Very Important Paper

Understanding the Role of Chalcogens in Ether-Based Luminophores with Aggregation-Induced Fluorescence and Phosphorescence

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In memory of Prof. Dr. Carsten Schmuck (1968-2019)

We describe the role of chalcogen variation (O, S, Se and Te) on the photoluminescence properties of ether-based luminophores showing aggregation-induced fluorescence and phosphorescence. To this end, a library of eleven different compounds with varying substitution patterns was synthesized and analyzed in terms of their photophysical properties. Ortho- and tetraselenoethers revealed remarkable phosphorescence properties. To the best of our knowledge, these are one of the first phosphorescent organic selenium-containing compounds featuring AIE properties. Besides photophysical investigations, X-ray diffractometric analyses were performed, yielding the molecular structures of nine compounds in a crystalline environment, facilitating a direct correlation between the packing and the emission performances. All experimental results were supported by quantum chemical calculations providing an in-depth understanding of the role of chalcogens within this class of compounds.

1. Introduction

The term aggregation-induced emission (AIE) was coined in 2001 when Tang et al. showed that pentaphenylsiloles reveal striking photoluminescence properties in the aggregated state (e.g. in poor solvents), as crystals or as amorphous solid materials, while losing their emission upon dissolution.[1] Ever since, the field of AIE emitters has progressed dramatically and has become one of the hottest topics in current organic, biological and materials chemistry.[2] In this blossoming field, numerous systems with these unique properties have been developed in the past decade.[3] Usually, AIE emitters bear highly motile aromatic rotors, which mainly convert the absorbed light energy into kinetic energy. Upon restriction of internal rotation (RIR) or restriction of intramolecular vibration (RIV) in hindered or overcrowded systems, these compounds act as efficient luminophores.[4] Besides fluorescence, a current research topic in this field is the design and investigation of AIE emitters that are capable of photoluminescence from excited triplet states, i.e. long-lived phosphorescence.[5] Up to now, several systems with this feature have been described in the literature, mainly based on expensive metal complexes such as iridium, platinum or europium.[6] The current need for purely organic, easy to synthesize and high performing luminophores is one of the most challenging disciplines in modern organic chemistry. A class of compounds, so-called thermally activated delayed fluorescence emitters (TADF), have attracted much interest in the last decade, since they are able to harvest singlet and triplet excitons.[7] This feature is especially interesting for the conception of new organic light emitting diodes. In this context, elements from the third, fifth and sixth main group have attracted attention, and several systems bearing heteroatoms from these groups with aggregation-induced phosphorescence have been described so far.[8,9] Boron-containing phosphors, such as iminoketones[10] or boronic acid[11] derivatives, have been described to show efficient phosphorescence emission in either doped polylactide (PLA) films or as crystalline material with lifetimes up to seconds. In addition, phosphorus-containing compounds, such as triphenylphosphine[12] derivatives bearing carbonyl units enabling fast intersystem crossing, reveal lifetimes in the microsecond range along with quantum...
yields up to 27%. More recently, chalcogens have been investigated in detail starting with an extensive study of thiophosphorus by Ceroni et al.,[10] who used hexathiophosphorus equipped with terpyridines as receptors for metal ions such as magnesium.[11,12] These thiophosphorus revealed quantum yields of up to 100%, depending on the substitution pattern. In a recent study their scope was extended by the introduction of functional groups showing a bathochromic shift in emission which went along with a decrease of photoluminescence quantum yield (PLQY).[13] Rivard and co-workers were the first group to describe the use of tellurium for purely organic phosphors.[14] To this end, a series of tellurophanes were synthesized showing strong phosphorescence emission with lifetimes in the microsecond range.[15] This first example of the higher chalcogens as efficient AI emitters showed that the influence on the emission of these elements is poorly understood and requires further investigation. One of first selenium containing phosphor was described by Bonifazi in 2015.[16] Here phosphorescence was observed in a glassy matrix at 77 K. Recently, our group was able to synthesize a library of thioether-based AIE luminophores[16] which were used for different purposes, such as supramolecular assembly into organogels,[17] micelles[18] and nanorods,[19] as well as their application in molecular recognition of small bioactive ligands.[20] Within this library, two compounds were identified as photorecursive compounds with excited state lifetimes reaching up to 5 μs and emission in the yellow-orange region of the electromagnetic spectrum. Herein, we expanded our scope to a whole series of chalcogens including oxygen, sulphur, selenium and tellurium to understand the role of these heteroatoms on the emission wavelength, photoluminescence quantum yields and excited state lifetimes.

2. Results and Discussion

2.1. Synthesis

In this contribution, eleven compounds with different substitution patterns (ortho, para and tetra) bearing two nitrile groups were synthesized by the formation of ethers (see SI). To this end, 1,2-dichlorophthalonitrile, tetrachlorophthalonitrile, and 1,4-dichlorophthalonitrile, which can be synthesized in a straightforward three-step reaction route, were used as starting compounds.

In the case of oxygen, sulphur and selenium, these core units were reacted with the corresponding phenol, thiophenol and benzeneselenol in the presence of potassium carbonate to yield the desired compounds (1–3, 5–7 and 9–11). For the tellurothiophenes, a different strategy was introduced, since tellurothiophenes were not commercially available. Compound (4) was synthesized starting from elemental tellurium which was reacted with a phenylgrignard species, yielding the activated tellurium intermediate which was readily reacted with 1,2-dichlorophthalonitrile to yield compound (4). Compound (8) was synthesized from diphenylditelluride, which was reduced by sodium borohydride, followed by the reaction with 1,4-dibromoterephthalonitrile towards compound (8) (See SI).

Interestingly, the tetra-tellurothiophene cannot be synthesized under these conditions, due to the high steric demand of the resulting compound as well as its sensitivity towards molecular oxygen, leading to rapid oxidation. With these eleven compounds in stock, we explored their spectrally and temporally resolved photoluminescence properties. To investigate the influence of oxidation on the emission properties, compound (3) was oxidized, using meta-chloroperbenzoic acid (mCPBA). We succeeded in obtaining the mono-oxidized selenoethers (3-O) and the doubly oxidized seleno-ether (3-O₂) in a pure fashion after careful column chromatography separation (Figure S105 and 106).

2.2. Photophysical Properties

The synthesized compounds (1)–(8) appear as off-white to slightly yellow powders, in good agreement with their UV-Vis absorption spectra revealing relative maxima between 300 nm and 400 nm.

Interestingly, compounds (10) and (11) are bright yellow and orange with absorption maxima between 420 nm and 440 nm. Besides the UV-Vis absorption spectra of dispersions in water-DMF mixtures (99:1), the photoluminescence properties were also investigated (see SI, Figure S18–S33).

Photographs of fluid dispersions, as powders and as finely dispersed solids in a silicone matrix, were recorded under UV-light excitation (Figure 1). Interestingly, no detectable or weak emission was observed for the tellurium compounds (4) and (8) as well as for the para-selenium species (7). This phenomenon is attributed to a fast intersystem crossing favoured by the heavy atom effect. The para-substituted compounds (5)–(7) show only blue emission with a slight red shift upon increasing the chalcogen size (Table 1 and Figures 1 and 2). The ortho-compounds (1)–(3) show the same trend, but with a broader emission distribution from 340 nm to 520 nm with Stokes shifts of up to 11862 cm⁻¹ for compound (3). Our interest in this context was to investigate the influence of oxidation on the emission properties of (3).

We found that, if compared with the pure compound (3) showing an emission maximum at 567 nm, the photoluminescence intensity of the oxidized species decreased significantly (Figure S114) which points to an oxidation-induced quenching.
Furthermore, we observed a hypsochromic shift of the luminescence (e.g. (3-O) at 374 nm, (3-S2) at 469 nm). Most interestingly, the tetra-compounds (10) and (11) reveal yellow to orange emission (Figures 1 and 2, Table 1). Since a classical AIE-behaviour is expected for all the investigated compounds, dilution experiments from 0%–99% water content were performed and monitored by photoluminescence spectroscopy and photography. As can be seen in Figure 3, an emission enhancement is observed upon aggregation of compound (3). This was also detectable for all the other compounds (Figure S25–S33), even though varying amounts of water were necessary to induce the emission as a consequence of solubility differences. Ortho- and para- compounds revealed higher solubilities, leading to an aggregation at water concentrations between 70 and 80%, whereas the tetra-compounds (9–11) aggregate at lower water contents due to a poorer solubility. Furthermore, for nearly all compounds, a drop of the photoluminescence intensity was observed for water contents above 90%, which was attributed to a precipitation leading to a decreased effective concentration of the sample. The size of the luminescent aggregates was investigated by dynamic light scattering (DLS) in 99% water and 1% of DMF (Figure S40 and Table S1). The average sizes correlate well with the observed aggregation tendency of all compounds investigated herein. Here, the ortho-compounds reveal average sizes between 62 nm–114 nm, along with the aggregation and luminescence induction at high water ratios (typically between 60%–70%), whereas the para-compounds (average size around 120 nm) tend to aggregate at 50% of water and the tetra-compounds (average size between 114–252 nm) at 30% water content. Besides emission and absorption spectra, we focussed our attention on the photoluminescence quantum yields (ΦL) and excited state lifetimes (Table 1 and Figure S34–S39). Most of the compounds reveal moderate ΦL between 1 and 8%, except for compound (1) showing an increased value of around 21% with an emission maximum in the UV region of the

\[ \text{Table 1. Photophysical properties of the compounds investigated in this study.} \]

| λ_em [a,b] (nm) | λ_abs [a,b] (nm) | λ_exc [a] (nm) | Stokes shift [b] (cm⁻¹/µm) | ΦL [c] | τL [d] (µs) | τr [e] (µs) | k_av [f] (s⁻¹) | k_r [g] (s⁻¹) |
|----------------|----------------|----------------|-----------------------------|--------|-------------|-------------|--------------|-------------|
| 369            | 2613           | 369            | (0.08 ± 0.01) µs            | 0.18    | 1.7         | 15          | 25.7         |              |
| 372            | 281            | 372            | (0.10 ± 0.01) µs            | 0.17    | 1.4         | 10          | 20.5         |              |
| 379            | 296            | 379            | (0.12 ± 0.01) µs            | 0.14    | 1.2         | 8           | 15.5         |              |
| 387            | 301            | 387            | (0.14 ± 0.01) µs            | 0.12    | 1.0         | 5           | 12.5         |              |
| 398            | 309            | 398            | (0.16 ± 0.01) µs            | 0.10    | 0.8         | 2           | 9.5          |              |
| 409            | 313            | 409            | (0.18 ± 0.01) µs            | 0.09    | 0.6         | 1           | 8.5          |              |
| 420            | 317            | 420            | (0.20 ± 0.01) µs            | 0.08    | 0.5         | 0.5         | 7.5          |              |
| 431            | 319            | 431            | (0.22 ± 0.01) µs            | 0.07    | 0.4         | 0.3         | 7.0          |              |
| 442            | 321            | 442            | (0.24 ± 0.01) µs            | 0.06    | 0.3         | 0.2         | 6.5          |              |
| 453            | 323            | 453            | (0.26 ± 0.01) µs            | 0.05    | 0.2         | 0.2         | 6.0          |              |
| 464            | 325            | 464            | (0.28 ± 0.01) µs            | 0.04    | 0.2         | 0.2         | 5.5          |              |
| 475            | 327            | 475            | (0.30 ± 0.01) µs            | 0.03    | 0.2         | 0.2         | 5.0          |              |
| 486            | 329            | 486            | (0.32 ± 0.01) µs            | 0.02    | 0.1         | 0.1         | 4.5          |              |
| 497            | 331            | 497            | (0.34 ± 0.01) µs            | 0.01    | 0.1         | 0.1         | 4.0          |              |

[a] Measured in DMF/water 1:99 v/v in aerated solutions. [b] Lowest energy maximum. [c] Amplitude-weighted average lifetime values in square brackets correspond to deaerated solutions. [d] Longest lifetime component, values in square brackets correspond to deaerated solutions. [e] Calculated from the λ_exc and λ_abs. [f] These data have been described in parts before.[14] [g] Average radiative rate constant calculated using the equation k_r = ΦL/τL based on the amplitude-weighted average lifetime. [h] Average radiationless rate constant calculated using the equation k_r = [1−ΦL/τL] based on the amplitude-weighted average lifetime (see Supporting Information). [i] The upper limit for the ΦL is used for the calculations. Concentrations were in all cases 100 µM.
electromagnetic spectrum ($\lambda_{\text{em}} = 385 \text{ nm}$). Moreover, we analysed the time-resolved photoluminescence decays, since the aggregated tetra-sulphur compound (10) showed phosphorescence emission peaking at 566 nm with long lifetimes even in aerated solvents, as described before.\textsuperscript{[18]} Interestingly, it was observed that in deaerated solvents, the photoluminescence lifetime increases only marginally. We hypothesize that the formation of aggregates leads to a shielding from diffusional quenching by triplet molecular oxygen (Dexter energy transfer), preventing the concomitant non-radiative deactivation pathway. Due to this fact, we focussed here exclusively on aerated solutions. Interestingly, the ortho- and tetra- selenium compounds (3) and (11) with emissions at 567 nm and 578 nm, respectively, showed prolonged lifetimes. Compound (3) reveals an amplitude-weighted average lifetime of around 915 ns in aerated solutions. Furthermore, an amplitude-weighted lifetime of 359 ns was also detected for compound (11). We also investigated the influence of molecular oxygen on the phosphorescence of (3) and (11). We found only marginal enhancement of the excited state lifetimes in deaerated solutions (Figure S35 and S39), which can be explained by external shielding from molecular oxygen within the aggregates. It is noteworthy that these two compounds are some of the first ever-described phosphorescent AE-\textit{e}active compounds containing selenium. These examples showed that the influence of the chalcogens on the excited state properties is quite significant, leading to a need for further investigation of the correlation between the molecular arrangement in the crystal and the photoluminescence quantum yields and excited state lifetimes. We assume that a short-range order is needed for randomly packed aggregates in aqueous media, leading to non-covalent interactions such as $\pi\cdots\pi$, chalcogen-chalcogen and CH-$\pi$ contacts. To this end, we investigated the molecular packing of the monomers in the crystal and focussed on the role and position of the chalcogens in relation to the aromatic systems.

2.3. X-Ray Diffractometric Crystallography

All eleven compounds synthesized were obtained as single crystals, which enabled us to analyse the influence of the molecular packing as well as of the short and long-range order on the photo-physical properties (Figure S45–S54). The ortho-compounds show two different molecular conformations. In the sulphur (2) and selenium (3) (Figure 4) species, both CH groups of the central ring form an intra-molecular CH-$\pi$ bond to the phenyl rings of the residual groups.

In the oxygen (1) (Figure 4) and tellurium (4) compounds, only one conformation is present, while in (1) the other residual phenyl ring is the donor for a CH-$\pi$ bond to the central ring. These interactions yield a chiral molecular conformation.

Both (1) and (4) are racemic, even though (1) crystallises in the Sohnke space group $P2_1$. In this case, the asymmetric unit comprises both enantiomers. The two independent molecules in (1) form a dimeric unit via non-classical hydrogen bonds and a CH-$\pi$ interaction.

The neighbouring units related by the 2$_1$ are connected by CH–N hydrogen bonds and form a corrugated layer (Figure 5). These layers are stacked parallel to $a$ and held together by CH–$\pi$ and CH–N interactions of the residual groups. The resulting stacking of the molecules with the CN groups and the chalcogen above the central ring system can be found in a similar way in all ortho-compounds except for (2)\textsuperscript{[18]} (Figure 6 and Figure S48). For compound (3), the molecules are stacked in this way parallel to a weak Se–$\pi$ bond between adjacent molecules, and weak CH–Se interactions from phenyl rings of a neighbouring stack connect the molecules within the stack. Non-classical CH–N hydrogen bonds between the stacks complete the three-dimensional connectivity (Figure 6). In (4), again chalcogen–$\pi$ interactions connect the molecule to form a stack. Unlike in the case of (3), these interactions are not limited to the central phenyl’s $\pi$-system, but also involve one of the Te–Ph residues. This residue becomes available because of the differing conformation of the molecule. The resulting Te–$\pi$ interaction replaces the second intramolecular CH–$\pi$ interaction observable in (1) (Figure S49). The neighbouring stacks are
cross-linked by non-classical hydrogen bonds (Figure S48) and a weak N–Te interaction. In all para-compounds, the molecule is placed on a centre of inversion. The angle between the plane of the central phenyl-ring and the one of the residual group is significantly smaller in the oxo-compound (5) (5: 60.21(7)°, 6: 73.71(3)°, 7: 74.75(10)°, 8: 79.47(5)°). The packing of (5) may be described as molecules forming chains parallel to a via CH–N hydrogen bonds. These are connected by CH–N interactions. The resulting layers are oriented parallel to (011) (Figure S51) and cross-linked by CH–π interactions. (7) (Figure 7) is isomorphous to the already published sulphur compound (6). [18] In (8), the dominant motif is a Te–π interaction which yields strings parallel to [1 0 1], CH–π interactions from the Te–Ph groups to the central ring and the nitrile groups lead to the formation of layers perpendicular to b (Figure 7, Figure 8 and Figure S52).

The N atoms are located on the surface of these layers. However, no strong hydrogen bonds to connect the layers can be found. The shortest H–N contact is ~0.1 Å longer than the sum of the van der Waals radii with a rather small angle at the hydrogen atom (~120°) which suggests a low impact on the packing. It is noteworthy that neither in the ortho-substituted compounds (1)–(4) nor in the para-substituted products (5)–(8), chalcogen-chalcogen interactions were observed in the crystal lattice (sum of the van der Waals radii > 4.0 Å). This might also be the reason for the phosphorescence emission of compound (3), since contacts between the larger chalcogens are known to lower the phosphorescence quantum yield due to triplet quenching by enhanced radiationless decay (intersystem crossing from the excited triplet state back to the ground state) favoured by clustering and close contact of heavy atoms (i.e. external heavy atom effect). [23]

Compared to other recently described systems, no emission for the tellurium derivatives was found. [24] This finding cannot be explained easily, and we investigated this behaviour by quantum chemical calculations (see last section).

All tetra-substituted compounds (9–11) form the interaction pattern already observed for the thioethers [18] i.e. the ortho-H...
of the residual groups interact with the nitrile N, yielding a chain with the CN group and the central ring’s π-system oriented in parallel. The parallel shift grows with the atomic number of the heteroatom and an approximation of the chalcogen to a residual phenyl ring is observed. This suggests an increasing relevance of E···π interactions within the chains. In addition, the shortest E···E distances decrease (ΣvdW + 0.5 Å (9), +0.2 Å (10), −0.2 Å (11)).

The arrangements of the chains differ for the compounds. Here, chalcogen-chalcogen interactions play a crucial role leading to decreased ΦL, in line with a triplet quenching by enhanced radiationless decay mediated by the larger chalcogens (sulphur and selenium).

In the oxo-ether compound (9) (Figure 9), CH···N interactions involving the nitrile group connect the chains, which in the thio- and seleno-compounds (10) and (11) (Figure 9, Figure 10 and Figure S54) are mediated by CH···π interactions between the residual groups. Thus, the conformations of the molecules are different – most obvious for (10) being centrosymmetric. Depending on the strength of the E···π interactions, they probably cause the different conformations. In this case, the differing packing would be the result of the altering conformations – not its cause.

### 2.4. Quantum Chemical Calculations

The structures of all molecular species (1)–(11) were optimized in the electronic ground state using density functional theory (DFT) (see Computational Details, Figures S55–S104). At the equilibrium geometry, UV-vis absorption spectra were calculated using time-dependent DFT (TDDFT). Fluorescence wavelengths for the 0-0 transition were determined by taking the difference between the minimum S0 and S1 energies. The latter was obtained by geometry optimization in the S1 state using TDDFT. The results are summarized in Table 2. The optimized structure of a single molecule of species (1) is shown in Figure 11, its theoretical absorption spectrum is displayed in Figure 12 together with the experimental data. Although the calculation reproduces the double peak structure found in the experiment, the main feature at ca. 210 nm is blue-shifted by

![Figure 9. Molecular structure of A) (9) and B) (11) in the crystal, as obtained by X-ray diffractometric analysis. Thermal displacement ellipsoids are shown with 50% probability.](image)

![Figure 10. Molecular structure of (11) as a dimer as well as all secondary interactions such as Se-Se contacts, as obtained by X-ray diffractometric analysis. Thermal displacement ellipsoids are shown with 50% probability.](image)

| Compound | λabs (nm) | λem (nm) |
|----------|-----------|----------|
|          | monomer / dimer | monomer / dimer |
| (1)      | 309       | 307/303  | 385 | 378/379 | 499 |
| (2)      | 330       | 307/323  | 462 | 447    | 544 |
| (3)      | 339       | 334/344  | 567 | 506    | 613 |
| (4)      | 348       | 385/375  | 582 | 412    | 571/580 |
| (5)      | 362       | 333/350  | 437 | 412    | 587 |
| (6)      | 391       | 371/382  | 442 | 441    | 590 |
| (7)      | 404       | 400/408  | 442 | 441    | 590 |
| (8)      | 420       | 432/457  | 472 | 472    | 587 |
| (9)      | 373       | 367      | 400 | 399    | 590 |
| (10)     | 426       | 400      | 556 | 551    | 620 |
| (11)     | 502       | 473/481  | 578 | 606/612 | 403 |

[a] Measured in DMF/water 1:99 v/v; [b] Most red-shifted maximum.
about 30 nm from the corresponding experimental peak. The secondary peak at ca. 300 nm, on the other hand, is roughly at the right position, but its intensity is much too low.

The agreement is significantly improved when an optimized dimer of species (1) is considered (Figure 12). As can be seen, the position of the theoretical double peak matches the experimental one very well. In addition, the low-energy peak at 302 nm has a much stronger intensity compared with the monomer spectrum. We therefore conclude that aggregates of species (1) are dominant in aqueous solution.

The calculated emission wavelength of the monomer at the optimized geometry in the S1 state is 379 nm, almost identical with that of the dimer (378 nm). However, we have monitored the S0–S1 energy gap during a molecular dynamics simulation of the monomer in the S1 state and found that it vanishes at certain geometries (Figure 13). Comparison of the time evolution of the S0–S1 energy gap (Figure 13 top) with that of the dihedral angle between the two CN groups (Figure 13 bottom) reveals a strong correlation between the two. This finding suggests that non-radiative decay paths are easily accessible in the monomer, quenching its fluorescence. In aggregates, on the other hand, the structure is more rigid due to intermolecular interactions. The optimized dimer structure (Figure 14) has two intermolecular hydrogen bonds (CH–N and CH–O) restricting, to some extent, out-of-plane deformations. In larger aggregates, the conformational freedom is expected to be reduced further. The experimentally observed fluorescence is therefore likely to originate from aggregates rather than monomers.

For species (2) (Figures S63–S66), the same qualitative conclusions hold as for species (1). The calculated absorption and emission wavelengths can be found in Table 2 and are seen to agree well with experimental numbers. Further details, including optimized ground and excited state structures, are contained in the SI.

The conclusions for species (3) (Figures S67–S70) are broadly the same as for species (1) and (2). However, the deviation of the calculated fluorescence wavelength (506 nm) from the experimentally measured value of 572 nm is unusually large. Since the Se atoms introduce stronger spin-orbit coupling, we have also considered the possibility of intersystem crossing with subsequent phosphorescence. Indeed, the calculated emission wavelength from the T1 state of 544 nm is more in line with experiment.

Intersystem crossing is even more likely to occur in the Te-containing species (4) (Figures S71–S74). Our calculations predict a phosphorescence wavelength of 613 nm, whereas fluorescence would occur at 599 nm. In view of the small vertical T1–S0 gap at the T1 minimum of 1.35 eV, non-radiative decay appears quite probable. It was found that decreasing HOMO-LUMO gaps correlate well with a continuous red-shift in emission from (1) (385 nm) to compound (3) (567 nm) (Figure 15, Table 2).
Figure 15. Molecular orbital isosurface plots of compounds (1), (2), (3) and (4) (from left to right) including the HOMO and LUMO energies and the HOMO-LUMO gap [eV] as well as the corresponding experimental photo-luminescence quantum yields.

The calculated absorption and emission wavelengths for the para-substituted species (5)-(8) can also be found in Table 1. In this case, the dimer absorption spectra agree only marginally better with experiment than the monomer spectra (see Si, Figures S81–95). The most stable dimer structure is π-stacked rather than hydrogen bonded.

For compound (7), the calculated S\textsubscript{1} emission wavelength (441 nm) agrees well with the experimental value of 442 nm. The theoretical T\textsubscript{1} emission wavelength (571 nm), on the other hand, strongly deviates from experiment, suggesting that the measured signal indeed stems from fluorescence rather than phosphorescence. The corresponding theoretical values for compound (8) are 472 nm (S\textsubscript{1}) and 587 nm (T\textsubscript{1}), respectively.

Due to the presence of Te, one would expect phosphorescence to dominate in this case. However, ab initio molecular dynamics simulations in the T\textsubscript{1} state revealed that the S\textsubscript{T1}−T\textsubscript{1} energy gap frequently adopts values of around 1 eV, making non-radiative decay very likely, which might explain why no signal was detected in experiment. Here, the finding that increased HOMO-LUMO gaps go along with a hypsochromic shift also applies (Figure S103, Table S2).

For the tetra-compounds (9) and (10), only monomer structures were considered, reproducing the experimental absorption and emission wavelengths fairly well (Table 1, Figures S96–107). Following the trend observed for the ortho- and para-species, the agreement is likely to improve for aggregates. For compound (11), a dimer structure was also optimized and its spectroscopic properties computed. As can be seen from Figure S101 (SI), the absorption spectrum of the dimer does not reproduce the main experimental peak, in contrast to the monomer. It is possible, however, that a mixture of monomers and dimers are present in the experiment. We have again verified that the emission wavelength of the dimer (612 nm in the case of fluorescence) is very close to that of the monomer (606 nm). On the other hand, the theoretical results would also support phosphorescence, the wavelength calculated with the unrestricted Kohn-Sham method being 612 nm (620 nm with TDDFT).

3. Conclusions

To conclude, we performed an in-depth analysis of ether-based luminophores and discovered, one of the first examples of the missing link in the series oxygen, sulphur and tellurium as phosphorescent emitters with aggregation-induced luminescence turn-on. Two of the selenium compounds revealed average lifetimes of up to 1 μs in aerated solutions with emission maxima in the yellow-orange part of the visible spectrum. The compounds were synthetically easily accessible (one-step synthesis) and were obtained in good yields. The molecular structures and packing of the compounds were obtained by X-ray diffractometric analysis of single crystals and their photophysical properties were explained by quantum-chemical calculations. Good overall agreement was found between experimental and theoretical absorption and emission wavelengths. In addition, we compared our findings with nine more compounds from the family containing O, S, Se and Te as ether bridges. This study regarding structure-property-relationship constitutes a unique example of this kind and enabled us to gain a deeper understanding of the role of chalcogens regarding their influence on photophysical properties of Al-emitters. Phosphorescent selenium compounds are promising candidates for the future development of bioimaging probes, since they are suitable for time-gated detection techniques and phosphorescence lifetime microscopy. This approach is part of an ongoing study requiring further research efforts and analysis.

Notes and References

The crystal structures of all discussed compounds were deposited in the Cambridge crystallographic database under the following numbers: 1898414 (1), 1898415 (3), 1898058 (4), 1898416 (5), 1898417 (7), 1898418 (8), 189419 (9), 189420 (11).

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Conflict of Interest

The authors declare no conflict of interest.

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