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Aggregation Induced Emission – Emissive Stannoles in the Solid State⁺

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The optoelectronical and structural properties of six stannoles are reported. All revealed extremely weak emission in solution at 295 K, but intensive fluorescence in the solid state with quantum yields (Φ_F) of up to 11.1% in the crystal, and in thin film of up to 24.4% Φ_F).

Fluorescent compounds are very useful for biological and medical applications as well as in materials science. However, in the literature, many luminescent compounds are described to exhibit aggregation-caused quenching (ACQ), which reduces or destroys the fluorescence quantum yields. This makes such compounds difficult to use in devices, even if they appear promising in solution. However, for other compound classes aggregation induced emission (AIE) is observed, which was described the first time in 2001 by Tang and co-workers.¹ One of these interesting classes consists of the group 14 metalloles.1c, 2 In the past, only siloles have received much attention due to their promising optoelectronic properties in the fields of materials science,³ biological imaging,⁴ biological sensors,⁵ explosives sensors⁶ and device applications,⁷ but germoles, stannoles and plumboles were little investigated with respect to their emission properties and applications.^{1c, 2a,} 6b. 8

All of the group 14 metalloles (containing Si, Ge, Sn, Pb) exhibit narrower highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps compared to their carbon analogues as well as broad red-shifted absorption maxima.⁹ The reason for this is a strong $\sigma^*-\pi^*$ conjugation, also known as hyperconjugation, in the molecule.^{9a, 10} However, within group 14, from Si and Ge to the heavier element Sn, the emission is weakened to non-existent. This is most likely due to the heavy element effect of Sn and the elongated Sn--C bonds that enhance molecular vibration.^{2a, 2c, 8a, 9c, 11} In general, group 14 metalloles (containing Si, Ge, Sn) display higher quantum yields (Φ_F) in the aggregated state in dioxane or tetrahydrofuran/water mixtures caused by AIE, but again, Φ_F for the Sn analogues is the lowest (e.g. Φ_F , in 90% water fraction: Silole-Ph₆ 38%, Germole-Ph₆ 10%, Stannole-Ph₆ 1%).^{2a} About the fluorescence behaviour of plumboles little is known so far.^{9b}

In comparison to classical stannoles, fused-ring systems as stannafluorenes and dithienostannoles are (highly) emissive in solution (examples by Yang and co-workers, Tilley and co-workers, Ohshita and co-workers, $\Phi_{\rm F}$: 0.9-65%).¹¹⁻¹² The dithienostannoles by Ohshita and co-workers are also efficient emitters in the crystalline state ($\Phi_{\rm F}$: 21-56%).^{11a} So far, it is not reported that classical non-fused stannoles show quantum yields higher than 1% in fluid-phase aggregates and 3.8% in dispersed phase in glasses of sucrose octaacetate, respectively.^{2a}

In this study, we present a set of classical stannoles (Figure 1) that show unexpected high quantum yields in the crystalline state of up to 11.1% and in thin films of up to 24.4%.



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Herein, we report on the synthesis and crystal structures of four new stannoles ST1, ST2, ST3, and ST6, the optical properties, in particular the fluorescence properties in fluid solutions, frozen solutions, in water/tetrahydrofuran mixtures, thin films and crystalline states of in total six stannoles ST1-ST6. Theoretical results by DFT and TD-DFT calculations support our experimental results.

The synthesis of the stannoles analysed in this work was straightforward: Reactions of Rosenthal's zirconocene with alkynes 8, 10, or 13 and di-alkynes 17, 18 or 19 (see alkynes in the ESI) led to zirconacyclopentadienes, which were used for further transmetalation reactions with dichlorodimethylstannane, dichlorodiphenylstannane and di-(p-hexylphenyl)dichlorostannane (22) in the presence of copper(I) chloride to furnish ST1-ST6 in yields ranging from 22% to 70% (see all procedures in the ESI).13

The molecular structures of ST1, ST2, ST3 and ST6 are illustrated in figures S1, S5, S9, S13 (ESI) and confirm the identity of the compounds; tables S3 and S4 (ESI) summarise the crystal data, selected bond distances and angles. The molecular structures of ST4 and ST5 have already been reported by us.^{9a, 13c} The optimised DFT geometries of **ST1-ST3** and ST6 are in agreement with the molecular structures as derived from crystal data. All compounds show small HOMO-LUMO energy gaps in the range of 3.2-3.4 eV. HOMO and LUMO are delocalised over the whole backbone and with the exception of ST6, the Sn atoms are involved in the LUMO at the displayed isovalue (leading to efficient $\sigma^* - \pi^*$ conjugation), while the substituents at the Sn atom are hardly involved (Figure 2; Figures S111-S116 ESI).9a, 9c The structure of the LUMO of stannole ST6 appears to have the same characteristics as our previous calculated stannole with 5nitro-thiophenyl substituents in the 2- and 5-position of the stannole ring.9a



All stannoles showed absorption in the short-wave region < 280 nm and a major absorption band with vibrational finestructure with $\lambda_{abs, max}$ in the order 412 nm (ST3)< 413 nm (ST1)< 414 nm (ST2) < 418 nm (ST5)< 425 nm (ST6)< 442 nm (ST4) in solutions of chloroform, toluene and 2methyltetrahydrofuran (10⁻⁵ M) at 295 K (ESI Table 5). These bands can be assigned to $\pi \rightarrow \pi^*$ transitions, involving the π and π^* -orbitals of the stannole ring. The polarity of the solvent had no effect on

 $\lambda_{abs. max}$. All compounds exhibited high extinction coefficients ranging from 9146 mol·L⁻¹·cm⁻¹ (ST2) to 44500 mol·L⁻¹·cm⁻¹ (ST4) (ESI Table 5). Our theoretical results from TD-DFT calculations employing TD-PBE1PBE1-GD3BJ/6the

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311++G(2d,2p) //PBE1PBE1-GD3BJ/6-311++G(2d,2p)//tic model chemistry and SDD pseudo potentiନ୍ୟା: 16403 ଅନି^{0C}ମିହି⁴⁵ ଅନିବ experimental data well.¹⁴ Main electronic transitions are located around 425 nm (ST1) to 456 nm (ST4) and correspond to a direct HOMO-LUMO transition. Because calculations of single molecules in the gas phase were used, the absorption maxima are slightly red-shifted about 7 nm to 19 nm compared to the experimental results (ESI Table S8).

The luminescence of the six stannoles was extremely weak in solution (10⁻⁵ M, in chloroform, toluene, tetrahydrofuran) at 295 K with $\Phi_{\rm F}$ <0.1% in almost all cases and $\lambda_{\rm em, max}$ in the order 501 nm (ST3)< 507 nm (ST6)< 509 nm (ST5)< 513 nm (ST1) < 517 nm (ST2)< 530 nm (ST4). However, two exceptions were **ST4** and **ST6** with $\Phi_F = 1.0\%$ and $\Phi_F = 0.4\%$, respectively, in toluene. Similar to the observations for the absorption spectra, the polarity of the solvent had little to no effect on Φ_F or λ_{em} , max (ESI Table 5). Stokes shifts ranged from 3706 cm⁻¹ (ST4, toluene) to 4939 cm⁻¹ (ST1, toluene) and all fluorescence halflifes were between $\tau_{295 \text{ K}}$ < 80 ps and 0.13 ns (ESI, Table S5, S6). The luminescence of ST1 and ST5 was also measured in different solution mixtures of tetrahydrofuran/water at 295 K, in which these compounds are expected to aggregate. Thus, this technique can be used to investigate the phenomenon of AIE of stannoles in fluid-phase aggregates. The intensity of the emission maximum increased slowly from 0% (Φ_{F} : <0.1%) to 50%/ 60% water fraction for ST1/ ST5, respectively, then stronger until the water fraction was at 98% ($\Phi_{\rm F}$: 0.4%) for **ST1** and 85% water fraction (Φ_F : 2.5%) for **ST5** (Figure 3). Dispersed particles [µm size] were observed in the solvent mixtures at a water fraction of 70% as indicated by a change from a clear to a cloudy solution. At 80% water fraction, the mixtures became homogenous again [nm particles] and with water fractions higher than 80%, again visible large aggregates were observed making the suspension completely inhomogeneous. In the case of ST5, the emission intensity decreased again at 90% water fraction (Figure 3). These observations are similar to the findings of Mullin and co-workers for their group 14 metalloles.^{2a, 2b} Micrographs primarily show needles for ST1 and mixtures of needles and plates for ST5 (ESI, Figures S98-S104).



Figure 3. a) Emission spectra of ST1 and c) of ST5 in tetrahydrofuran/water with different water fractions at 295 K. b) Plot of maximum intensity against water fraction (vol %) of ST1 and d) of ST5.

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Furthermore, the emission behaviour of **ST1-ST6** was investigated in a solution of 2-methyltetrahydrofurane (10^{-5} M) at various temperatures (**ST2** Figure 4, ESI Figures S46, S55, S64, S73, S84, S93). While the photoluminescence intensity increased slowly from 280 K to 160 K for **ST1-ST3**, it increased extremely strongly from 140 K to 80 K. The intensity at 280 K to 80 K was in total increased by a highly significant factor of 158 to 620 for **ST1-ST3**. Compared to 280 K, $\lambda_{em, max}$ was blue-shifted about 4 nm to 33 nm, which is consistent with earlier reports.^{2a}



Figure 4. a) Temperature dependent emission spectra of **ST2** in 2-methyltetrahydrofuran. b) Picture of the irradiated frozen solution of **ST2** at 80 K. c) Plot of maximum intensity against the temperature. d) Plot of the maximum wavelength against the temperature.

Analysing the temperature-intensity dependency for **ST4**, **ST5** and **ST6**, it could be observed that the intensity increased little from 280 K to 200 K, then very rapidly from 220 K to 80 K. Compared to 280 K, the intensity was increased by a very high factor of 87 to 334 for **ST4-ST6** at 80 K. From 280 K to 80 K, all three compounds (**ST4**, **ST5** and **ST6**) exhibited a blue-shift of $\lambda_{em, max}$ about 5 nm to 17 nm. The irradiated frozen solutions of **ST1-ST6** at 80 K are illustrated in Figure 4 and in the ESI, figures S19, S22, S25, S28, S32, S35 and show intense luminescence.

For all structures, upon cooling, the broad emission band at 280 K split up into at least three larger and one small defined emission bands. This is most likely caused by suppression of intramolecular degrees of freedom. Furthermore, the observed colour of fluorescence of the frozen solution depended on the intensity ratio of the three main bands. All were in the range of turquois blue to green. Fluorescence half lifes were between $\tau_{80 \text{ K}} = 0.90 \text{ ns} (33.4\%)$, 2.77 ns (66.6%) and $\tau_{80 \text{ K}} = 3.83 \text{ ns}$, significant higher than at 295 K (ESI, Table S6).

Most importantly, and the first time described for classical stannoles, all structures showed visible luminescence in the solid state (Figure 5). **ST1**, **ST2** and **ST5** showed green emissions from 519 nm to 538 nm with Φ_F 1.2% to 10.2% in the crystalline state and Φ_F 1.8% to 18.8% in thin film. **ST3** exhibited turquois-green emission with $\lambda_{em, max} = 510$ nm, $\Phi_F = 0.5\%$ in the crystalline state and $\Phi_F = 1.0\%$ in thin film. **ST4** displayed greenish-yellow emission with $\lambda_{em, max} = 557$ nm, $\Phi_F =$

3.9% in the crystalline state and $\Phi_{\rm F}$ = 9.3% vin thin film (Figure 5). Compared to $\lambda_{\text{em, max}}$ in solution 1030/20508,458% maximum was red-shifted by up to 87 nm in the solid state. The compound with the largest shift in the emission maximum (ST6) showed orange photoluminescence with $\lambda_{em, max}$ = 594 nm, Φ_F = 11.1% in the crystalline state and even Φ_F = 24.4% in thin film. In comparison to ST1-ST5, ST6 has thiazolylsubstituents in the 2- and 5-positions. In summary, Φ_F are 5 to 111 times higher in the crystalline state than in solution at 295 K and even higher in film indicating strong AIE. Except for **ST2**, $\Phi_{\rm F}$ were 1.8 to 4.2 times higher in thin film than in the crystalline state and 10 to even 244 times higher than in solution at 295 K. Going from solution to solid state, $\lambda_{em, max}$ are red-shifted; this is most probably due to enhanced conjugation within the molecules in the solid state as compared to isolated, non-aggregated molecules in solution, in which the aryl-substituents can rotate with respect to the

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stannole core.^{1c} The fluorescence half lifes were between $\tau_{295 \text{ K}} < 0.20 \text{ ns}$ and $\tau_{295 \text{ K}} = 0.53 \text{ ns}$ and all stannoles exhibited small stokes shifts of $\Delta \nu = 1094 \text{ cm}^{-1}$ to 1997 cm⁻¹ with regard to the excitation maximum in the solid state (Table 1). During our experiments, we never observed long living triplet emission (phosphorescence), neither at 295 K in solution or solid state nor at 80 K in frozen solution.

In general, $\Phi_{\rm F}$ values are higher for **ST4-ST6** with aromatic rings at the Sn atom than for **ST1-ST3** with methyl groups on Sn. Furthermore, $\lambda_{\rm em,\ max}$ are red-shifted, which was also observed by Mullin and co-workers for similar systems.^{2a} The thiophenyl/thiazolyl rings in the 2- and 5-positions of the stannole ring make the overall backbone of the structure more planar, which means better conjugation within the system as compared to twisted backbones, e.g. for HPSn/ DMTPSn. This leads to a red-shift in $\lambda_{\rm abs,\ max}$ and $\lambda_{\rm em,\ max}$ as compared to twisted structures such as HPSn/ DMTPSn and also to an increased emission intensity.^{1c, 2a} While for **ST1-ST3** no π - π interactions between the molecules in the crystal unit cell were observed, **ST6** exhibits π - π stacking between the thiazolyl-groups of two stannole molecules with an interplanar distance of 3.493 Å and a slip angle of 76.7 ° (ESI, Figure S17).



Figure 5. a) Steady-state fluorescence spectra in the solid state of **ST1-ST6** at 295 K. b) CIE 1931 chromaticity plot with emission colour coordinates of **ST1-ST6**; images of **ST1-ST6** under irradiation at 366 nm.

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Normally, π - π stacking quenches emission, but in our case, **ST6** had the highest Φ_F . The substituents in the 3- and 4-positions are not involved in the HOMO and LUMO and have only a small effect on the emission; but they are important for the crystal unit cell packing, therefore causing larger differences in Φ_F between **ST1-ST3** (for further discussions see ESI).^{2b}

A possible reason for the phenomenon of AIE can be the restricted intramolecular rotation (RIR) in these molecules. Therefore, the non-radiative pathways are reduced, while the emissive pathway becomes dominant and the photoluminescence increases dramatically.^{1a, 1d, 2a, 2b}

In conclusion, we experimentally and computationally investigated the optical properties and crystal structures of six stannoles **ST1-ST6**. Specifically, their fluorescence properties in fluid and frozen solutions and solid state were investigated. With this work, classical stannoles with Φ_F up to 11.1% in the crystalline state and 24.4% in thin film were reported for the first time. We also observed different colours of emissions ranging from blue turquois to green in frozen solutions at 80 K and turquois green to orange in the solid state. Future work will see an in-depth analysis of structure-property relationships to further increase the emission in the solid state and eventually the application in organic light-emitting diodes.

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Conflicts of interest

There are no conflicts to declare.

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For the first time, six classical stannoles with photoluminescence quantum yields up to 11.1% in the crystalline state and 24.4% in thin film are presented.

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