Rationally designed synthesis of bright AgInS$_2$/ZnS quantum dots with emission control

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ABSTRACT

In the blossoming field of Cd-free semiconductor quantum dots (QDs), ternary I–III–VI QDs have received increasing attention due to the ease of the environmentally friendly synthesis of high-quality materials in water, their high photoluminescence (PL) quantum yields (QYs) in the red and near infrared (NIR) region, and their inherently low toxicity. Moreover, their oxygen-insensitive long PL lifetimes of up to several hundreds of nanoseconds close a gap for applications exploiting the compound-specific parameter PL lifetime. To overcome the lack of reproducible synthetic methodologies and to enable a design-based control of their PL properties, we assessed and modelled the synthesis of high-quality MPA-capped AgInS$_2$/ZnS (AIS/ZnS) QDs. Systematically refined parameters included reaction time, temperature, Ag:In ratio, S:In ratio, Zn:In ratio, MPA:In ratio, and pH using a design-of-experiment approach. Guidance for the optimization was provided by mathematical models developed for the application-relevant PL parameters, maximum PL wavelength, QY, and PL lifetime as well as the elemental composition in terms of Ag:In:Zn ratio. With these experimental data-based models, MPA:In and Ag:In ratios and pH values were identified as the most important synthesis parameters for PL control and an insight into the connection of these parameters could be gained. Subsequently, the experimental conditions to synthesize QDs with tunable emission and high QY were predicted. The excellent agreement between the predicted and experimentally found PL features confirmed the reliability of our methodology for the rational design of high quality AIS/ZnS QDs with defined PL features. This approach can be straightforwardly extended to other ternary and quaternary QDs and to doped QDs.

KEYWORDS
quantum dot, core/shell nanoparticle, silver indium sulfide, microwave-assisted synthesis, design of experiment, photoluminescence

1 Introduction

Cd-free ternary I–III–VI semiconductor quantum dots (QDs) have emerged as promising alternatives for nanocrystalline emitters that can circumvent the inherent drawback of II–VI and IV–VI binary semiconductor QDs, namely the presence of toxic constituents such as Cd, Hg or Pb, and the lack of environmentally friendly synthetic routes for high quality III/V QDs like InP [1–5]. Among these ternary QDs, Cu–In–S (CIS) and Ag–In–S (AIS) QDs are particularly interesting [2, 6, 7]. Their attractive photoluminescence (PL) properties include high PL quantum yields (QYs) ≥ 50% in the entire visible to near infrared (NIR) region from about 400 nm to about 1,000 nm after passivation with e.g., a ZnS shell [8–10]. Other interesting features of these ternary QDs, that also show size confinement effects [11], are broad PL bands with full width at half-maximum (FWHM) of more than 100 nm in this wavelength region, which only slightly overlap with the rather unstructured absorption spectrum lacking the sharp first excitonic feature of II/VI and III/V QDs [12–14]. Moreover, they show long PL lifetimes of several hundred nanoseconds, which are not sensitive to the presence of oxygen.

The ternary QDs emission features, ascribed to either the radiative recombination of donor–acceptor pairs [15, 16], a self-trapped exciton model [17], the recombination of a localized hole with a conduction band electron as derived for CIS QDs [18] or a combination of these models [19], can provide the basis for many future applications of CIS and AIS QDs. Although the broad PL spectra are not ideal for some multiplexing applications, they can be advantageous, e.g., for the construction of sensor systems, solid state lighting (light emitting diodes) [10, 20], photovoltaics (photovoltaic cells [21]; light-harvesting systems/solar concentrators [22]), photocatalysis [23, 24], and luminescent probes for bioimaging [25–27].

From a chemical point of view, the most prominent characteristic of CIS and AIS QDs is their compositional and structural versatility, as they are able to accommodate non-stoichiometric ratios of their constituents and can have different
data, a mathematical model can be established to describe the reaction with high probability [29]. Challenges in the synthesis of CIS and AIS QDs arise from the different reactivity of the constituting metal ions as a result of their distinct hard and soft Lewis acid and base (HSAB) character [3]. For example, in the case of AIS QDs, which are in the focus of this article, In(III) is a “hard” while Ag(I) is a “soft” Lewis acid [30]. Consequently, the synthesis of AIS QDs requires a non-stoichiometric ratio of the metal ions with indium being used in excess [3]. The precursor ratio also considerably influences the PL properties of the resulting AIS QDs [11, 30–32]. Additionally, the deposited ZnS shell often does not merely play a protective role but can also initiate a cation exchange (CE) between the zinc ions added during the shell deposition procedure and the metal ions forming the QD core. This can lead to alloy formation, yielding a hybrid between a ternary and a quaternary nanomaterial [32–35]. Seeking a balance between the different cation reactivities is a demanding task, independent of the chosen synthetic route, e.g., hot-injection or aqueous-based synthesis. The synthesis of high quality QDs in water, which is increasingly preferred to meet environmental concerns, presents an additional challenge. Besides their role in colloid stabilization, typically employed small water-soluble thiol ligands such as 3-mercaptopropionic acid (MPA) form complexes with Ag(I) [36], In(III) [37], and Zn(II) [36], with the complex stoichiometry depending on ligand concentration [38]. Therefore, the initially used or so-called feeding thiol:In(III) ratio is also important for balancing the thiol binding strength to the different metal cations present in the reaction mixture [30]. For all aqueous syntheses, pH is a crucial parameter, as it controls the thiol protonation state and the formation of metal hydroxides, present either as soluble complexes or as precipitates [3]. Bearing in mind that the hydroxide ion is a typical hard base, the effective concentration of free indium(III), for example, can largely depend on the pH. Other synthetic parameters affecting the PL features of the resulting AIS/ZnS QDs are temperature and reaction time during the AIS core and the ZnS shell synthesis. For the preparation of high quality AIS/ZnS QDs in water, microwave (MW)-assisted methods are very attractive. These methods have been widely explored for the synthesis of water-soluble binary II–VI QDs [39–43], but were scarcely used for AIS QDs until now [44–48]. This is related to the efficient absorption of MW irradiation by the solvent water and the metal ion precursors. Moreover, MW synthesizers enable a rapid and homogeneous increase in temperature, which reduces the possibility of a temperature gradient in the reaction mixture, consequently yielding a more efficient, uniform, and controlled nucleation and growth of the nanoparticles [49, 50]. MW heating also expands the reaction temperature range due to water superheating, allowing reactions to be performed above its boiling point [51], and enabling automation.

Contrary to binary II–VI QDs where the emission color can be easily tuned by changing the reaction time, the manifold of parameters affecting the synthesis of ternary QDs, like AIS nanocrystals (NCs), and their unknown interplay render the rational design of AIS QDs almost impossible. A useful tool to rationally guide the optimization of complex processes is the design of experiment (DoE) approach. Its cornerstone is the assumption that the outcome of a reaction can be described by a mathematical equation [52, 53]. Based on the experimental data, a mathematical model can be established to describe the studied system and, consequently, to predict the experimental conditions, which provide the optimum outcome [54–56]. This encouraged us to study the applicability of DoE for the rationally driven MW-assisted synthesis of MPA-capped AIS/ZnS QDs in water with optimum PL features. Subsequently, we performed a “top-down” optimization, where the reaction parameters were systematically narrowed, guided by mathematical models developed based on our experimental data. This allowed us to predict different outcomes of the underlying reactions, that were then validated by new experiments. Consequently, a methodology was developed to rationally design high quality AIS/ZnS QDs with control over elemental composition and PL properties like emission color and PL decay kinetics and to better understand the relationship between the reaction conditions and these features.

2 Experimental

2.1 Chemicals

Silver(I) nitrate (AgNO₃, 99.8%, Bernd Kraft), anhydrous indium(III) chloride (InCl₃, 98%, abcr GmbH), 3-mercaptopropionic acid (MPA, 98%, Merck KGaA), sodium sulfide nonahydrate (Na₂S·9H₂O, 98%, Acros Organics), zinc(II) nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99.998%, Alfa Aesar), ammonium hydroxide solution (NH₄OH, 25%, Merck KGaA), and ethanol abs. (p.a., Chem-Lab NV) were used without further purification. All precursors were used as 1 mol·L⁻¹ solution. Indium(III) chloride (InCl₃, 98%, abcr GmbH), 3-mercaptopropionic acid (MPA, 98%, Merck KGaA), sodium sulfide nonahydrate (Na₂S·9H₂O, 98%, Acros Organics), zinc(II) nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99.998%, Alfa Aesar), ammonium hydroxide solution (NH₄OH, 25%, Merck KGaA), and ethanol abs. (p.a., Chem-Lab NV) were used without further purification. All solutions were prepared using bidistilled water with a resistance not exceeding 18 MΩ·cm. InCl₃ was used for the synthesis as 1.0 mol·L⁻¹ solution containing 0.1 mol·L⁻¹ HNO₃. The remaining precursors were used as 1 mol·L⁻¹ solution.

2.2 MW-assisted AIS QDs synthesis

AIS synthesis was performed using a modified procedure of the synthesis reported by Raevskaya et al. [11]. In a typical synthesis, AgNO₃ (0.04 mmol), MPA (1 mmol) and NH₄OH (1 mmol) were added in a 35 mL reaction vessel with 25 mL of water. InCl₃ (0.2 mmol) was then added dropwise and the pH was adjusted to 8.5 by the addition of small amounts of NH₄OH. Na₂S (0.5 mmol) were then added and the resulting solution was MW-heated in a CEM Discover SP Microwave Synthesizer. An initial power output of 200 W was applied until the desired temperature of 100 °C was reached, which was maintained for 50 min. After this heating period, MPA (0.2 mmol), NH₄OH (0.2 mmol) and Zn(NO₃)₂·6H₂O (0.2 mmol) were added to the reaction mixture, which was then heated for 30 min at 100 °C. For the precipitation of the obtained QDs, ethanol (50 mL) was added and the dispersion was centrifuged for 5 min at 10,000 RCF with a Rotina 380R centrifuge (Hettich Lab Technology), the precipitate was collected and re-dispersed in water, and the procedure was repeated two times. The obtained QDs samples were stored in amber glass vials at room temperature.

2.3 Design of the experiments

This encouraged us to study the applicability of DoE for the rationally driven MW-assisted synthesis of MPA-capped AIS/ZnS QDs in water with optimum PL features. Subsequently, we performed a “top-down” optimization, where the reaction parameters were systematically narrowed, guided by mathematical models developed based on our experimental data. This allowed us to predict different outcomes of the underlying reactions, that were then validated by new experiments. Consequently, a methodology was developed to rationally design high quality AIS/ZnS QDs with control over elemental composition and PL properties like emission color and PL decay kinetics and to better understand the relationship between the reaction conditions and these features.
 points, with six axial points at a distance of $\alpha = 1.682$ and five center points. Five different responses were used. The statistical analyses of the fractional factorial design and of CCD were performed with Design Expert v. 11 (Stat-Ease Inc. Minneapolis, MN, USA). The suitability and significance of the models were evaluated by analysis of variance (ANOVA) with Fisher’s $F$-test. The terms with $p$-value > 0.05 were considered significant. The goodness of fitting was evaluated by a Lack-of-Fit test and by adjusted-$R^2$ and predicted-$R^2$ values.

### 2.4 Characterization of the QDs

Elemental analysis was done using the inductively coupled plasma optical emission spectrometer (ICP-OES) SPECTRO ARCOS (SPECTRO Analytical Instruments GmbH., Kleve, Germany). The zeta potential was measured with the Zetasizer ARCOS (SPECTRO Analytical Instruments GmbH., Kleve, Germany). The zeta potential was measured with the Zetasizer ARCOS (SPECTRO Analytical Instruments GmbH., Kleve, Germany) in standard 1.0 cm optical quartz cuvettes. The PL decays of the QDs were fitted with a multi-exponential model, see Eq. (1)

$$I(t) = \sum n \alpha_n e^{(-t/\tau_n)}$$  

where $\alpha_n$ are the amplitudes and $\tau_n$ the lifetimes of the respective decaying species. These data were calculated with a reconvolution fitting procedure using the FLS-920 spectrometer software. The fit quality was evaluated from the corresponding $\chi^2$ values. Biphasic or triexponential fits were done as the resulting $\chi^2$ values were closer to 1 than for mono-exponential fits. The average lifetimes were calculated as an amplitude-weighted average, see Eq. (2) [57]

$$< \tau > = \frac{\sum_n A_n \tau_n}{\sum_n A_n}$$  

where, $\tau_n$ are the lifetimes of each component and $A_n$ the corresponding relative fractional amplitudes. Further details about the experiments are provided in the Electronic Supplementary Material (ESM).

### 3 Results and discussion

#### 3.1 Parameter definition

The first step to design a methodology for the synthesis of AIS/ZnS QDs with rationally envisaged properties is the definition of the reaction parameters. We envisioned an unprecedented approach by considering all parameters, independent of their expectable importance for the outcome of the synthesis of AIS and AIS/ZnS QDs. This included the feeding ratios of Ag:In, S:In, Zn:In, and MPA:In as well as pH, time for the synthesis of the AgInS$_2$ core, time, and temperature of the ZnS shell, and temperature. For each parameter, the working range was defined (Table 1) considering the reaction mechanism and related requirements, e.g. a suitable pH, the feeding ratios reported for similar synthetic procedures [11, 30, 32, 58], and the results from preliminary screening studies (Table S2 in the ESM).

### 3.2 Time and temperature optimization

The reaction time was optimized first, while the other parameters were kept constant. Subsequently, the temporal evolution of the optical properties of the AIS QDs was assessed assuming for each parameter the average value between the corresponding lower and upper limits, given in Table 1 (Ag:In ratio of 0.16; S:In ratio of 1.5; Zn:In ratio of 1.5; MPA:In ratio of 6; pH of 9.5). The reaction temperature was fixed at 100 °C, while the reaction time was varied. The PL features of the resulting QDs were used as main screening tools to evaluate QD performance. A feature typically found in the synthesis of QDs including the reaction time was varied. The PL features of the resulting QDs were fitted with a multi-exponential model, see Eq. (1)
A representative absorption spectrum of our AIS QDs is shown in Fig. 1(a) underlining the previously mentioned lack of a sharp first excitonic peak and the long, so-called Urbach tail below the bandgap energy \( E_g \). This tail is ascribed to phonon-assisted optical transitions \([61, 62]\). As displayed in Fig. 1(a), the prepared AIS QDs revealed the expected Urbach tail at a wavelength of about 500 nm. The absorption spectrum, however, also showed a sharp absorption peak at 289 nm. The surprisingly pronounced structure of this absorption peak is not typical for AIS QDs and it was only found under these specific conditions. This feature was evident from the beginning of the synthesis (Fig. 1(b), 10 min) up to a reaction time of 50 min but became less pronounced for reaction times exceeding the optimum reaction time (see Fig. 1(b)). The assignment of this absorption peak at around 289 nm is not clear yet. One possible explanation could be the formation of ternary or alloyed nanoclusters intermediates, that have been reported e.g. for \( \text{Zn}_{x}\text{Cd}_{y}\text{Se}, \) semiconductors \([63]\). The intermediate nature of these species follows immediately from the temporal course of the absorption peak at about 290 nm, as this feature eventually disappears at longer reaction times or at higher reaction temperatures (Fig. S3 in the ESM).

The formed AIS QDs displayed broad emission bands ((FWHM) of \( \sim 0.5 \) eV), see Fig. 1(c), when compared with traditional II–VI QDs. For example, the absorption and emission spectra of monodisperse hydrophobic thick shell CdSe/CdS QD in hexane with a QY close to 1 show a FWHM of the first sharp excitonic absorption maximum of about 37 meV and a FWHM of the emission band of 65 meV \([64–67]\). The spectral widths of the emission bands were obtained assuming a symmetric shape of the emission spectra that were only recorded up to 790 nm. The origin of the broad PL of AIS QDs has been described by different models like the donor–acceptor model \([15, 16]\), the self-trapped exciton model \([17]\), a free-to-bound charge carrier recombination mechanism \([18, 68]\), and a model combining all these models recently suggested by us \([19]\). The PL intensity of the AIS QDs (Fig. 1(c)) and the QY values increased as function of the reaction time (Fig. 1(d)), while the maximum of the PL emission was slightly blue shifted (Fig. 1(c)). A maximum QY value of 0.24 was reached after 50 min. PL emission band also narrowed as function of the reaction time, which is attributed to annealing. Parallel performed measurements of the zeta potential revealed a drop during the reaction from \(-40\) to \(-30\) mV, possibly due to thiol decomposition. Nevertheless, this zeta potential is still sufficient to guarantee a good colloidal stability (Fig. 1(d)).

Time-resolved PL measurements of the AIS QDs at different reaction times always revealed complex decay kinetics. The PL

![Figure 1](https://example.com/figure1.png)

**Figure 1** Temporal evolution of the optical and structure-analytical features of AIS QDs during synthesis. (a) Absorption spectra of the AIS QDs obtained after 50 min as representative absorption spectrum of AIS QDs. (b) Evolution of the absorption spectra of the AIS QDs resulting after 10 min (yellow), 50 min (blue), and 60 min (dark blue); (c) PL emission spectra; (d) QY (blue triangles) and zeta potential (green squares) of the AIS QDs as a function of reaction time. (e) PL lifetime of the short-lived component (\(\tau_1\); blue triangles) and the long-lived component (\(\tau_2\); red circles) derived from the biexponentially fitted decay curves of the AIS QDs as a function of reaction time. (f) Fractional amplitudes (in percent) of both decay components derived from the biexponentially fitted decay curves as a function of reaction time. (g) FTIR spectra of the MPA-capped AIS QDs (blue) and the ligand MPA (yellow); the dashed rectangle marks the absorption range of the SH group and the dotted rectangle the absorption range of the \(\text{COO}^-\) group. (h) Low-magnification TEM image of the AIS QDs resulting after 50 min; showing an overview of the QDs. (i) XRD diffraction pattern of the AIS QDs before heating (0 min, blue) and after 50 min of heating (50, red) in comparison to the XRD pattern of bulk chalcopyrite \(\text{AgInS}_2\).
decays could satisfactorily be fitted with bi-exponential kinetics (Table S3 and Fig. S4 in the ESM), yielding a short-lived component with a fluorescence lifetime of about 110 ns and a long-lived component with a fluorescence lifetime of about 450 ns (Fig. 1(e)). These fits present, however, a simplification of the AIS photophysics and do not really imply that there are only two well defined emissive species present, but rather reflect a distribution of long-lived and short-lived species as previously described by us [19]. The observed decay kinetics and long fluorescence lifetimes of the AIS QDs exceed those of II/VI semiconductors like CdSe and CdTe, which have radiative lifetimes in the range of 20 to 40 ns [69–71]. This behavior agrees very well with the PL lifetimes of ternary AIS QDs observed by other groups and previously reported by us [19] and the PL decay kinetics of CIS QDs [29]. During the course of the reaction, the lifetimes of the short and the long decay component increased (Fig. 1(e)), while their relative fractions, referred to here as fractional amplitudes, remained constant (Fig. 1(f)).

The surface passivation of the AIS cores by the organic ligand shell was confirmed by FTIR, see Fig. 1(g). The FTIR spectrum of the MPA-capped AIS QDs revealed the presence of MPA on the QD surface as indicated by the absence of the S–H stretching vibration in the range of 2,600–2,550 cm−1 and the presence of the asymmetric and symmetric stretching vibrations of the COO− group at 1,554 and 1,380 cm−1. In comparison to free MPA, the MPA-capped AIS are lacking the broad and intense O–H stretching vibration and the carbonyl absorption band is shifted. This underlines the deprotonation of the carboxylic acid group in the case of MPA-stabilized AIS QDs.

TEM analysis of AIS QDs obtained at reaction times of 50 min revealed approximately tetrahedral shaped and crystalline AIS QDs with an average diameter of ca. 2.7 nm (Fig. 1(h) and Fig. S5 in the ESM). The relatively broad particle size distribution was attributed to the aqueous based synthetic route and the lack of a size-selective precipitation. TEM images obtained at different reaction times did not show a clear difference in terms of size (Fig. S5 in the ESM depicts the comparison between AIS QDs after 10 and 50 min). Although it is known that the size distribution of QDs contributes to the spectral width of the PL band, but as demonstrated, e.g. by our recently performed single-particle measurements, a relatively broad PL band is an intrinsic feature of AIS QDs [14]. Therefore, the AIS QDs particle size is not so relevant as it is for binary II–VI QDs. To assess the temporal evolution of the crystallinity of the QDs during synthesis, the XRD pattern determined for weakly fluorescent AIS QDs (data not shown), prepared without heating, were compared with those derived for brightly emissive AIS QDs during ZnS shell growth is depicted in Fig. 2. Upon addition of the shell precursor, the emission peak was blue shifted. This observation is attributed to the diffusion of Zn(II) ions into the AIS lattice, yielding quaternary alloyed/doped NCs [6, 30] in addition to the formation of an inorganic surface passivation shell of ZnS around the QD core (Fig. 2(b)). Cation diffusion

The elemental composition of the AIS QDs determined with ICP-OES (Fig. 2(a)) revealed a decrease in Ag:In ratio with increasing reaction time. This indicates that AIS QDs grew by incorporating more “hard” Lewis acid indium than “soft” Lewis acid silver, which is in accordance with the blue shift of the PL emission (Fig. 1(c)).

To prepare core-only AIS QDs with shorter reaction times, the ability of the MW-synthesis in a closed vessel was exploited to perform reactions above the water boiling point (Fig. S6 in the ESM). Optimum conditions, which provided the highest QY of the AIS QDs, were found for a temperature of 100 °C and relatively long reaction times (Fig. S6 in the ESM, QY of 0.24 at 50 min). However, a moderate QY of 0.19 could be achieved at 110 °C with a relatively short reaction time of 10 min (Fig. S6 in the ESM).

The temporal evolution of the optical features of the AIS QDs during ZnS shell growth is depicted in Fig. 2. Upon addition of the shell precursor, the emission peak was blue shifted. This observation is attributed to the diffusion of Zn(II) ions into the AIS lattice, yielding quaternary alloyed/doped NCs [6, 30] in addition to the formation of an inorganic surface passivation shell of ZnS around the QD core (Fig. 2(b)). Cation diffusion...
into the AIS core is limited because at longer reaction time, no further blue-shift in emission was observed (data not shown). Similarly, the QY values increased considerably during the first minutes of the reaction, followed by a slow increase until a maximum value of 0.50 was reached (Fig. 2(c)). As the reaction proceeded, the PL lifetime also increased and the fluorescence decay kinetics became more complex, revealing at least triexponential decay kinetics (Fig. 2(c)). The change in the elemental composition of the AIS QDs after ZnS addition was confirmed by ICP-OES (see Fig. 2(a)). As Zn(II) is a relatively “soft” Lewis acid [3], it was expected that cation exchange occurred preferentially to yield Ag-richer NCs. The XRD diffraction pattern also support the formation of an alloy or quaternary doped QDs (Fig. 2(d)). All diffraction peaks are located between those of bulk tetragonal AgInS₂ and cubic ZnS, but the corresponding peaks are slightly shifted to larger angles, as is typical for the incorporation of Zn(II) ions into chalcopyrite AIS [30, 59]. The average crystal size calculated using the Scherrer equation was 2.3 nm. The HR-TEM images of the AIS/ZnS QDs show a slight increase in size to c.a. 3 nm after Zn(II) shelling (Fig. 2(e)). This subtle size increase found by HR-TEM was not congruent with the formation of complete monolayer of ZnS. Therefore, our AIS/ZnS QDs can be most likely regarded as a quaternary alloy directly at the AIS core/shell interface rather than a pure core/shell assembly.

3.3 Screening of the synthesis parameters

Subsequently, the influence of the synthesis parameters like the molar ratios of the AIS/ZnS-constituting components (Ag:In, S:In, Zn:In), the capping ligand ratio (MPA:In), and the pH were screened. The goals were to (i) evaluate the influence of each parameter on the optical properties of the resulting AIS QDs, (ii) quantify the relevance of each parameter with respect to the application-relevant features of the QDs obtained, and (iii) assess possible interferences between the parameters. To achieve these goals, a two-level multivariate DoE was performed, in which more than one parameter was studied simultaneously. The lower and upper limits of the parameters used are summarized in Table 1. For each synthesis of the 2⁻¹ fractional factorial design approach (Table S4 in the ESM), a complete optical characterization was done by measuring \( \lambda_{\text{max}} \) of the PL, QY, and the PL decay kinetics (Table S5 in the ESM). QY was considered the best parameter to assess the quality of the synthesized QDs. It was thus used as an outcome to construct a mathematical model, which was subsequently used for the fitting of the experimental data. More details are provided in the ESM (Table S4 in the ESM).

\( t \)-statistics were used to assess the influence of the different optimization parameters on QY. Their interferences are summarized in Fig. 3. In this figure, the \( t \)-value presents a measure for the absolute difference, in terms of standard deviation, between the mean and null hypothesis that the effect is zero. Therefore, the size of the \( t \)-value correlates with the relevance of the effect, with higher \( t \)-values implying a higher importance. As the chart displays the absolute values of the effects, a color code is used to represent positive and negative effects by green and blue bars, respectively. Apparently, the MPA:In ratio is the most important parameter. It has a negative effect, meaning that a decrease of the MPA:In ratio promotes an increase in QY. The MPA:In ratio, the Ag:In ratio, the interplay between the Ag:In ratio and pH (Ag:In × pH), the interplay between the MPA:In ratio and pH (MPA:In × pH), and the pH were considered in a statistically significant manner as they are above the calculated threshold line (Fig. 3, red line) of 2.23 with the currently selected terms and an alpha risk level of 0.05. The remaining terms were regarded as insignificant and subsequently neglected.

The results are in accordance with the chemistry behind the synthesis. The reactivity of In(III) is the major reaction limiting factor. Considering the aqueous medium used for the synthesis and the hardness of In(III), this cation reacts preferentially with the hydroxide ion, forming In(OH)₃, rather than being incorporated into the AgInS₂ structure [3]. In(III) can form stable complexes with MPA, and at alkaline pH, the thiol group of MPA is able to form polynuclear complexes with Indium(III) (In[MPA]₃⁻, In[MPA]₄⁻, In[MPA]₅⁻, and In[MPA]₆⁻ species) [38, 72]. Therefore, depending on the MPA:In ratio, the In[MPA] complex which is formed can affect the In(III) reactivity, and thus dramatically influence QY. Considering the Ag(I) and In(III) softness mismatch, the preparation of AIS/ZnS QDs requires the use of a non-stoichiometric amount of In(III). Therefore, the extent of non-stoichiometry, expressed by the Ag:In ratio, is directly related to the quality of the synthesized QDs. In the presence of cation mismatch, the pH plays a major role in the formation of alloyed QDs [3]. The pH can influence the MPA charge and then eventually on the formation of indium(III) hydroxide or zinc(II) hydroxide. Therefore, it is reasonable to assume that the interaction of the pH value with the MPA:In ratio, and the interaction of the pH with the Ag:In ratio was more significant than the pH value itself. On the other hand, the sulfide ions were present in excess compared to the amount of limiting reagent Ag(I), providing a sufficient chalcogenide pool concentration. The evidence of sulfide excess also supports the formation of a chalcopyrite AgInS₂-based nanostructure instead of a cubic AgInS₃-based nanostructure. Similarly, Zn(II) was also present in excess and its diffusion into the AIS lattice rapidly reached a saturation point. Therefore, the S:In and Zn:In ratios used seemed not to be important for the QY values obtained for the AIS/ZnS QDs (Fig. 3). Contrary to the Ag:In and MPA:In ratios, the interplay between pH and S:In or Zn:In ratios were also not relevant for the QY of the AIS QDs. This suggests that the pH does not influence the HS⁻/S²⁻ equilibrium nor the formation of zinc(II) hydroxide to an extent that reduces the required effective ion concentrations. As these parameters had a negative effect on QY, both were set to a value below 1 during the subsequent optimization.
3.4 Modelling of the AIS/ZnS QDs synthesis

Once the three most important parameters were identified, they were fine-tuned by a central composite design (CCD) comprising 19 experiments. This multivariate design of experiment was chosen because it involves replicated synthesis to improve the model predictability and to estimate experimentally related errors [73, 74]. Each parameter was evaluated at five different levels and under extreme conditions [75] (Table S7 in the ESM). For one of the extreme conditions, namely performing the reaction with a MPA:In ratio of 2.6 (entry 11, Table S7 in the ESM), a white precipitate, possibly indium hydroxide, was formed during synthesis (data not shown). This indicates that a MPA:In ratio of at least 4 is required to guarantee the complete dissolution of In(III). The QD samples obtained under these conditions were thus not used for the construction of the models. The remaining 18 samples were fully characterized by steady-state (λ_{max} and QY) and time-resolved PL measurements (average lifetime, <τ>) and in terms of the elemental composition of the obtained QDs (QD(Ag:In) and QD(Zn:In)) by ICP-OES (Table S8 in the ESM). For the sake of a more practical method, the PL emission maxima were expressed on a wavelength scale (λ_{max}) using the spectra directly provided by the spectrophotometer. Based upon this large collection of experimental data, five models were predicted, one for each outcome of the reaction (Table 2).

A quadratic equation was the best fitting model for all the different sets of our experimental data (Table 2). The model equations predict the response value by substituting a, b, and c for the corresponding experimental parameters Ag:In ratio, MPA:In ratio, and pH. Within the range of the experimentally varied parameters used in this work, the predicted response was within the validated response range (Table 2). All models were significant with p-values > F lower than 0.0001 (ANOVA analysis). The goodness of the fits, assessed by the adjusted-\(R^2\) and the predicted-\(R^2\) values, was considered excellent based on the size of the obtained adjusted- and predicted-\(R^2\) values exceeding 0.9 and 0.8, respectively [76]. Moreover, the Lack-of-Fit test, used to evaluate the goodness of the fits (in addition to \(R^2\)), yielded insignificant results (\(p\)-value > \(F\) higher than 0.05). This finding indicated that our models were valid. Adequate precision and a metric of signal-to-noise ratio indicated a suitable model discrimination (desirable > 4) [77]. More details and further analysis of the statistics behind our models are provided in the ESM (Tables S9–S13 in the ESM).

3.5 Optimization to QY

As previously stated, QY is the best parameter to assess the quality of the synthesized AIS/ZnS QDs. Therefore, based on the developed QY model, a rational design of ternary QDs was done with special emphasis on AIS/ZnS QDs with the highest QY.

The correlation between the QY values and different synthetic parameters previously identified is depicted in Fig. 4. Based on our experimental data-based QY model, highly luminescent AIS/ZnS QDs, with QY > 0.5 can be obtained by performing the synthesis at a pH between 8.5 and 9.5 (Fig. 4(a)), a MPA:In ratio between 4.5 and 6.5 (Fig. 4(a)), and an Ag:In ratio between 0.13 and 0.22 (Fig. 4(b)), respectively. The numeric resolution of the QY model focused on the highest QY values predicted for the following reaction conditions: an Ag:In ratio of 0.18, a MPA:In ratio of 5.77, and a pH of 8.91. Subsequently, five replicated syntheses were performed using these conditions in order to experimentally validate the QY model. The predicted and experimentally obtained QY values are summarized in Fig. 4(c). The excellent agreement between these values confirm the accuracy of our experimental-based model.

Our model was developed based on syntheses performed using time and temperature for the screening conditions (MW irradiation for 10 min at 110 °C plus 5 min at 100 °C). By employing optimum conditions for these parameters, like a MW irradiation for 50 min at 100 °C plus 30 min at 100 °C, AIS/ZnS QDs with QY of 0.6 were obtained. Considering that the AIS/ZnS were directly synthesized in water without a post-synthesis purification, the obtained QY values are high and it is superior to the one found on previously reported MPA-capped AIS/ZnS QDs [78]. Although AIS/ZnS QDs with a higher QY have been reported so far, these QDs were synthesized by a hot-injection method in an organic solvent [10, 79, 80]. This procedure is known to typically lead to the highest QY values, yet it is more complex and requires also ligand exchange, silanization or micellar encapsulation to render the resulting QDs water-dispersible. The experimentally determined QY data shown in Fig. 4(c) were obtained from three independent syntheses. The small standard deviations underline the excellent batch-to-batch repeatability of our MW-assisted synthesis method (see Table S14 in the ESM). The optical properties of the highly emissive MPA-capped AIS/ZnS QDs (best-AIS/ZnS QDs) are summarized in Fig. 4(d). The elemental analysis of the composition of the QY-optimized AIS/ZnS QDs gave a Ag:In ratio of 0.61 and a Zn:In ratio of 1.64 (the agreement of the experimental and predicted values is further discussed in the next chapter). Apparently, the most luminescent AIS/ZnS QDs correspond to QDs with Ag:In:Zn ratios near 1:1:5.3.

Table 2  Summary of the regression models predicted for each PL response of the central composite design (CCD)

| Model equations | Validated response range | Model \(F\)-value | Model (\(p\)-value > \(F\)) | Lack-of-fit (\(p\)-value > \(F\)) | Adjusted \(R^2\) | Predicted \(R^2\) | Adequate precision |
|-----------------|-------------------------|-----------------|-----------------|-----------------|----------------|----------------|-----------------|
| QY = -3.64 + 2.68a + 0.24b + 0.72c + 0.03ab + 0.04ac | 0.205–0.524 | 44.31 | < 0.0001 | 0.2375 | 0.9582 | 0.8538 | 19.62 |
| \(\lambda_{max} = 1144.99 + 1797.47a - 3.606 - 166.23c - 6.23ab - 157.50bc - 0.626b - 60.98a^2 + 0.30b^2 + 11.50c^2\) | 617–733 nm | 86.32 | < 0.0001 | 0.2128 | 0.9783 | 0.9065 | 35.31 |
| QD(Ag:In) = -2.28 + 3.52a + 0.01b + 0.50c - 0.03ab - 0.09a + 0.01bc + 2.11bc - 0.06bc | 0.25–1.04 | 538.96 | < 0.0001 | 0.3285 | 0.9965 | 0.9865 | 84.39 |
| QD(Zn:In) = -8.71 - 8.40a + 0.20b + 2.53c - 0.07ab - 0.04ac + 0.01bc + 14.49a^2 - 0.01b^2 - 0.15c^2 | 0.56–1.92 | 84.90 | < 0.0001 | 0.5112 | 0.9780 | 0.9285 | 37.91 |
| \(<\tau> = 645.6 + 5186.3a - 14.3b - 141.8c + 3.5ab - 328.3ac - 2.8bc + 742.1a^2 + 3.7b^2 + 13.6c^2\) | 398–619 ns | 35.43 | < 0.0001 | 0.1444 | 0.9480 | 0.8037 | 21.98 |

*In the model equations a is the feeding Ag:In ratio used for the QD synthesis, which was validated for values between 0.1 and 0.3; b is the feeding MPA:In ratio, which was validated for values between 4 and 8; c is the pH of the reaction, which was validated for values between 8.5 and 10.5. QD(Ag:In) and QD(Zn:In) refers to the corresponding ratios present in the resulting AIS/ZnS QDs.
defined emission wavelength and a known chemical composition. Luminescent AIS/ZnS QDs, but also AIS/ZnS QDs with a rational design was developed, that provides not only highly elemental composition of the resulting AIS/ZnS NCs. Therefore, used in the reaction mixture can be different from the actual stoichiometric ratios, it is expected that the precursor ratios of the precursors. However, due to the use of non-stoichiometric ratios, this can introduce a certain uncertainty into the derived chemical composition, the Ag:In ratio effectively present in the QDs (QD(Ag:In) ratio) decreased slightly (Fig. 5(f)). This finding is attributed to a higher exchange rate of Zn(II) for Ag(I). The low Ag-pH-focused strategy of keeping the Ag:In ratio constant at 0.1 and increasing the pH from 8.5 to 10.5 also led to a red shift of λ_max (Fig. 5(a), grey arrow). For the low Ag-based strategy, the Ag:In ratios maintained constant at a low value (Ag:In ratio of 8.5), while the pH is increased (Fig. 5(a), dashed arrow). The identification and use of more than one strategy to achieve the same goal emphasizes the role of DoE and its multivariate nature, as such predictions are only possible when more than one parameter is studied at the same time.

Following the low pH-focused strategy by fixing the pH at 8.5 and increasing the Ag:In ratio from 0.1 to 0.3, λ_max was red-shifted from about 630 to 700 nm (Fig. 5(a), grey arrow). Under these conditions, the MPA:In ratio was not that relevant for the emission tunability, as λ_max did not change significantly for the different MPA:In ratios used (Fig. 5(d)). In a similar manner as λ_max, also <τ> increased with increasing Ag:In ratio from 0.1 to 0.3 and a pH of 8.5 (Fig. 5(d)). Independent of the optimization strategy employed, a red shift is always associated with PL broadening (see Fig. S12 in the ESM). However, the large FWHM originates mainly from an intrinsic inhomogeneous PL broadening [19] with possible (smaller) contributions from the size polydispersity, distribution in composition, and Ostwald ripening. Moreover, the MPA:In ratio also did not have a significant impact on the response of <τ> (Fig. 5(e)). In terms of chemical composition, the Ag:In ratio effectively present in the AIS/ZnS QDs (QD(Ag:In) ratio) increased with increasing Ag:In ratio used in the reaction mixture (Ag:In ratio) (Fig. 5(c)), a feature frequently found on I–III–VI QDs [81], while the effective Zn:In ratio found in the AIS/ZnS QDs (QD(Zn:In) ratio) decreased slightly (Fig. 5(f)). This finding is attributed to a higher exchange rate of Zn(II) for Ag(I). The low Ag- in the AIS/ZnS QD emission, can mainly be achieved by a low pH-focused and a low Ag(I)-focused strategy using a low value (pH of 8.5), while the Ag:In ratio is increased (Fig. 5(a), grey arrow). For the low Ag-based strategy, the Ag:In ratios maintained constant at a low value (Ag:In ratio of 8.5), while the pH is increased (Fig. 5(a), dashed arrow). The identification and use of more than one strategy to achieve the same goal emphasizes the role of DoE and its multivariate nature, as such predictions are only possible when more than one parameter is studied at the same time.

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3.6 Optimization of the tunability of PL emission

The emission of the AIS/ZnS QDs can be tuned by the feeding ratios of the precursors. However, due to the use of non-stoichiometric ratios, it is expected that the precursor ratios used in the reaction mixture can be different from the actual elemental composition of the resulting AIS/ZnS NCs. Therefore, a rational design was developed, that provides not only highly luminescent AIS/ZnS QDs, but also AIS/ZnS QDs with a defined emission wavelength and a known chemical composition. Additionally, also <τ> was considered. However, this value is not as relevant as the parameters QY and λ_max, and eventually also the FWHM of the PL band and additionally considering the multiexponential nature of the PL decay kinetics (and hence its challenging to fit) together with its often pronounced dependence on emission wavelength (and possibly also on excitation wavelength that was, however, beyond the scope of this study) can introduce a certain uncertainty into the derived PL lifetimes.

The correlation between the different parameters examined and the features derived from our models are shown in Fig. 5 as surface and contour plots. The surface plots were generated as a function of two parameters while the third parameter was kept constant. Visual inspection of the surface plot allows the rational design of AIS/ZnS QDs with the desired PL properties, while the exact value can be predicted by substitution of the equation parameters provided in Table 2.

Considering the target of this optimization, the tunability of the AIS/ZnS QD emission, can mainly be achieved by a low pH-focused and a low Ag(I)-focused strategy using a low value (pH of 8.5), while the Ag:In ratio is increased (Fig. 5(a), grey arrow). For the low Ag-based strategy, the Ag:In ratios maintained constant at a low value (Ag:In ratio of 8.5), while the pH is increased (Fig. 5(a), dashed arrow). The identification and use of more than one strategy to achieve the same goal emphasizes the role of DoE and its multivariate nature, as such predictions are only possible when more than one parameter is studied at the same time.
experimental data, the variability in the experimental data like the relative standard deviations found for QY, PL decay measurements or the determination of the zinc(II) amount by ICP-OES were automatically reflected by the model's accuracy of predicting certain properties or reaction conditions to realize certain features. Although the prediction accuracy for most of the desired PL features can be still refined, our goal to describe the highly complex correlation between the different synthetic parameters and the optical properties for ternary core/shell QDs consisting of four different constituents and an organic ligand shell was achieved.

The range of emission wavelengths obtained with our $\lambda_{\text{max}}$ model was also affected by the choice of the synthesis parameters and their allowed range in variation used for developing this experiment-based model, namely the range of considered variations in the Ag:In ratio (from 0.1 to 0.3). Utilizing the low-pH strategy, we expanded our $\lambda_{\text{max}}$ model by exploring different combinations of pH and Ag:In ratios (Table S15 in the ESM). Figure 7(b) shows the PL emission spectra of AIS/ZnS QDs obtained with Ag:In ratios varying from 0.01 to 0.325. This led to QDs with $\lambda_{\text{max}}$ changing from 565 to 725 nm for Ag:In of 0.01 and 0.325. A blue emission ($\lambda_{\text{max}} < 500$ nm) could not be realized, as the AIS/ZnS QDs synthesized with a very low amount of silver(I) showed only a very weak luminescence (QY of 0.05 for QDs with Ag:In of 0.01, Table S15 in the ESM). High QYs in the red region of the visible spectrum and the near infrared region were satisfactorily achieved (QY of 0.24

**Figure 5**  Surface and contour plots of the response functions of the PL features to changes in the different parameters affecting AIS/ZnS QD performance. The relation between pH, Ag:In, and $\lambda_{\text{max}}$ (a), $\tau_{\text{av}}$ (b), QD(Ag:In) (c), and QD(Zn:In) (f), when MPA:In is fixed at 8. The relation between MPA:In, Ag:In, and $\lambda_{\text{max}}$ (d), and $\tau_{\text{av}}$ (e), when pH is fixed at 8.5.

**Figure 6** Comparison between the predicted and experimentally determined PL features of AIS/ZnS QDs designed with a target PL emission wavelength. The 95% prediction interval represents the interval in which 99% of the QD population lay with a 95% confidence.

**Figure 7** (a) AIS/ZnS QDs excited with a UV lamp. (b) PL emission of AIS/ZnS QDs synthetized with different Ag:In ratios; the Ag:In ratios are given in the legend. (c) XRD diffraction pattern of AIS/ZnS QDs synthetized with different Ag:In ratios.
for QDs with Ag:In of 0.325, see Table S15 in the ESM). As expected, extrapolating outside of the design space increased the prediction uncertainty because of the lack of experimental data collected for such PL properties and used for developing a model (Fig. S14 in the ESM). When the reaction is performed at low pH with increasing Ag:In feeding ratio, the Ag:In ratio present in the QDs is increased (Figs. 5(c) and 5(f)). This stoichiometric elemental composition was also reflected in the XRD pattern of the resulting QDs, as AIS/ZnS QDs synthesized with increasing Ag:In feeding ratios showed diffraction peaks of increasing sharpness shifted to smaller angles (Fig. 7(c)).

### 3.7 Relationship between QDs structure and PL properties

The developed models also allow to establish the relationship between the synthesis experimental conditions, the obtained AIS QDs chemical structure, and the resulting PL properties. Figure 8 summarizes three paradigmatic examples of this relationship. In the first example, AIS QDs synthesis were designed using the lowest Ag:In ratio and pH of our experimental settings (Ag:In = 0.1, pH = 8.5). These conditions yield AIS/ZnS QDs with non-stoichiometric Ag:In:Zn ratios of about 1:3:4, which emit around 620 nm, with relatively short PL lifetimes, considering the range of decays typically found for AIS/ZnS QDs (Fig. 8). A synthesis design where the Ag feeding ratio is kept low and the pH is increased (Ag:In = 0.1, pH = 10.5), leads to QDs with almost similar Ag:In:Zn ratios, while increasing the feeding Ag content at a pH of 8.5 (Ag:In = 0.3, pH = 8.5) results in almost stoichiometric AIS QD structures with Ag:In:Zn ratios of about 1:1:1 (Fig. 8). Apparently, the silver amount used in the QD synthesis is the limiting reactant for the incorporation of Ag(I) into the AIS nanocrystals, independently of the pH used for the synthesis. However, the different chemical compositions of the AIS/ZnS QDs obtained show almost the same PL emission. This effect might possibly arise from the underlying PL emission mechanism of these ternary QDs. For this complex system, it seems reasonable to assume that, depending on the synthesis conditions used, different PL mechanisms can assume a predominant role. For example, the PL red shift achieved with stoichiometric AIS/ZnS QDs could be possibly ascribed to a change in the defect sites within the QD volume. This is also reflected by changes in the PL lifetimes found in this series with values of $\tau$ of about 600 ns vs. 500 ns. For QDs synthesized with the conditions of pH = 8.5/Ag:In = 0.3 and pH = 10.5/Ag:In = 0.1, these effects are more pronounced than for AIS QDs with a non-stoichiometric Ag:In:Zn ratio of 1:3:4. Considering its complex and heterogeneous lattice structure and the lack of defined PL mechanism, the establishment of a well-defined relationship is daunting, and further research is required to better understand how these properties are interlinked.

### 4 Conclusions

To fulfill the high expectations imposed on cadmium-free ternary I–III–VI semiconductor QDs, a rational approach to their preparation with respect to the targeted PL features like PL emission color, spectral linewidth, QY, and for some applications involving lifetime encoding and time-gated emission, even PL decay kinetics/PL lifetime, is needed. Although ternary core–shell QDs like AIS/ZnS QDs can be obtained in high quality by a facile synthetic route in water, the proper choice of the many experimental parameters affecting the optical properties of the resulting QDs and the resulting AIS/ZnS QDs under different synthesis conditions, that QY can be steadily increased by refining the reactions conditions, emission tunability, also with consequences in terms of PL lifetime and QD elemental composition, can be achieved either by a low pH-focused or low Ag-focused approach. Moreover, the large set of data collected in this work confirms features already described for AIS/ZnS QDs in the literature. This includes the role played by the QDs chemical composition and the proposed PL mechanisms accounting for the broad PL emission band.

In summary, we could successfully model the highly complex correlation between the different synthetic parameters and the optical properties for ternary core/shell QDs. These developments in the predictive and experiment-based modelling of the synthesis of more complex QDs, like ternary QDs containing three different metal ions with varying reactivities and a shelling step, are expected to pave the road to a deeper understanding of fundamental properties of this class of semiconductors. In the future, we plan to refine these models to further improve their prediction accuracy and to apply them also to other ternary QDs, like core and core–shell Cu–In–S (CIS) and Hg–In–S (HIS) QDs.

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