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Synthesis and functionalisation of silicon nanostructures: General discussion

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**Synthesis and functionalisation of silicon nanostructures: general discussion**

P. Ceroni, C. Crucho, A. Fucikova, A. Goyal, Y. He, A. Reza Kamali, K. Kusova, G. Morselli, K. Dohnalova, J. Paulusse, H. Stephan, W. Sun, M. Lee Tang, H. Zuilof

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## Synthesis and functionalisation of silicon nanostructures: general discussion

Paola Ceroni, Carina Crucho, Anna Fucikova, Ankit Goyal, Yao He, Ali Reza Kamali, Katerina Kusova, Giacomo Morselli, Katerina Dohnalova, Jos Paulusse, Holger Stephan, Wei Sun, Ming Lee Tang and Han Zuilof

**Anna Fucikova** opened a general discussion of the paper by Han Zuilhof: Really nice article. Could the authors please tell us if they tried to dry their samples and redissolve them, and did they maintain their optical properties?

**Han Zuilof** replied: Thank you for the compliment. No, we did not try to dry up our samples, as evaporating the 2.5 ml of DMSO in which the particles were dispersed would take at least 2 days of heating at 80 °C and 1 mbar. During this time, oxidation of the particles (especially the nanoparticles capped with smaller silanols) will take place, which would also affect the optical properties. For the nanoparticles capped with decyldimethylsilanol, this experiment could perhaps be tried, but it was not attempted for the current work.

**Carina Crucho** said: A few years ago, I developed an approach to track silica surface modification and quantify functional group coverage using only solution NMR on silica nanoparticles.<sup>1</sup> Looking at your NMR spectrum, the signals are quite visible. I think it would be interesting to do a quantification and calculate the number of molecules per nanoparticle. Knowing the number of Si-H bonds, it would be possible to see how many Si-H groups had reacted and whether the ligands were monolayered or adsorbed on the surface. The broadening of the NMR peaks is due to restricted mobility of the species.

<sup>1</sup> C. I. C. Crucho, C. Baleizão and J. P. S. Farinha, *Anal. Chem.*, 2017, 89(1), 681–687, DOI: 10.1021/acs.analchem.6b03117.

**Han Zuilof** answered: First of all, that method is really nice – great work! It would indeed be very interesting to be able to quantify the number of molecules per nanoparticle as obtained *via* our method. While quantification might be somewhat limited in accuracy, this would certainly be of interest for future studies!

**Ming Lee Tang** remarked: Hello. Nice to meet you virtually – I've read many of the papers from your group. Too bad we couldn't meet in person. (1) Have you done XRD to verify that this microwave synthesis does indeed produce Si? I see there is TEM data but I am just curious. (2) Do silanols without flanking dimethyl groups work for this functionalization, *i.e.* R-CH<sub>2</sub>SiOH, not R-CMe<sub>2</sub>SiOH presented here?

**Han Zuilof** responded: Thanks for your comments! XRD was performed on the nanoparticles produced using this microwave method; those data were published in a previous paper from our group.<sup>1</sup> We also considered using silanols without flanking dimethyl groups due to the reduced steric hindrance, but did not include them in the present paper. Our main concern with the use of such “unflanked” silanols was the stability, as the Si-H bond present in such silanols might also react with another silanol or environmental oxygen, leading to multilayers and oxidation.

<sup>1</sup> S. P. Pujari, H. Driss, F. Bannani, B. van Lagen and H. Zuilhof, *Chem. Mater.*, 2018, **30**, 6503–6512.

**Katerina Dohmalova** remarked: First, I would like to voice great collegial appreciation for the fact that the authors are contributing to the difficult and complex research field of the bottom-up synthesis of Si nanoparticles. They are offering an interesting synthesis and capping routes, which seem very up-scalable and “simple”. Nevertheless, I am of the opinion that the authors do not offer any evidence that the emissive material is truly the Si nanoparticles. It is beyond doubt that the authors produced a material that emits brightly, and they show Si content in the solution, but there is no evidence that it is the silicon content that emits. Independent of that, there are also further doubts because (i) none of the existing theoretical models suggest that crystalline (or amorphous) Si nanoparticles of ~6 nm mean diameter could have visible emission with fast radiative rates, and (ii) recently many critical papers have appeared proving that bottom-up Si nanoparticle synthesis routes are “plagued” with highly emissive carbon nanomaterial by-products (including the cited paper by Oliinyk *et al.*<sup>1</sup>), especially when the synthesis route involves organic material and some form of heating (including microwaves). Given this landscape, I am of the opinion (open to debate) that the presented evidence does not show that brightly emissive Si nanoparticles can be produced using the proposed method and would like to ask for (1) supporting evidence for this claim (such as correlative optical-Raman/AFM/STM/SEM microscopy, or similar), plus (2) a repeated microwave synthesis without the Si precursor (as the simplest step).

<sup>1</sup> B. V. Oliinyk, D. Korytko, V. Lysenko and S. Alekseev, *Chem. Mater.*, 2019, **31**, 7167.

**Han Zuilof** replied: First of all, thanks for the comments – they point at a recent discussion on the nature of the NPs produced by these wet-chemical methods induced by Oliinyk *et al.*<sup>1</sup>, and we think both points strike at the heart of this scientific discussion.

The complete characterization of the particles used in this study was published previously by our group.<sup>2</sup> Since the synthesis of the particles is not the main focus of the current paper, such extensive characterization was not repeated here. We



did perform a control reaction without the silicon compound, and the optical properties of this mixture were significantly different (about 50 nm blue-shifted). In addition, the XPS of our NPs does not display N, thereby excluding that we are looking at  $C_wN_xSi_yO_z$  species with a high value of  $x$ . Since we form significant amounts of NPs in our method (typically, 100s of mgs of isolated NPs per experiment), significant sources of elements are needed to get to a substantial contribution to the composition of the NPs. Of course, all this primarily only shows that the species formed with the Si source present is different to those formed without its presence, but this at least indicates that the fluorescent species contains silicon and no nitrogen. In addition, upon exposure to ambient air, the fluorescence of the silicon mixture displays a large blue-shift, and a white precipitate (confirmed to be  $SiO_2$  by XPS) forms in the solution. If the solution is exposed to air or water for longer times, the fluorescence drops in intensity as the precipitate sinks to the bottom of the cuvette. Therefore, we would argue that the fluorescent material in our study is indeed a silicon species. If the fluorescent material was carbon nanoparticles, the fluorescent properties would likely not change readily or upon removal of  $SiO_2$ . Finally, it is evident that more work is clearly needed in this field, also in view of the still wide-ranging variation in optical properties and deviations between experiment and theory. Collaborative efforts between synthetic chemists, spectroscopists and theoreticians are likely to be the most fruitful to clarify the issues at hand here.

- 1 B. V. Oliinyk, D. Korytko, V. Lysenko and S. Alekseev, *Chem. Mater.*, 2019, **31**, 7167–7172.  
2 S. P. Pujari, H. Driss, F. Bannani, B. van Lagen and H. Zuilhof, *Chem. Mater.*, 2018, **30**, 6503–6512.

**Ali Reza Kamali** opened a general discussion of the paper by Ankit Goyal: In this work, silicon nanoparticles with particle sizes of less than 20 nm were ball-milled with attrition ball-milling equipment using WC balls for 20 h. It is mentioned that the temperature is raised to 500 °C during the ball-milling process. I have three questions: (1) How could the temperature inside the ball-milling jar be estimated? (2) In my opinion, 500 °C is very difficult to reach during normal ball-milling processes. One simple consequence of such a high temperature is that the high pressures caused by the expansion of gas inside the milling jar lead to either an explosion or a leakage problem. Can you comment on this please? (3) What was the level of W and C contamination from the WC milling media, and what was its effect on the optical performance of the Si nanoparticles?

**Ankit Goyal** responded: Thank you for the questions. We used ~20 micrometer particles as a starting powder. (1) Local temperatures at the surface of the sub-microscopic particles could reach up to 500 °C. In existing commercial or modified home-made ball-mills (such as ours), there is no provision for measuring the actual temperature inside the mill. Even if one could measure the temperature inside the chamber, maybe using IR detectors, it is very difficult to measure sub-microscopic temperatures during a continuous random process. 500 °C is a theoretical estimate. (2) In commercial ball-mills where sealed jars are used, it is very difficult to mill silicon or any hard materials. As you say, that could lead to a very high temperature and cause an explosion, but in our case, we have a modified ball-mill where we have a provision for continuous cooling to avoid too

much heat and continuous gas flow so the milling jar is not pressurized at any moment during the process. (3) I haven't seen any traces of tungsten in the sample. I saw SiC formation in the FTIR so I would assume some carbon would have come from the milling media, but exact quantification wasn't done. I assume it would be less than one part per thousand (ppt). Carbon caused the formation of a Si-C surface on the silicon core, which could be one possible reason for the multi-phononic PL peak we saw in the PL spectrum, but it could also be due to the presence of metallic impurities so this part is still to be figured out.

**Holger Stephan** opened a general discussion of the paper by Giacomo Morselli: Have you carried out dynamic light scattering (DLS) measurements with ammonium-terminated silicon nanocrystals suspended in methanol/water in order to get information about the size distribution and zeta potential?

**Giacomo Morselli** replied: We performed both the analyses suggested by the kind reader. However, in an aqueous solution of KCl (1 mM) we observed aggregation (DLS size about 100 nm and zeta potential +14 mV), a slight quenching and blue-shift over time, probably due to the oxidation of the surface. This is the reason why we aimed to further functionalize the surface with amide bonds (to carboxymethyl PEG or other biological molecules), capping all the amino groups and protecting the surface. Moreover, amino-functionalised SiNCs are reported to be cytotoxic, and this is another reason to carry out the amide coupling. We didn't perform the DLS measurements in methanol, in which the nanocrystals seem to be more stable (well-suspended and maintaining their photoluminescence after more than one year). This could be interesting and we thank the reader very much for the suggestion.

**Holger Stephan** remarked: Are coupling reactions of ammonium-terminated silicon nanocrystals with biological molecules such as peptides also planned? This would be very interesting.

**Giacomo Morselli** answered: Yes, we are planning to functionalise SiNCs with peptides and, more generally, each molecule that we aim to link to the SiNC surface could be interesting for ameliorating their properties and widening their applications.

**Carina Crucho** asked: I wonder if the authors tried to do a quantification of the amine groups with the ninhydrin test? This is an important result. It is also important for the complete characterization of the material. In addition, this is widely used in the characterization of amine functionalized silica nanoparticles, as for example in the work developed by Sun *et al.*<sup>1</sup> The authors could then compare the results with the ones in the paper by Stephan and coworkers from the present Faraday Discussion (DOI: 10.1039/c9fd00091g).

1 Y. Sun, F. Kunc, V. Balhara, B. Coleman, O. Kodra, M. Raza, M. Chen, A. Brinkmann, G. P. Lopinski and L. J. Johnston, *Nanoscale Adv.*, 2019, **1**, 1598–1607, DOI: 10.1039/c9na00016j.

**Giacomo Morselli** responded: We performed a quantification of the amino groups from the NMR spectra, comparing with a standard at a known



concentration. About 2 chlorosilanes out of 3 reacted with the trityl amine. This is due to the steric hindrance of the triphenylmethyl group.

**Carina Crucho** commented: I work with silica nanoparticles and I use quantification by solution-state  $^1\text{H-NMR}$  to quantify organic moieties (hydrophobic and hydrophilic) attached to the nanoparticle surface.<sup>1</sup> I know from experience that in the case of amine groups, as the protonated amines have solubility in water, it is possible to see the NMR peaks of the protons attached to the carbon next to the amine group or next to the silicon atom (even without dissolution of the silica matrix) if the NMR spectra are recorded in  $\text{D}_2\text{O}$ . In Fig. 1 of the paper (DOI: 10.1039/c9fd00089e), spectra (a) and (b) were recorded in different NMR solvents, so we can't compare. I wonder if the authors tried different NMR solvents or mixtures of NMR solvents, for example, DMSO and  $\text{D}_2\text{O}$ .

<sup>1</sup> C. I. C. Crucho, C. Baleizão and J. P. S. Farinha, *Anal. Chem.*, 2017, **89**(1), 681–687, DOI: 10.1021/acs.analchem.6b03117.

**Giacomo Morselli** replied: Unfortunately, the tritylamine functionalised SiNCs and the deprotected ones could not be suspended in the same solvent. So, we could only assess the fading of the aromatic groups in the second spectrum. We thank the reader for the suggestion.

**Carina Crucho** remarked: I wonder if the authors considered using zeta potential measurements to monitor changes on the particle surface?

**Giacomo Morselli** answered: We performed zeta potential measurements in 1 mM KCl (aq), yielding a potential of +14 mV (DLS measurements confirmed slight aggregation of the nanoparticles in the same solution). Moreover, a slight quenching and blue-shift was observed in aqueous solution over time, probably due to the oxidation of the surface. This is the reason why we aimed to further functionalize the surface with amide bonds (to carboxymethyl PEG or other biological molecules), capping all the amino groups and protecting the surface.

**Ankit Goyal** remarked: I have some questions regarding the photophysical properties of the synthesized SiNCs: 1. The PL spectrum shown in Fig. 4(a) of the paper (DOI: 10.1039/c9fd00089e) looks very broad (~520 nm to 1000 nm) which suggests a broad size distribution. Have you measured the size distribution or done some size separation to see size dependant emission? What does the PLE look like for the obtained PL spectrum, and please mention the excitation wavelength used to obtain this PL spectrum.

**Giacomo Morselli** responded: The emission spectrum looks very broad because it is reconstructed and the band shape is affected by this procedure: due to the position of the emission of the sample, we had to record it with two different detectors, one for visible light (excitation at 452 nm) and one for the NIR spectral range (excitation at 610 nm), and then combine the two spectra. Unfortunately, the maximum lies exactly in the middle of the sensitivity zones for the two detectors, resulting in a hollow at about 750 nm. With our analysis software

we could “flatten” the zone, but there should be a maximum instead. The PLE spectrum is the green line in Fig. 8 of the paper (DOI: 10.1039/c9fd00089e).

**Ankit Goyal** commented: 2. In Fig. 5 of the paper (DOI: 10.1039/c9fd00089e), the absorption spectrum also looks shifted along with the PL of the SiNCs. Could you please comment on how oxidation happened in water but not in ethanol? I assume “A” is absorbance here?

**Giacomo Morselli** replied: It is really difficult to assess if the absorbance is shifted: the sample was more dilute than the one in ethanol and so the curve is lower. Anyway, the oxidation also occurs in ethanol, but at a much slower rate.

**Ankit Goyal** remarked: 3. You mentioned that upon excitation at 340 nm, 70% of light is absorbed by pyrene and 30% of light is absorbed by the silicon core. Could you please comment on how you quantified light absorbance here?

**Giacomo Morselli** responded: The absorption spectrum of pyrene-functionalised silicon nanocrystals closely matches the absorption spectrum of the pyrene chromophore and the pristine silicon nanocrystals, demonstrating no significant interaction between the chromophores and the silicon core in the ground state. Therefore, superimposing the absorption spectra of pyrene-free silicon nanocrystals and pyrene-functionalised silicon nanocrystals with the same silicon concentration (Fig. 6 of the paper, DOI: 10.1039/c9fd00089e), the difference in the absorbance at 340 nm is due to the pyrene moieties, which is 70% of the total.

**Ankit Goyal** commented: 4. You have mentioned that: “The same value (3.7 ns) corresponds to the rise time in PL emission of the SiNCs at 700 nm upon excitation at 340 nm, which proves the occurrence of energy transfer from the pyrenes to the silicon core.” This is quite unclear. In which figure do you see emission at 700 nm?

**Giacomo Morselli** responded: The emission of the silicon core at 700 nm is visible in Fig. 7a and b (dashed green line) of the paper (DOI: 10.1039/c9fd00089e).

**Holger Stephan** opened a general discussion of the paper by Yao He: Have you investigated how stably europium is bound within Eu@SiNPs in cell medium in the presence of challenging proteins?

**Yao He** replied: Thanks for your valuable comments. In our case, the Eu@SiNP nanothermometer maintains stable fluorescence intensity for 48 h of storage in cell media (DMEM and RPMI 1640).

**Holger Stephan** commented: Do you believe that the Eu@SiNP-based nanothermometer can also be used *in vivo*, for example to differentiate between normal and highly proliferative cells?



**Yao He** responded: The Eu@SiNP-based nanothermometer is useful for *in vitro* applications but it is not suitable *in vivo* due to its blue emission. To address this issue, we plan to design new kinds of NIR-emitting nanothermometers in the future, which would be available for *in vivo* applications.

**Wei Sun** remarked: Prof. He is a very well-known expert in the field of bio-applications of silicon nanostructures. This work is also innovative in its nanothermometer use. I would just like to draw his attention to the fact that a recent report has different thoughts on the synthesis, optical properties and definition of SiNPs synthesized using APTMS and trisodium citrate dihydrate (Na<sub>3</sub>Cit) under microwave heating.<sup>1</sup> The authors showed that even without a Si source, similar luminescent nanomaterials were also generated under the reaction conditions. The paper by de Cola and coworkers in this issue of *Faraday Discussions* (DOI: 10.1039/c9fd00127a) has also reported similar concerns. Personally, I think the luminescence obviously did not originate from the band gap of SiQDs, and the NPs synthesized seem to be a composite of Si, C, N and O, as seen from the XPS results where Si appeared to be mostly in its higher oxidation states, very different from the Si(0) nanoparticles synthesized from thermal disproportionation or non-thermal plasma. Nevertheless, since the particles contained Si and performed well in the demonstrated applications, I appreciate the work, so this is just something interesting with respect to the description and definition of "SiNPs" that I would like to mention.

1 B. V. Oliinyk, D. Korytko, V. Lysenko and S. Alekseev, *Chem. Mater.*, 2019, **31**, 7167–7172.

**Yao He** answered: We agree with these opinions that the luminescence did not originate from the band gap of SiQDs, and the NPs synthesized seem to be a composite of Si, C, N, and O. Based on the optical characterization (*e.g.*, Fig. 4 and 5, DOI: 10.1039/c9fd00088g) and previous reports,<sup>1–4</sup> we deduce that the luminescence of Eu@SiNPs is contributed by both the quantum-size effect and surface properties (*e.g.*, surface defects and surface ligands). On the other hand, we thank you for your kind reminder about the recent report regarding the difference between SiNPs and CNPs (carbon NPs). We actually noted the paper several months ago, and then made a systematic comparison between SiNPs (synthesized using APTMS and trisodium citrate dihydrate) and CNPs (synthesized without a Si source). Based on our experimental data, both SiNPs and CNPs produce similar luminescence; however, they show distinctive differences in terms of optical stability (*e.g.*, pH and storage stability) and biological effects (*e.g.*, intracellular distribution). Moreover, XPS and element analysis provide convincing evidence that the SiNPs contain Si element, consistent with the above comment (*i.e.*, "the NPs synthesized seem to be a composite of Si, C, N, and O").

We really appreciate these precious comments and suggestions, thanks again!

1 X. Shen, B. Song, B. Fang, X. Yuan, Y. Li, S. Wang, S. Ji and Y. He, *Nano Res.*, 2019, **12**, 315–322.

2 S. Ciampi, J. B. Harper and J. Gooding, *Chem. Soc. Rev.*, 2010, **39**, 2158–2183.

3 M. Dasog, J. Kehrle, B. Rieger and J. G. C. Veinot, *Angew. Chem., Int. Ed.*, 2016, **55**, 2322–2339.

4 J. M. Lauerhaas and M. J. Sailor, *Science*, 1993, **261**, 1567–1568.

**Ming Lee Tang** opened a general discussion of the paper by Anna Fucikova: Hi there. I read your 2014 *ACS Photonics* paper<sup>1</sup> and was very surprised to see the narrow linewidth of the silicon nanoparticles in your report since my group routinely measures broad photoluminescence linewidths. Here you show similar experimental observations – very intriguing. You include TEM, but is there XRD data showing that nanocrystalline Si is present?

<sup>1</sup> I. Sychugov, A. Fucikova, F. Pevere, Z. Yang, J. G. C. Veinot and J. Linnros, *ACS Photonics*, 2014, **1**, 998–1005.

**Anna Fucikova** responded: Thanks for the question. We were surprised by the narrow linewidths as well, therefore we tried to do XRD but there were too few nanoparticles present in the sample so we could not get reliable data. Although the synthesis produces perfect nanocrystals, it does not produce a sufficient amount of them for mass characterization methods. Therefore, we decided to test our idea differently: we prepared a set of samples which only differed in the length of the molecule and had a ketone group in the molecule (we used acetone, methyl isobutyl ketone, and ethyl acetate) – our results are summarized in this *Faraday Discussions* paper (DOI: 10.1039/c9fd00093c). We confirmed that the shorter the molecule, the thinner the shell and the narrower the linewidth, which is in agreement with our theory from the 2014 *ACS Photonics* paper.<sup>1</sup> The crystallinity of the nanoparticles was confirmed with TEM but also indirectly *via* optical characterization of the single silicon nanocrystals. They have the same properties as silicon nanocrystals with a silicon oxide shell except for the linewidth. They blink, spectral hopping is observed, they respond similarly to higher excitation power, and their luminescence properties respond in the same way to lowering the temperature except that we do not observe any phonon replicas in the spectra of single nanocrystals. This might contribute to the even narrower linewidth and also indicates that the shell is uniform and rigid.

<sup>1</sup> I. Sychugov, A. Fucikova, F. Pevere, Z. Yang, J. G. C. Veinot and J. Linnros, *ACS Photonics*, 2014, **1**, 998–1005.

**Paola Ceroni** remarked: Q1: Would it be possible to liberate your SiNCs from the surrounding matrix and make measurements by dispersing them in solution?

**Anna Fucikova** responded: Thank you for this question. We successfully liberated the silicon nanocrystals from the matrix and the photoluminescence study of the individual nanocrystals showed the same photoluminescence linewidth distribution as the nanocrystals in the matrix. Unfortunately the sample concentration was not sufficient to perform the measurements in solution.

**Paola Ceroni** asked: Q2: Do you know the emission quantum yield of your particles?

**Anna Fucikova** answered: Since the amount of sample produced is so low, we could not measure the absolute quantum yield. We have just a rough estimate based on a comparison of the spectral blinking of individual nanocrystals with thin shells and silicon nanocrystals with silicon oxide shells: our samples blinked



2-3 times less than the ones with silicon oxide shells. Based on this, the QY is higher than 30% as a minimum.

**Paola Ceroni** remarked: Q3: What is the experimental evidence for spectral hopping? How can you estimate a 3% spectral hopping?

**Anna Fucikova** responded: The spectral hopping was observed by photoluminescence spectral studies of single nanocrystals. More than 200 nanocrystals were spectrally analysed for each sample, and out of these spectra of individual nanocrystals, around 3% showed spectral hopping.

**Ali Reza Kamali** opened a general discussion of the paper by Jos M. J. Paulusse: In this research, the synthesis of Si QDs by oxidation of magnesium silicide ( $Mg_2Si$ ) with bromine ( $Br_2$ ) is reported. Also, a control sample is prepared without the involvement of the Si source. The reaction involving  $Mg_2Si$  produced 24.4 mg of a dark brown material. On the other hand, the reaction without the presence of  $Mg_2Si$  also produced 24.5 mg of a dark brown material. The Si amount in the Si QDs and the control sample was found to be 2.2 and 0.4 wt%, respectively. 1. Considering that there was no Si source ( $Mg_2Si$ ) involved in the preparation of the control sample, what is the source of the Si observed in the elemental analysis of the control sample?

**Jos Paulusse** responded: The detected Si content is low. We think the source of Si in the control reaction is possibly grease or lubricants on the glassware/equipment used (though care was taken to avoid the use of silicone-based grease).

**Ali Reza Kamali** asked: 2. Which kind of elemental analysis was used to evaluate the silicon content of the samples?

**Jos Paulusse** replied: The Wurzschnitt digestion was used for digestion of silicon, followed by UV-Vis analysis.

**Ali Reza Kamali** asked: 3. How was the formation of crystalline silicon confirmed? Which characterization technique was used to confirm this?

**Jos Paulusse** responded: The formation of crystalline silicon was not confirmed. TEM was used to detect any crystalline silicon, but no crystalline materials were observed.

**Katerina Kusova** remarked: This publication questions the wet-chemical synthesis of SiQDs by the oxidation of  $Mg_2Si$  with  $Br_2$  and calls for a critical assessment of other synthesis techniques. I have more of a comment than a question here. When I measured a sample prepared by the solution-phase reduction of  $SiCl_4$  with  $LiAlH_4$ , I compared the PL of the sample and that of a pure solvent. The PL was about 100x higher in the sample, suggesting that the observed PL came from SiQDs. However, a more thorough analysis (spectra, decays, several excitation wavelengths) showed that the PL of the SiQD sample and that of the pure solvent were exactly the same, this time proving that the



product of the synthesis only amplified the (very weak) PL of the solvent. Do the authors have experience with a similar problem?

**Jos Paulusse** replied: We indeed have indications that the reduction synthesis also produces small molecule materials with blue fluorescence emission. These molecules are possibly based on only several silicon atoms instead of larger clusters.

## Conflicts of interest

There are no conflicts to declare.