Insights into Excimer Formation Factors from Detailed Structural and Photophysical Studies in the Solid-State

Timo Schillmöller, Regine Herbst-Irmer, and Dietmar Stalke*

Solid-state luminescent materials are essential for the development of optoelectronic devices like lasers, sensors, and organic light-emitting diodes. Organic molecules reveal several benefits like stability, costs, and environmental compatibility compared to metal-based materials. As common organic fluorophores often suffer from aggregation-caused quenching, different strategies have been established to overcome this quenching, which are mainly based on intramolecular modifications. Controlling the photophysical properties via intermolecular interactions is more challenging and less investigated. The formation of excited dimers (excimers) bears great potential for obtaining efficient solid-state luminescent materials. As the excimer-formation process is strongly dependent on the non-covalent interactions, a full understanding of the structure–property relationship is essential. In this study, structurally simple thiophosphoranyl anthracene excimers and the dependency of the photophysical properties on the solid-state arrangement are investigated. Through crystallization of polymorphs and co-crystals, the resulting intermolecular interactions have been modulated over a broad range. Novel insights into the excimer formation factors and the dependence of the photophysical properties on the intermolecular interactions are obtained. This study will help in the development and controlling the photophysical properties of solid-state luminescent materials.

1. Introduction

The development of organic materials with solid-state photoluminescence is essential for optoelectronic devices like organic light-emitting diodes (OLEDs), lasers, and sensors. Photophysical properties of common organic fluorophores have been investigated widely in solution, but a transfer of these results to the condensed phase is usually not easy, because the intermolecular interactions in the solid-state influence the excited state in many ways. Often a complete quenching of chromophores with intense solution-emission is observed in the solid-state which is ascribed to strong intermolecular interactions and known as aggregation-caused quenching. Opposite behavior with an emission enhancement upon aggregation of the fluorophores is also known, but early reports are rare. This phenomenon is coined aggregation-induced-emission (AIE) and became more popular through the work of Tang and co-workers since the early 2000s. A plethora of molecules with AIE-behavior was investigated and a general understanding of their photophysical properties was achieved. The emission quenching is referred to internal motion of suitable substituents like tetr phenylethylene and hexaphenylsilole at the fluorophore. Rotation and vibration of these groups open non-radiative pathways which result in radiationless decay in solution. Aggregation confines the flexibility of the substituents to restrict the internal motion. Consequently, the non-radiative pathways are blocked, and the emission enhances in highly aggregated-solutions and in the solid-state. Further strategies for obtaining solid-state luminescent materials aim at the introduction of bulky substituents at the fluorophores to prevent strong interchromophoric interactions. These approaches are mainly based on intramolecular modifications and therefore the resulting fluorescence of the aggregates can be considered to be close to the emission from a monomeric state of the fluorophores.

Controlling photophysical properties through non-covalent interactions (NCIs) is more challenging. In early works, Jelley and Scheibe observed the appearance of new absorption and emission bands in pseudoisocyanine solutions with increasing dye-concentration, which were attributed to the formation of aggregates. More recently a different approach for controlling and optimizing the photophysical properties of polyaromatic hydrocarbons in the solid-state has been successfully introduced. Instead of avoiding intermolecular interactions, molecules are designed, which allow specific interactions between their fluorophores in the aggregated state. The occurring π–π interactions lead to the formation of an excited dimer (excimer) after irradiation. The formation of excimers in solution is well known since the investigations of the pyrene excimer by Förster and Birks. The typical features of spectral broadening and increased lifetime are also well investigated. In recent publications, this approach was successfully transferred to efficient solid-state emitters. Through control of the NCIs, the formation of excimers or exciplexes in the solid-state is possible and allows tuning of the photophysical properties.
Several polyaromatic hydrocarbons have been reported, which show an efficient excimer emission in the solid-state.[22–26] The fluorescence is mainly determined by the NCIs and set in relation to the monomer emission. Usually, a broad structureless and red-shifted emission band is observed for the excimer. For a wider rational application in organic optoelectronics, the understanding and mapping of the ingredients to NCI excimer formation is substantial. Therefore, several studies recently examined those fundamental features. A combined experimental and theoretical study by Fischer, Röhr, et al. focused on the formation of the pyrene excimer as the prototype of excimers.[27] Yang et al. investigated the excimer properties of pyrene and anthracene model systems in more computational studies.[28,29] In this paper, we present a more experimental approach to obtain further insights into the excimer formation process and especially focus on the influence of the NCIs on the luminescence properties.

Recently, we reported three positional isomers of a structurally simple thiophosphoranyl anthracene.[30] The isomer substituted in the 1-position revealed an unusual large bathochromic shift resulting in a yellow emission in the solid-state, which could be assumed to be an excimer state. For further understanding of the excimer formation process and the dependence of the photophysical properties on NCIs in the current paper, we investigate the structural and photophysical properties of the [1-[S]PPh2-(C14H9)] (3) isomer in more detail. We were able to identify several polymorphs and co-crystals of 3, which differ drastically in the observed intermolecular interactions and photophysical properties. The variety of different structures allows a comprehensive study of the structure/property relationship and novel insights in the excimer formation process of the anthracene fluorophore.

2. Results and Discussion

2.1. Structural Properties

For a clear understanding of the aggregation and stability of the polymorphs of 3, the parent phosphane [1-PPh2-(C14H9)] (1) will be presented first. [1-PPh2-(C14H9)] was synthesized from 1-chloroanthracene via nucleophilic substitution with lithium diphenylphosphane similar to reported procedures for the 1,8-bis(diphenylphosphane)anthracene (Scheme 1).[31] After aqueous workup, the phosphane was obtained in good yields and single crystals suitable for structure determination were obtained by recrystallization from dichloromethane (DCM). The compound crystallizes in the triclinic space group P\textsuperscript{T} with one molecule in the asymmetric unit. The phosphorous atom adopts a pyramidal geometry and the anthracene core is nearly planar. The P-C bond is slightly shortened in comparison to its 9-isomer (1.8430(14) Å versus 1.8510(17) Å), which was investigated in our previous study.[32] The shortening of the P–C bond together with a more relaxed orientation of the phenyl groups indicates a less strained structure when the substituent moves from the center to the outer anthracene ring (Figure 1 and Figure S1, Supporting Information).

The phosphane 1 can easily be oxidized with hydrogen peroxide or elemental sulfur to the corresponding oxo- or thiophosphoranyl anthracene (Scheme 1). The oxophosphoranyl anthracene [1-[O]PPh2-(C14H9)] (2) is obtained after aqueous workup and recrystallization from DCM. It crystallizes also in the triclinic space group P\textsuperscript{T} with one molecule in the asymmetric unit but with distinctly different cell parameters compared to the parent phosphane 1 (Table S1, Supporting Information). The anthracene scaffold is nearly planar. The oxygen atom replaces the phosphorous lone pair at an O-P-C9A torsion angle of 47.96(15)°. NCIs reveal a columnar stacking of the anthracene moieties with a π–π distance of 3.470 Å and an overlapping area of the anthracene planes of about 20% (Figure S2, Supporting Information).

When 1 is oxidized with elemental sulfur in toluene the pale-yellow oxidation product [1-[S]PPh2-(C14H9)] (3) precipitates from the reaction mixture and can be recrystallized under various conditions resulting in three different polymorphs. The α-polymorph crystallizes through slow diffusion of n-hexane into a solution of crude 3 in toluene. The resulting crystals are isomorphous to those of the parent phosphane 1. The overlay of the two structures illustrates the similarities regarding the orientation of the substituent with only a slightly different orientation of one phenyl group (Figure S4, Supporting Information). The S-P-C1-C9A torsion angle of 47.96(15)°

\begin{align*}
\text{Scheme 1. Synthesis of the phosphane } [1-\text{PPh}_2-(C_{14}H_{9})] (1) \text{ and its oxo- and thiophosphoranyl homologs } [1-[\text{O}]\text{PPh}_2-(C_{14}H_{9})] (2) \text{ and } [1-[\text{S}]\text{PPh}_2-(C_{14}H_{9})] (3).\end{align*}
in relation to the O-P-C1-C9A torsion angle in 2. Furthermore, the sulfur atom occupies almost the same position as the lone pair in the phosphane. The α-form of 3 and the parent phosphane 1 adopt a sheet structure with all anthracenes parallel oriented (Figure S4, Supporting Information). This arrangement allows no π−π interactions between the anthracene scaffolds. This way the C−H⋯π contacts are the predominant NCIs.

The α-3 polymorph could not be crystallized exclusively without the additional crystallization of one of the other polymorphs. Several crystallization methods and conditions were investigated but the β- or γ-polymorph always crystallized together with the α-form. The crystals could be distinguished by morphology and color (Figure S3, Supporting Information). The β- and γ-polymorphs of 3 could be obtained by various crystallization methods, for example, recrystallization from toluene (β-3) or DMF (γ-3). The β- and γ-polymorphs are very similar with regard to their structural properties. Both forms crystallize in the monoclinic space group P2₁/c, but with different cell parameters. The molecular structure itself changes only slightly in comparison to the α-form. The phenyl groups rotate moderately and the S-P-C1-C9A torsion angle rises by about 10° to 64.06(14)° (β-3) and 66.75(13)° (γ-3) (Figure 2a). The most drastic changes are found in the crystal packing and the NCIs. For the α-form, no direct interactions between the anthracene π-systems were observed and the intermolecular interactions were dominated by C−H⋯π interactions. For the two other polymorphs, strong direct anthracene–anthracene interactions were found, which are crucial for excimer formation. In both structures, a dimeric motif with an antiparallel orientation of the anthracenes is present (Figure 2b). The π−π distance is about 3.3 Å like in graphite and therefore in a typical range for π−π interactions between polyaromatic hydrocarbons. The overlap area of the anthracenes was estimated to 42.3% (β-3) and 45.9% (γ-3), respectively. While for the β-form the dimer offset along the short (dₓ) and long (dᵧ) anthracene axes equally is 1.0 Å, the offset dₓ in γ-3 decreases to 0.9 Å, and the offset along the long axes slightly increases to 1.3 Å (Figure 2b and Table 1). Besides the dominant π−π interactions between the anthracenes, various C−H⋯π interactions among neighboring molecules can be found in both solid-state structures and result in an overall different packing motif for the two polymorphs (Figure S5, Supporting Information).

From the observations made during the crystallization processes, the stability of the polymorphs can be estimated. The

---

**Figure 1.** Changed orientation of the diphenylphosphane substituent in the two positional isomers a) [1-PPh₂-(C₁₄H₉)] (l) and b) [9-PPh₂-(C₁₄H₉)] (structure already reported earlier).[^32]

**Figure 2.** a) Structural overlay of the α- (grey) and β-polymorph (black) of 3. b) Dimeric motif with decent overlap of the anthracene planes and resulting in direct anthracene–anthracene interactions as found in the solid-state structures of β-3 and γ-3.
Table 1. Structural parameters and photophysical data of the polymorphs and co-crystals of the thiophosphoranyl anthracenes 3 and 4 in the solid-state.

| Space group | Guest | Overlap [%] | \(d_{\pi,\pi}[\text{Å}]\) | \(d_{\pi}[\text{Å}]\) | \(d_{\pi}[\text{Å}]\) | \(\lambda_{\text{ex}}/\text{[nm]}\) | \(\tau/\text{[ns]}\) | \(\Phi_{\text{f}}/\text{[%]}\) |
|-------------|-------|-------------|----------------|-------------|-------------|----------------|-------------|-------------|
| \(\alpha\)-3 | \(\rho\uparrow\) | – | 0 | – | – | – | 437 / 458 / 493 | 6.6 | <1 |
| \(\beta\)-3\(^{[b]}\) | \(P2_1/c\) | – | 42.3 | 3.33 | 0.89 | 1.34 | 546 | 30.0 | 5.7 |
| \(\gamma\)-3 | \(P2_1/c\) | – | 45.9 | 3.35 | 1.19 | 3.19 | 462 | 21.4 | 12.3 |
| 3a | \(\rho\uparrow\) | Benzene | 25.3 | 3.23 | 1.07 | 1.06 | 545 | 29.0 | 5.9 |
| 3b | \(\rho\uparrow\) | Pyridine | 31.3 | 3.32 | 1.07 | 2.77 | 512 | 2.9 | <1 |
| 3c | \(\rho\uparrow\) | Aniline | 25.5 | 3.26 | 1.21 | 3.04 | 491 | 38.2 | 16.6 |
| 3d | \(\rho\uparrow\) | Quinoline | 22.3 | 3.36 | 1.38 | 2.91 | 458 | 2.8 | <1 |
| 4 | \(P2_1/n\) | – | 38.5 | 3.34 | 1.06 | 1.47 | 539 | 16.4 | 2.1 |
| 4a | \(C2/c\) | Benzene | 34.0 | 3.44 | 0.97 | 2.88 | 490 | 6.3 | 3.9 |
| 4b | \(C2/c\) | Toluene | 33.7 | 3.45 | 0.98 | 2.87 | 493 | 8.4 | 4.4 |
| 4c | \(C2/c\) | Chlorobenzene | 33.4 | 3.47 | 0.98 | 2.90 | 493 | 4.8 | 5.4 |
| 4d | \(\rho\uparrow\) | Cyclohexane | 52.5 | 3.42 | 0.82 | 1.10 | 542 | 13.2 | <1 |
| 4e | \(\rho\uparrow\) | EtOAc | 52.9 | 3.42 | 0.83 | 1.05 | 541 | 25.7 | 2.9 |
| 4f | \(\rho\uparrow\) | CHCl3/Hexane | 52.3 | 3.43 | 0.84 | 1.04 | 542 | 21.7 | 2.2 |
| 4g | \(P2_1/n\) | DCM | 52.9 | 3.45 | 0.72 | 1.34 | 540 | 26.0 | 2.0 |
| 4h | \(\rho\uparrow\) | Benzene | 51.4 | 3.43 | 0.83 | 1.16 | – | – | – |

\(^{[a]}\) \(\lambda_{\text{ex}} = 375\text{ nm}; ^{[b]}\) data has already been reported earlier.\(^{[30]}\)

\(\alpha\)-form could not be crystallized exclusively and was obtained only together with the other polymorphs. The best method to enrich this polymorph is vapor diffusion of \(n\)-hexane into a toluene-solution of the crude precipitated reaction product. The crystallographic analysis revealed plenty of similarities in the solid-state structures of the parent phosphane 1 and \(\alpha\)-3. According to the Ostwald's step rule, we assume that the \(\alpha\)-form is the metastable polymorph that is initiated by the oxidation process because 1 and \(\alpha\)-3 are very close in energy.\(^{[33]}\) From the photophysical study, we could also confirm that the solid which precipitates during the reaction consists mostly of the \(\alpha\)-polymorph. When the precipitate is dissolved and crystallized from hot solutions the \(\beta\) and \(\gamma\)-polymorph are the dominant crystallizing forms and are therefore assumed to be more stable. With the reported procedure by Spackman et al., we calculated the lattice energies of the polymorphs at a very basic level of theory.\(^{[34]}\) As expected, all polymorphs are very close in energy and the calculated lattice energies are in a range of around 4.4 kJ mol\(^{-1}\). According to the calculations, the \(\gamma\)-polymorph is the most stable form of 3, and about 2.7 kJ mol\(^{-1}\) more stable than the \(\alpha\)-form and further 1.7 kJ mol\(^{-1}\) compared to \(\beta\)-3, which is surprising as the latter was the first identified polymorph and could be crystallized in a pure form in contrast to \(\alpha\)-3. However, these calculated differences should not be overinterpreted, because they are very small and could be caused by approximations in the calculation.

During the screening for polymorphs and evaluating the crystallization conditions we identified the ability of the thiophosphoranyl anthracene \([1-(S)PPh_2(C_{12}H_8)]]\) for co-crystal formation with small aromatic molecules. Through recrystallization from the corresponding solvent four co-crystals with benzene (3a), pyridine (3b), aniline (3c), and quinoline (3d) could be obtained and investigated. Further small benzene derivatives like toluene, fluorobenzene, and chlorobenzene were also used for crystallization, but no co-crystals were obtained. All co-crystals exist in the triclinic space group \(\rho\uparrow\), while 3a and 3c can be considered as isomorphous with very similar cell parameters. Although, only the co-crystallized solvent varies for the other co-crystals clearly different structures are obtained. For all four host-guest complexes one molecule of 3 and one solvent molecule is found in the asymmetric unit resulting in a 1:1 host-guest ratio. The arena is located above the anthracene plane in a T-shaped manner and forms several weak C–H \(\cdots\) \(\pi\) interactions (Figure 3a). \(\pi\)-stacking between the solvents and the anthracenes \(\pi\)-system could not be observed and therefore a strong electronic interaction like a charge-transfer (CT) between the solvent and the anthracene system can be excluded. Instead, the co-crystallization induces a change in the crystal packing and the occurring intermolecular interactions between the anthracene chromophores. The dimeric motif, which was found in the polymorphs \(\beta\)-3 and \(\gamma\)-3 is still present in the co-crystals, but with clearly reduced \(\pi\)-\(\pi\) interactions between the two anthracenes. The overlap is reduced to values between 22% and 32%. The smaller overlapping area goes along with an increase of the molecular offset \(d_{\pi}\) along the long anthracene axes up to 3.2 Å. The offset \(d_{\pi}\) along the short
Therefore, we synthesized \[1-(S)PPh_2-4-Ethyl-(C_{14}H_8)\] anthracene. We investigated this effect also for the thiophosphoryl substituent due to the inductive effect of the alkyl group. We observed that the overlapping area upon alkyl-substitution in the para-position of the anthracene chromophores (Figures S6 and S7, Supporting Information). For the polymorphs and co-crystals of 3 already a wide range of varying intermolecular interactions are found, which can be seen in the overlap ratios of the anthracenes, which range from 0–45%.

In our previous work on the 9,10-substituted thiophosphoranyl anthracenes, we observed a drastic increase of the overlapping area upon alkyl-substitution in the para-position of the thiophosphoryl substituent due to the inductive effect of the alkyl group. We investigated this effect also for the \[1-(S)PPh_2-4-Ethyl-(C_{14}H_8)\] in order to increase the already large overlapping area and verify the results obtained by the investigation of 3. Therefore, we synthesized \[1-(S)PPh_2-4-Ethyl-(C_{14}H_8)\] starting from 1,4-dibromoanthracene via stepwise lithium–halogen exchange adopting previously reported procedures (see Supporting Information for synthetic details). 4 could be crystallized from various organic solvents and under various conditions. Slow diffusion of n-hexane into a solution of 4 in toluene afforded pure crystals of 4 without any co-crystallized solvent present. 4 crystallizes in a monoclinic space group \(P2_1/n\) with one molecule in the asymmetric unit. The anthracene moiety shows a small deviation from planarity with a small bending of the aromatic plane.

The thiophosphoranyl substituent reveals a slightly different orientation compared to 3 with a decreased S-P-C1-C9A torsion angle of 48.3(18)°. The ethyl group in the 4-position is more orthogonal to the anthracene with a torsion angle of 72.7(3)°. When 4 is crystallized from hot solutions of various solvents co-crystals form as already seen for 3. While the co-crystals 3a–3d revealed three different structures, those of 4 can be divided into two groups with isomorphous members. Aromatic solvents like benzene (4a), toluene (4b), and chlorobenzene (4c) crystallize in a monoclinic crystal system in the space group \(P2_1/n\) with one molecule and half a solvent molecule in the asymmetric unit. When aliphatic solvents like cyclohexane (4d), EtOAc (4e), or CHCl_3/hexane (4f) are used for crystallization the triclinic space group \(Par{1}\) again with one molecule and half a solvent molecule in the asymmetric unit is preferred. A monoclinic system was only observed for the smaller DCM (4g), which crystallizes with one and a half solvent molecules in the asymmetric unit in space group \(P2_1/n\). The ethyl group in the 4-position probably prevents a dense packing resulting in larger crystal voids compared to 3, which can be filled by a plethora of guest molecules. For benzene as the guest also the triclinic structure, isomorphous to 4d–f, could be determined (4h), but the crystals seem to transform into the monoclinic system upon storage for a few days and reproduction of these crystals was not successful. Therefore, the monoclinic form seems to be the favored crystal system when aromatic solvents are co-crystallized and aliphatic guests prefer the triclinic crystal system.

The basic structural parameters of the co-crystals 4a–4e differ only a little from the guest-free structure 4. The S-P-C1-C9A torsion angle for 4a–4c and 4g is slightly increased by 10° to values of about 57° and the anthracene plane is nearly planar. The orientation of the ethyl group in the 4-position changes as it now lies in the anthracenes plane with a torsion angle near 0°. For the structures with non-aromatic solvent co-crystallized 4d–4f an enlargement of the S-P-C1-C9A torsion angle up to 70° is observed and the phenyl groups are therefore slightly rearranged (Figure S8, Supporting Information).

The intramolecular structural parameters are only slightly dependent on the co-crystallized solvent. The NCIs and therefore the crystal packings are more affected by the co-crystallization of different guest-molecules. The dimeric motif with antiparallel overlapping anthracenes as seen for 3 is maintained, but overlap ratios and offsets differ. The guest-free structure of 4 reveals a slightly decreased overlap compared to \(\alpha\) and \(\beta\) with an overlapping area of 38.5%. The offsets along the anthracene axes are therefore a little larger. Crystals of 4 in the space group \(C2/c\) with the aromatic solvent co-crystallized reveal an overlap ratio of the anthracene dimer of approximately 33–34% with offsets of 0.98 Å (\(d_\alpha\)) and 2.87 Å (\(d_\beta\)).

**Figure 3.** a) T-shape orientation of the co-crystallized solvent in the crystal structure of 3b and b) reduced overlap of the anthracene dimer upon co-crystallization.
comparable to the co-crystals 3a–3d (Table 1). Again, the offset along the long molecular axis ($d_\parallel$) is significantly increased compared to the solvent-free structure, while the offset $d_\perp$ is only slightly changed. The co-crystals 4d–4g reveal an anthracene overlap of nearly 53% with a reduced offset $d_\parallel$ along the long molecular axes to values of around 1.1 Å. The expected increase of the overlap through ethyl-substitution in the 4-position can be confirmed for 4d–4g but cannot exclusively be ascribed to a change of the electrostatic potential induced by the ethyl group. The NCIs to the co-crystallized guests play a key role. Weak C=H \cdots \pi interactions between neighboring thiophosphoranyl anthracenes or between the anthracene and co-crystallized arenes reduce the \pi-\pi interaction between the anthracene dimers. When aliphatic solvents are co-crystallized these interactions are less pronounced resulting in stronger \pi-\pi interactions between the anthracene moieties.

From the presented two structural simple thiophosphoranyl 3 and 4 anthracenes a plethora of different solid-state structures with drastically different intermolecular interactions could be obtained. Through no or only marginal changes in the molecular structure, the electronic properties of all structures are nearly identical. This fact allows a detailed study of the influence of the intermolecular interactions on the photophysical properties. Especially, the overlap ratio, which could be varied over a broad range from 0–55%, is of great interest as this structural motif is suitable for excimer formation.

2.2. Photophysical Properties

Investigation of the photophysical properties in diluted solutions gives information about the absorption and emission behavior of the monomeric form of the compounds as intermolecular interactions can be neglected. The oxidized phosphoranes 2 and 4 reveal typical absorption and emission spectra for structurally simple anthracene derivatives (Figure 4) as also seen for 3 in our previous work.\[30\] The S$_0$–S$_1$ absorption which is assigned to a \pi-\pi$^*$ transition located on the anthracene can be found as a structured band from 325 to 400 nm (anthracene fingers). The ethyl substituent in para position in 4 induces a slight bathochromic shift of the absorption. The emission spectra also reveal vibronic bands in the blue region from 400 to 470 nm and are therefore only slightly red-shifted compared to unsubstituted anthracene and the shape of both spectra is nearly identical. The lifetimes are in a range of a few nanoseconds and CT-processes or contribution of a triplet state can be excluded and the emission occurs therefore mainly from the locally excited singlet state. The quantum yield of the oxophosphoranyl anthracene 2 in solution is significantly higher and reaches values up to 42.8%. Emission of the sulfur derivatives 3 and 4 in solution is nearly completely quenched, which was explained earlier by the photo-induced electron transfer (PET) from the sulfur lone pairs to the chromophore.\[36\] The oxygen lone pairs in 2 are not suitable in energy for a PET and therefore a comparable high quantum yield is observed in diluted solution.

While the photophysical properties in diluted solution are typical for structurally simple anthracene derivatives the emission behavior in the solid-state reveals some uncommon characteristics (Table 1). The unusual yellow emission of $\beta$-3 was reported in our communication before and assigned to an excimer formation in the solid-state.\[30\] Nearly identical behavior was observed for the structurally comparable $\gamma$-polymorph. The broad, structureless emission spectrum ranges over 200 nm and peaks in the yellow region at around 545 nm (Figure 5). Together with the elongated lifetime up to 30 ns an excimer emission can also be confirmed for $\gamma$-3. The dimer structural motif of the $\beta$- and $\gamma$-polymorph with the large overlap of the anthracene $\pi$-systems seems to be ideal for an efficient excimer formation in the solid-state. The $\alpha$-polymorph shows a completely different emission behavior. A vibronic structure is present in the spectrum and the bathochromic shift of the emission wavelength is only small resulting in an emission in the blue region with maximum emission intensities at wavelengths of 437 and 458 nm. They differ by more than 100 nm from the emission of the $\beta$- and $\gamma$-polymorph. The obtained lifetime is also decreased to a few ns indicating the absence of any CT participation in the excited state. The described properties are found as well for single crystals, which were clearly identified as the $\alpha$-polymorph as well for the bulk sample, which

![Figure 4](image)

**Figure 4.** a) Normalized UV–Vis absorption and b) normalized emission spectra of 2 (green) and 4 (blue) in diluted THF solution ($10^{-5}$ M).

![Figure 5](image)

**Figure 5.** Normalized solid-state emission spectra of polymorphs and co-crystals of 3 and 4. For the isomorphous co-crystals 4a–4c and 4d–4g only one example each is shown.
precipitates from the reaction mixture and was therefore considered to consist mostly of the α-form as evaluated above. As the photophysical properties of α-3 are very similar to the obtained results from diluted solution we determined the emission of α-3 in the solid-state to a monomer emission from the locally excited state. This assignment goes hand in hand with the described solid-state structure where no π-π interactions between the anthracene moieties were found, which could influence the excited state and the emission properties as seen for the β- and γ-polymorph. The change of the packing motif for the α- and β-polymorphs (Figure 5). No vibronic structure is present in the emission spectra but the spectral broadening is less pronounced than seen for the β- and γ-polymorph. The broadening can be quantified by the full width at half maximum (FWHM) and a clear increase within the series α-3 < 3a-3d < β/γ-3 can be found (Table S24, Supporting Information). For the isomorphous structures 3a and 3c also an increased lifetime is determined, while 3b and 3d reveal only short lifetimes. Nevertheless, the discussed properties indicate a contribution of the CT process in the excited state and the possible formation of an excimer even if it is less pronounced than in β/γ-3.

For [1-(S)PPh₃]₄-4-Ethyl-(C₆H₄) (4) and its co-crystals, a similar emission behavior as for 3 is observed. The isomorphous co-crystals 4a-4c with arenes as guests reveal a broad, structureless green emission of about 490 nm. Lifetimes and quantum yields of the three co-crystals are in a narrow range and therefore not dependent on the nature of the co-crystallized arene. Even if overlap of the anthracene moieties in the co-crystals 4d-4g was further increased the broad structureless emission peaks also at around 545 nm remain, similar to β- and γ-3. Elongated lifetimes and large FWHM indicate a CT contribution to the excited state. The several different structures of 4 can be organized into two groups along their solid-state emission profiles. The co-crystals 4a-4c show a green emission at about 490 nm while 4d-4g as well as the solvent-free 4 emit in the yellow region of the spectrum at about 540 nm.

2.3. Excimer Formation Factors

The investigation of the structural and photophysical properties could confirm the excimer formation of the thiophosphoryl anthracenes 3 and 4 in the solid-state except for α-3. The plethora of obtained structures allow a deeper insight into the mechanism of the excimer formation and the dependency of the photophysical properties on the NCIs. It is known that a decent overlap of the aromatic planes is required for the excimer formation. The resulting π-π interactions lead to the bathochromic shift of the emission wavelength. Hitherto, only few anthracene derivatives are reported which reveal an excimer emission in the solid-state. Most of them preclude a detailed investigation because only few comparable structures are known, or other factors clearly outnumber the π-π interactions. When considering the overlap ratio of the thiophosphoryl anthracenes, a strong correlation with the emission wavelength is obvious (Figure 6a). A larger overlap area of the anthracene residues causes a stronger bathochromic shift of the emission wavelengths. The excited state of anthracene dimers can be classified as a hybridized local and CT excited state.[28] When no interactions of the anthracene π-systems are present like in the structure of α-3 the excited state can be considered as the local excited state, which is dominated by the anthracene chromophore. Therefore, the emission in the solid-state resembles the emission in diluted solution, where strong NCIs can also be excluded. When a dimeric motif with a decent overlap is present the interactions of the π-systems result in a contribution of the CT to the excited state. The CT-state stabilizes the S₁ state and a red-shift of the emission wavelengths is the result. A closer look into the α-polymorph of 3 and its quinoline co-crystal 3d reveals an increase of the overlap from 0% (3) to 22% (3d). The emission wavelength shifts by only about 20 nm, which seems to be quite small. Compared to the β- and γ-polymorph with a similar increase of the overlap
area of further 22% to nearly 45% the emission wavelength increases by over 80 nm. A solely linear dependence of the emission wavelength from the overlap ratio seems therefore unlikely. Instead of linearity, a threshold for the excimer formation can be seen, which has also been postulated by Yang et al. in their computational study. Only when the CT-contribution to the excited state reaches a particular level a rapid increase of the emission wavelength can be observed, which goes along with an excimer formation.\[28\]

Comparing the data of \(\beta\) and \(\gamma 3\) with 4 and its co-crystals 4d–4g, an increase of the anthracene overlaps from 38% to 53% is observed, but the emission wavelength remains nearly constant at around 545 nm. From that, an upper limit for the bathochromic shift can be postulated like the lower threshold for excimer formation. When this limit is reached, the CT-contribution to the excited state seems not to increase any further, even when the overlap rises. Therefore, the emission wavelength remains constant at a particularly high level. For our investigated system the upper limit can be found at an overlap ratio of around 38% as found for the anthracene dimer in 4, which results in a maximum emission of around 545 nm.

A closer look into the solid-state structures can give further insight into the mechanism of the excimer-formation process. The overlap of the anthracene dimer is determined by the offsets along the short \((d_y)\) and long \((d_x)\) molecular anthracene axes. For a perfect co-facial dimer with 100% overlap, both offsets would be zero. Increasing the offset into one direction, therefore, reduces the overlap and the occurring \(\pi–\pi\) interactions. For the investigated compounds 3 and 4 including all polymorphs and co-crystals the offsets \(d_x\) range from 0.8 to 1.4 Å and are distributed nearly equally over this range (Figure 6b). For the offset \(d_y\), a different behavior is found. Of course, the observed range of offsets is larger from around 1.0 to 3.3 Å as the molecular axis is three times longer. It is of special interest here, that the shifts are not evenly distributed over the whole range. Instead, the observed offsets along the long molecular axis are clustered in two groups. The first group consists of the structures with \(d_y\)-values ranging 1.04 to 1.47 Å and for the second group offsets from 2.77 to 3.19 Å are found (Figure 6c). Taking the emission wavelengths into account it is evident, that for all compounds with the smaller offset \(d_y\) an emission wavelength of around 545 nm results, while for the second group a broader range of green emission is caused. From these findings, we assume that the ground-state geometry of the dimer determines the type of excimer formed in the excited state (Figure 7). For the compounds with the small \(d_y\) offset all three anthracene rings participate in the overlap and therefore in the \(\pi–\pi\) interactions. We suppose that the geometry of the dimer only slightly changes after excitation with shorter offsets in all three directions, which has been confirmed by computational results for different excimers.\[28\] Through the involvement of all three anthracene rings a large CT-contribution to the excited state can be considered, which results in the large bathochromic shift. When the offset is increased and only two rings of the anthracene overlap while the third ring is unaffected from strong \(\pi–\pi\) interactions the CT-contribution to the excited state is clearly lower and also the observed red-shift of the emission wavelength. Considering the structural and photophysical properties we assume that in the ground-state two types of dimer geometries are preferred and determine the nature of the excimer formed. When all three anthracene rings are involved in the overlap and in the \(\pi–\pi\) interactions an anthracene-type excimer is formed which reveals a large bathochromic shift of the emission wavelength to around 545 nm. When only two rings participate a naphthalene-type excimer can be considered with a clearly reduced red-shift of the emission wavelength and therefore less CT-contribution to the excited state.

3. Conclusion and Outlook

We synthesized and investigated a wide range of polymorphs and co-crystals of two simple but structurally different
were obtained on a Horiba Jobin-Yvon Fluoromax-4 spectrometer equipped with a 150 W xenon arc lamp as excitation source and a photomultiplier as detector. Lifetimes were measured with the TCSPC setup using a 375 nm pulsed laser diode. Absolute quantum yields were determined with the calibrated integrating sphere of the Quanta S setup.

Synthetic procedures and analytical data of compounds 1–4 are given in the Supporting Information. Co-crystals 3a–3d and 4a–4e and 4g were prepared through crystallization of the compounds from hot saturated solutions in the corresponding solvent. 4f was crystallized through slow diffusion of n-hexane into a solution of 4 in CHCl3. Formation of the co-crystals was confirmed by unit cell determination of several crystals.

Crystallographic data were collected on an Ag or Mo-IμS microfocus source or on a TXS-Mo rotating anode.[38] All data were integrated with SAINT[39] and a multiscan absorption (SADABS)[40] and if required a 3λ correction[41] was applied. Structures were solved by direct methods (SHELXTL)[42] and refined on F2 using the full-matrix least-squares methods SHELXL[43] within the ShelXle Gui. Disordered groups were modeled with DSR.[44] Crystallographic Information Files can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/, using the reference numbers 2 021 487–2 021 503.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge partial funding from the Danish National Research Foundation (DNRF93) funded Center of Materials Crystallography (CMC).

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that supports the findings of this study are available in the supplementary material of this article.

Keywords
aggregation-induced emission, excimer, host–guest systems, organic luminescence materials, polymorphism, solid-state luminescence.

Received: October 20, 2020
Revised: January 15, 2021
Published online: February 15, 2021

4. Experimental Section

Reactions with air- and moisture-sensitive compounds were performed under an atmosphere of N2 or Ar using standard Schlenk techniques.[37] Solvents were dried with standard laboratory techniques. The starting materials 1-chloroanthraquinone and 1,4-diaminoanthraquinone were used as purchased. Lithiumdiphenylphosphide was used as 0.5 M solution in THF as obtained. Chlorodiphenylphosphane was distilled prior to use. NMR-spectroscopic data were recorded either on a Bruker Avance III 500 MHz or Bruker Avance III 400 MHz spectrometer and referenced to the solvent signal. UV/Vis and fluorescence measurements in solution were performed in analytical grade solvents. UV/Vis spectra were recorded on an Agilent Cary 50 spectrometer. Fluorescence spectra

[1] a) J.-H. Lee, C.-H. Chen, P.-H. Lee, H.-Y. Lin, M.-k. Leung, T.-L. Chiu, C.-F. Lin, J. Mater. Chem. C 2019, 7, 5874; b) M. Aytan, G. Haykir, A. Battal, V. Jankus, S. K. Sugunan, F. B. Dias, H. Al-Attar, F. Türksoy, M. Tavasli, A. P. Monkman, Org. Electron. 2016, 30, 149; c) G. M. Farinola, R. Ragni, Chem. Soc. Rev. 2011, 40, 3467.
[2] a) J. Gierschner, S. Varghese, T.-L. Chiu, C.-F. Lin, Adv. Opt. Mater. 2019, 7, 5874; b) J. C. Kuhne, M. C. Gather, Chem. Rev. 2016, 116, 12823; c) I. D. W. Samuel, G. A. Turnbull, Chem. Rev. 2007, 107, 1272.
