c \approx 10^{-6}$ M.

Compound	**Temperature (°C)**	I_{ex}/I_m	**Difference between I_{ex}/I_m at 20 and 70 °C**
Mono-Naph	20	1.50	0.58
	25	1.36	
	30	1.29	
	35	1.26	
	40	1.28	
	50	1.19	
	60	1.08	
	70	0.92	
Di-Naph	20	1.90	0.49
	25	1.73	
	30	1.71	
	35	1.74	
	40	1.73	
	50	1.64	
	60	1.53	
	70	1.41	
Tetra-Naph	20	0.88	0.30
	25	0.85	
	30	0.81	
	35	0.77	
	40	0.73	
	50	0.67	
	60	0.61	
	70	0.58	

Fluorescence decay curves obtained for **Tetra-Naph** and **Di-Naph** in 10:90 DMSO:water (v:v) mixtures at wavelengths corresponding to fluorescence maxima can be fitted only by multiexponential models. To get detailed information about exact number of exponents required to describe observed decays, data were collected at ten wavelengths and global fitting was performed. The details can be found in the Supporting Information (Figures S21-S30 and Table S6-S9). In the case of **Di-Naph**, three exponents are essential to describe obtained data. Four exponents are needed for **Tetra-Naph** for the good agreement. The multiexponential character of decay curves indicates complex interaction of fluorophores in the ground and excited states in DMSO:water mixtures which can be attributed to formation of dimers and high order aggregates and their rearrangements after excitation.

The influence of temperature on the efficiency of excimer formation was investigated and the results are presented in Figure 10. For this purpose, the fluorescence spectra for solutions of **Mono-**, **Di-**, and **Tetra-Naph** in the DMSO:water mixture with water content 90 vol% were measured at various temperatures from 20 to 70 °C. As can be seen from Figure 10, **Mono**-, **Di-** and **Tetra-Naph** show a decrease in the excimer fraction as well as in general fluorescence intensity with an increase in temperature. I_{ex}/I_m ratios in **Mono-**, **Di-** and **Tetra-Naph** solutions in the mixture DMSO:water (10:90) at different temperature were calculated using formula (1) and summarized in Table 5 and Figure S34. The observed temperature dependences are typical for aryl excimers in solutions and are considered as a consequence of thermal dissociation of excimers. However, the decay of pre-excimers can also lead to the same dependence, especially since their binding energy is much lower. Assessing the contribution of both of these processes requires further study.

3. Conclusion

We have synthesized three new naphthalene derivatives based on siloxane matrices of linear and cyclic structures. In neat solvents, such as cyclohexane, dichloromethane, ethanol and DMSO, these compounds, which contain one, two or four naphthalene units, respectively, exhibit the absorption and fluorescence spectra characteristic of the naphthalene monomer. However, in the THF-water and DMSO-water mixtures, their emission spectra consist of both monomer and excimer bands due to formation of intermolecular or intramolecular excimers. The time-resolved emission data confirm the existence of excimers in solutions of **Di-** and **Tetra-Naph**. The position and intensity of the intramolecular excimer emission depend on the number of naphthalene units, solvent composition and water content of binary mixtures. In all cases, the intensity of excimer emission decreases with increasing temperature from 20 °C to 70 °C. Molecular modeling reveals that intramolecular complexes of the pre-excimer type can be formed in the derivative consisting of four naphthalene monomers.

Experimental Section

Experimental details, ^{1}H, ^{13}C, ^{29}Si NMR and IR spectroscopic data for all compounds are given in the supporting information.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: