Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In this manuscript, the authors represent a kind of supramolecular fluorescent sensor for liquefied petroleum gas sensing using self-assembled nanocubes with good selectivity and sensitivity, which was a development for detection of small neutral gases. It's interesting that the shape complementarity between LPG molecules and cube-shaped inner space induced selective responses of nanocube's fluorescence intensity without strong intermolecular interactions. In the study, the investigations of photophysical properties and sensing mechanisms were deep and detailed. However, some descriptions and conclusions were kind of unsupported and unprecise according to the results of experiments and the design of some experiments was not reasonable enough.
In summary, the study and results are meaningful for the field of gas sensing by using supramolecular self-assembled systems. However, several parts in the manuscript should be thought over and modified seriously. Therefore, I suggest major revision and consideration of acceptance by COMMUNICATIONS CHEMISTRY after the following points are addressed.

Below are several issues for the authors to consider for the revision:

1. Page 2, paragraph 1, "A main drawback of this type of sensors is low selectivity for LPG…". Here, some references should be cited to prove your conclusion.
2. Page 2, paragraph 2, "upon encapsulation of LPG, the fluorescence intensity was enhanced by 3.9 times than that before the encapsulation, which indicates great sensitivity for LPG…". A large increase of fluorescence intensity doesn't mean a good sensitivity directly, although the authors have proved its sensitivity after some experiments, they need to express the results more accurate here.
3. Page 3, paragraph 1, "Although the absorption spectra for the monomer GSA (1•Cl2) measured in methanol and the nanocube ([16]Cl12) in water are similar…". In general, the comparison of adsorption and emission spectra should be in the same solvent systems. However, as for this case, the monomers need to self-assemble in water to obtain the nanocubes. So here the authors should state it clearly.
4. Page 3, paragraph 1, line 7. The word "components" may should be "exponentials".
5. Page 3, paragraph 2. All the "firstly excited state" should be changed to "the first excitation state".
6. Page 3, paragraph 2. The data of fluorescence anisotropy should be marked in the figures (such as 0.16, 0.11, 0.12 ns, 0.20 ns). The conclusions drawn from fluorescence anisotropy measurement need some references to support and for readers to refer to.
7. Figure 2C. Why did the fluorescence anisotropy of 12+ monomers have more drastic fluctuation than that of the nanocubes?
8. Page 4, paragraph 1. "which would be due to weaker molecular meshing between the GSAs in the nanocube whose size became larger so as to fit the neutral guest molecules…". Maybe it's because the difficulties for larger guest molecules to enter inside the nanocubes so that the fluorescence intensity of a part of nanocubed couldn't be increased. So here it's better to provide the NMR spectra of nanocubes after introducing other LPG molecules to prove the encapsulation of larger LPG molecules.
9. Page 4, paragraph 1. The "Na2[10B12H12]" part. Is it possible that the attraction from anionic species induced the disassembly of nanocubes and decreased the fluorescence?
10. Figure 3A. From the fluorescence spectra, the emission wavelength didn't change, but from the photographs, the fluorescence changed from green to blue, why? If it's because the error from photography, it's better to take new photos to show the real fluorescence.
11. Page 5, paragraph 2. The concentration of nanocubes will also influence the results of LPG gas concentration dependence. I suggest that this experiment should be designed more reasonable or express more precise.
12. Figure 3E. Why did the difference of nanocubes' fluorescence intensity before and after

encapsulation of LPG obviously got smaller during recycling experiments?

Reviewer #2 (Remarks to the Author):

In this work, Zhan et al. report a supramolecular nanocube which shows fluorescence enhancement while the liquefied petroleum gas molecule is encapsulated into the cavity. Based on this observation, the authors designed a fluorescence sensor for the LPG. Since the nanocube structure has been reported in two previous papers by the same group (NATURE COMMUNICATIONS 2019, 10:1440; COMMUNICATIONS CHEMISTRY 2018, 1:14), the novelty of this work doesn't seem to warrant its publication on Communications Chemistry. It would fit better in other specialized journals. Also, the authors need to address the following questions/concerns before publishing this work somewhere else:

1. The self-assembly process of the monomer to nanocube in solution should be described in detail. The 1H NMR of the nanocube itself needs to be analyzed.
2. The authors claimed that the fluorescence of the nanocube was due to the AIE mechanism (the restricted motion of the aromatic rings). Further experiments need to be done to prove this speculation.
3. The detailed analysis/discussion about the mechanism of the fluorescence enhancement with the liquefied petroleum gas molecule inside of the cavity is needed.
4. Longer linear alkanes caused the decrease of the fluorescence. 1H NMR experiment should tell the encapsulation mode and the content.
5. It doesn't seem appropriate to call 3.9 times enhancement "high sensitivity".
6. The authors claimed that the “nanocube can detect LPG whose concentration is lower than the low explosive limit and that the concentration of LPG in the sample air can be determined by the fluorescence intensity of the nanocube.” Direct experimental evidence is needed, instead of the analysis of the concentration dependence of the fluorescence intensity.

Reviewer #3 (Remarks to the Author):

In this manuscript, the authors developed a supramolecular fluorescence sensor for LPG using a nanocube self-assembled from six molecules of gear-shaped amphiphiles in water. And this supramolecular fluorescence sensor exhibited high selectivity, high sensitivity, quick response and high stability for LPG. In general, this work is very interesting. All characterizations were performed very carefully and the results described here are very reasonable. I would recommend this paper to publish in Chemical Communications with the following suggestions.

1. The length of the manuscript is a little bit long. Some overdetailed descriptions and discussions, even explanations should be simplified appropriately.
1) For example, this part of content “It was found that…without any decomposition of the nanocube.” in the second paragraph of the Introduction section should be simplified and should not involve too many experimental details.
2) In the results section, the first three paragraphs were concentrated on the mechanism discussions of different fluorescent observations. I think these results should not be the focus of the present work and should be simplified appropriately.
2. According to the content of the main text, the detection of LPG and the corresponding potential used as commercial device were mentioned until the end of the manuscript, so Figure 1 should be divided properly and represented to well match the content described in the text.
3. Regarding the fluorescence changes encapsulated different guest molecules, the authors mentioned that “linear alkanes from n-propane to n-decane in the nanocube brought about the

increase in the fluorescence intensity from the nanocube", while the authors then also claimed that "those longer than n-butane the fluorescence intensity of the nanocube decreased with increase in the total volume of the linear". These results are confusing and should be re-described clearly. In addition, the authors claimed that "the reason why smaller alkanes than propane (methane and ethane) cannot be trapped in the nanocube would be due to entropic disadvantage arising from that more methane or ethane molecules should be needed to properly fill the inner space of the nanocube". This explanation is not convincing enough. It is likely that there exists a dynamic balance between their complexation and dissociation, which ultimately results in an unchanged fluorescence intensity.

4. For the quenched fluorescence when encapsulated anionic species ($Na_2[10B12H12]$), the authors deemed that it was due to the stronger ACQ caused by π-stacking. However, the above anionic species should not bring any significant impact on the intermolecular π-stackings.

Response to Reviewers for COMMSCHEM-19-0198-T

To reviewer 1

We are grateful for your careful review and valuable comments. Our response is as follows. Thank you again for your time in advance.

Reviewer 1's comments and our response

Comment:

In this manuscript, the authors represent a kind of supramolecular fluorescent sensor for liquefied petroleum gas sensing using self-assembled nanocubes with good selectivity and sensitivity, which was a development for detection of small neutral gases. It's interesting that the shape complementarity between LPG molecules and cube-shaped inner space induced selective responses of nanocube's fluorescence intensity without strong intermolecular interactions. In the study, the investigations of photophysical properties and sensing mechanisms were deep and detailed. However, *some descriptions and conclusions were kind of unsupported and unprecise according to the results of experiments and the design of some experiments was not reasonable enough.*

In summary, the study and results are meaningful for the field of gas sensing by using supramolecular self-assembled systems. However, *several parts in the manuscript should be thought over and modified seriously.* Therefore, I suggest major revision and consideration of acceptance by COMMUNICATIONS CHEMISTRY after the following points are addressed.

Below are several issues for the authors to consider for the revision:

1. Page 2, paragraph 1, "*A main drawback of this type of sensors is low selectivity for LPG…*". Here, some references should be cited to prove your conclusion.
2. Page 2, paragraph 2, "*upon encapsulation of LPG, the fluorescence intensity was enhanced by 3.9 times than that before the encapsulation, which indicates great sensitivity for LPG…*". A large increase of fluorescence intensity doesn't mean a good sensitivity directly, although the authors have proved its sensitivity after some experiments, they need to express the results more accurate here.
3. Page 3, paragraph 1, "*Although the absorption spectra for the monomer GSA (**1**•Cl_2) measured in methanol and the nanocube ([**1**$_6$]Cl_{12}) in water are similar…*". In general, the comparison of adsorption and emission spectra should be in the same solvent systems. However, as for this case, the monomers need to self-assemble in water to obtain the nanocubes. So here the authors should state it clearly.
4. Page 3, paragraph 1, line 7. The word "components" may should be "exponentials".
5. Page 3, paragraph 2. All the "firstly excited state" should be changed to "the first excitation state".
6. Page 3, paragraph 2. The data of fluorescence anisotropy should be marked in the figures (such as 0.16, 0.11, 0.12 ns, 0.20 ns). The conclusions drawn from fluorescence anisotropy measurement need some references to support and for readers to refer to.
7. Figure 2C. Why did the fluorescence anisotropy of 12+ monomers have more drastic fluctuation than that of the nanocubes?
8. Page 4, paragraph 1. "*which would be due to weaker molecular meshing between the GSAs in the nanocube whose size became larger so as to fit the neutral guest molecules…*". Maybe it's because the difficulties for larger guest molecules to enter inside the nanocubes so that the fluorescence intensity of a part of nanocubed couldn't be increased. So here it's better to provide the NMR spectra of nanocubes after introducing other LPG molecules to prove the encapsulation of larger LPG molecules.

9. Page 4, paragraph 1. The "$Na_2[^{10}B_{12}H_{12}]$" part. Is it possible that the attraction from anionic species induced the disassembly of nanocubes and decreased the fluorescence?
10. Figure 3A. From the fluorescence spectra, the emission wavelength didn't change, but from the photographs, the fluorescence changed from green to blue, why? If it's because the error from photography, it's better to take new photos to show the real fluorescence.
11. Page 5, paragraph 2. The concentration of nanocubes will also influence the results of LPG gas concentration dependence. I suggest that this experiment should be designed more reasonable or express more precise.
12. Figure 3E. Why did the difference of nanocubes' fluorescence intensity before and after encapsulation of LPG obviously got smaller during recycling experiments?

Comment 1:

Page 2, paragraph 1, "*A main drawback of this type of sensors is low selectivity for LPG…*". Here, some references should be cited to prove your conclusion.

Response to the reviewer

According to the reviewer's suggestion, an appropriate paper is cited as reference 11 in the revised manuscript.

Comment 2:

Page 2, paragraph 2, "*upon encapsulation of LPG, the fluorescence intensity was enhanced by 3.9 times than that before the encapsulation, which indicates great sensitivity for LPG…*". A large increase of fluorescence intensity doesn't mean a good sensitivity directly, although the authors have proved its sensitivity after some experiments, they need to express the results more accurate here.

Response to the reviewer

As the reviewer pointed out, the increase in the fluorescence intensity does not indicate the "sensitivity". This description is edited in the revised manuscript.

Comment 3:

Page 3, paragraph 1, "*Although the absorption spectra for the monomer GSA (**1**•Cl_2) measured in methanol and the nanocube ([**1**$_6$]Cl_{12}) in water are similar…*". In general, the comparison of adsorption and emission spectra should be in the same solvent systems. However, as for this case, the monomers need to self-assemble in water to obtain the nanocubes. So here the authors should state it clearly.

Response to the reviewer

As the reviewer pointed out, in general absorption and emission spectra measured under the same condition should be compared. In this case, since the monomer GSA and the nanocube exist in a different solvent, we cannot show the spectra measured in the same solvent. According to the reviewer's kind suggestion, we describe in the revised manuscript that the absorption and emission spectra were measured in different solvents with its reason.

Comment 4:

Page 3, paragraph 1, line 7. The word "components" may should be "exponentials".

Response to the reviewer

According to the reviewer's kind suggestion, the word is replaced in the revised manuscript.

Comment 5:

Page 3, paragraph 2. All the "firstly excited state" should be changed to "the first excitation state".

Response to the reviewer

According to the reviewer's kind suggestion, these phrases are corrected in the revised manuscript.

Comment 6:

Page 3, paragraph 2. The data of fluorescence anisotropy should be marked in the figures (such as 0.16, 0.11, 0.12 ns, 0.20 ns). The conclusions drawn from fluorescence anisotropy measurement need some references to support and for readers to refer to.

Response to the reviewer

According to the reviewer's suggestion, the data of the fluorescence anisotropy are added in the revised Figure 2c and cites two appropriate references.

Comment 7:

Figure 2C. Why did the fluorescence anisotropy of 12+ monomers have more drastic fluctuation than that of the nanocubes?

Response to the reviewer

The larger fluctuation of the fluorescence anisotropy for monomer GSA is probably due to the significantly weaker fluorescence intensity of the monomer GSA than that of the nanocubes. The average of three measurements does not show a significant fluctuation, so the average data are shown in Figure 2c in the revised manuscript.

Comment 8:

Page 4, paragraph 1. "*which would be due to weaker molecular meshing between the GSAs in the nanocube whose size became larger so as to fit the neutral guest molecules…*". Maybe it's because the difficulties for larger guest molecules to enter inside the nanocubes so that the fluorescence intensity of a part of nanocubed couldn't be increased. So here *it's better to provide the NMR spectra of nanocubes after introducing other LPG molecules to prove the encapsulation of larger LPG molecules.*

Response to the reviewer

The encapsulation of *n*-alkanes longer than *n*-butane was reported in our previous paper (*Nat. Commun.* **9**, 4530 (2018) [DOI: 10.1038/s41467-018-06874-y]) and the ^{1}H NMR of the nanocubes that encapsulate the *n*-alkanes are shown in Supplementary Figure 4 in the previous paper. According to the ^{1}H NMR spectra, all the nanocubes encapsulate *n*-alkanes after convergence and there were no nanocubes that do not encapsulate *n*-alkanes, even for long *n*-alkanes. To indicate that the encapsulation of the *n*-alkanes was reported in our previous paper, the reference is cited in the revised manuscript.

Comment 9:

Page 4, paragraph 1. The "$Na_2[^{10}B_{12}H_{12}]$" part. Is it possible that the attraction from anionic species induced the disassembly of nanocubes and decreased the fluorescence?

Response to the reviewer

As the reviewer proposed, when anionic species is added in a solution of the nanocube, the decomposition or disassembly of the nanocube may occur. However, $Na_2[^{10}B_{12}H_{12}]$ did not cause any decomposition nor disassembly, but was encapsulated in the nanocube, which is confirmed by the ^{1}H NMR spectrum obtained after the addition of $Na_2[^{10}B_{12}H_{12}]$ (Supplementary Figure 3).

Comment 10:
Figure 3A. From the fluorescence spectra, the emission wavelength didn't change, but from the photographs, the fluorescence changed from green to blue, why? If it's because the error from photography, it's better to take new photos to show the real fluorescence.

Response to the reviewer
According to the reviewer's suggestion, the photographs in Figure 3a were replaced with new ones in the revised manuscript.

Comment 11:
Page 5, paragraph 2. The concentration of the nanocubes will also influence the results of LPG gas concentration dependence. I suggest that this experiment should be designed more reasonable or express more precise.

Response to the reviewer
The linear relation between the fluorescence intensity and the logarithm of the percentage of LPG is not affected by the concentration of the nanocube. This linear relation is understandable qualitatively; the concentration of the nanocubes encapsulating LPG molecules increases with increase in the concentration of LPG, which enhances the fluorescence intensity. However, it is not simple to explain this linear relation quantitatively. If the fluorescence of the nanocube simply depends on the concentration of the nanocube encapsulating LPG molecules, the fluorescence intensity should linearly increase with the concentration of LPG in the solution. It is reasonable to expect that the concentration of LPG in water increase with the percentage of LPG in the gas injected in a solution of the nanocube, so the fluorescence of the nanocube would linearly increase with the percentage of LPG. Therefore, the dependence of the fluorescence intensity on the concentration of LPG in the sample gas is more complicated than expected under the assumption where the encapsulation of LPG by bubbling of the sample gas is in equilibrium, which suggests that the encapsulation of LPG is not perfectly under equilibrium. But, we do not have any clear idea to reasonably explain this relation.

Comment 12:
Figure 3E. Why did the difference of nanocubes' fluorescence intensity before and after encapsulation of LPG obviously got smaller during recycling experiments?

Response to the reviewer
As a matter of fact, the reason for decrease in the difference of fluorescence intensity after the cycles is still unclear. However, we have carried out following experiments to exclude several possibilities.

(1) The solution of the nanocube after the several cycles was monitored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra measured after the removal of and encapsulation of LPG in each cycle did not show any significant change, indicating that the nanocube is not decomposed nor disassembled into the monomer during the cycles. The ^{1}H NMR spectra are shown in Supplementary Figure 22 in the revised SI.

(2) LPG molecules are encapsulated in the nanocube in the presence of $NaHCO_3$ or Na_2CO_3 and any spectral change was observed by the addition of $NaHCO_3$ and Na_2CO_3. These results indicate that HCO_3^- and CO_3^{2-}, which would be produced after CO_2 was dissolved in a solution of the nanocube during the cycling, do not compete with LPG.
The above discussions are added in the revised manuscript.

To reviewer 2

We are grateful for your careful review and valuable comments. Our response is as follows. Thank you again for your time in advance.

Reviewer 2's comments and our response

Reviewer's Comment

In this work, Zhan et al. report a supramolecular nanocube which shows fluorescence enhancement while the liquefied petroleum gas molecule is encapsulated into the cavity. Based on this observation, the authors designed a fluorescence sensor for the LPG. 1*Since the nanocube structure has been reported in two previous papers by the same group (NATURE COMMUNICATIONS 2019, 10:1440; COMMUNICATIONS CHEMISTRY 2018, 1:14), the novelty of this work doesn't seem to warrant its publication on Communications Chemistry. It would fit better in other specialized journals.* Also, the authors need to address the following questions/concerns before publishing this work somewhere else:

1. The self-assembly process of the monomer to nanocube in solution should be described in detail. The ^{1}H NMR of the nanocube itself needs to be analyzed.
2. The authors claimed that the fluorescence of the nanocube was due to the AIE mechanism (the restricted motion of the aromatic rings). Further experiments need to be done to prove this speculation.
3. The detailed analysis/discussion about the mechanism of the fluorescence enhancement with the liquefied petroleum gas molecule inside of the cavity is needed.
4. Longer linear alkanes caused the decrease of the fluorescence. ^{1}H NMR experiment should tell the encapsulation mode and the content.
5. It doesn't seem appropriate to call 3.9 times enhancement "high sensitivity".
6. The authors claimed that the "nanocube can detect LPG whose concentration is lower than the low explosive limit and that the concentration of LPG in the sample air can be determined by the fluorescence intensity of the nanocube." Direct experimental evidence is needed, instead of the analysis of the concentration dependence of the fluorescence intensity.

Comment 1:

1Since the nanocube structure has been reported in two previous papers by the same group (NATURE COMMUNICATIONS 2019, 10:1440; COMMUNICATIONS CHEMISTRY 2018, 1:14), the novelty of this work doesn't seem to warrant its publication on *Communications Chemistry*. It would fit better in other specialized journals.

Response to the reviewer

As the reviewer pointed out, our papers concerning nanocube were published in *Nat. Commun.* (2019) and *Commun. Chem.* (2018). The paper published in *Commun. Chem.* in 2018 reported the thermodynamic stability of the nanocubes, which is affected by the substituents introduced in the gear-shaped amphiphile to discuss the main driving forces to stabilize the nanocube. The paper published in *Nat. Commun.* in 2019 reported a kinetic stability of the nanocube and based on this finding a reversible system between the ordered and disordered states by thermal energy was presented. In this paper, we discuss the photophysical property of the nanocube, which is affected by encapsulation of guest molecules. Although the same nanocube was used in these papers, the results obtained in this paper cannot simply be expected from the results published in our previous

papers. Indeed, this is the first time to discuss the possibility of the use of the nanocubes as a supramolecular sensor. Therefore, we believe that the results reported and discussed in this paper have sufficient novelty to be published in *Communications Chemistry*.

Comment 2:

The self-assembly process of the monomer to nanocube in solution should be described in detail. The ^{1}H NMR of the nanocube itself needs to be analyzed.

Response to the reviewer

The question about how the molecular self-assembly proceeds is one of the hot topics in molecular self-assembly. In our group, a novel method to discuss the self-assembly process, "Quantitative Analysis of Self-Assembly Process (QASAP)", was developed and we have reported 20 papers concerning coordination self-assembly processes since 2014. Thus, we ourselves are very interested in the self-assembly process of the nanocube. One of the difficulties in the analysis of the molecular self-assembly processes is that in most cases the intermediates that can be detected are very limited. Thus, in QASAP the information about the intermediates are obtained from the existence ratios of both the substrates and the products, which are quantified by ^{1}H NMR spectroscopy. In the case of the nanocube, the self-assembly of the GSA into the nanocube is very fast and finishes within a minute, so the time scale of the self-assembly of the nanocube is too fast for us to monitor the process by ^{1}H NMR spectroscopy. As far as we know, it is quite difficult or impossible now to experimentally investigate the self-assembly processes whose time scale is very fast like the nanocubes. Therefore, we investigated the self-assembly process of the nanocube computationally and have already published two papers last year (*J. Phys. Chem. Lett.* **9**, 6082–6088 (2018). [DOI: 10.1021/acs.jpclett.8b02624], *Phys. Chem. Chem. Phys.* **20**, 9115–9122 (2018). [DOI: 10.1039/C8CP00284C]). Though the topic of the molecular self-assembly processes is interesting, we think that the self-assembly process of the nanocube is far from the point of this paper concerning the sensing of LPG by a supramolecular host.

As to the analysis of the ^{1}H NMR spectrum of the nanocube, the ^{1}H NMR spectrum of the nanocube $[\mathbf{1}_6]^{12+}$ was already discussed based on H-H COSY and ^{1}H-^{1}H NOESY spectroscopy to assign the ^{1}H NMR signals of $[\mathbf{1}_6]^{12+}$ in our previous paper (*Commun. Chem.* **1**, 14 (2018).). The ^{1}H NMR spectrum of the nanocube encapsulating LPG (two molecules of *n*-butane and one molecule of *i*-butane) was also analyzed by ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, and ^{1}H DOSY spectroscopy, which are shown in the Supplementary Figures 13–16.

Comment 3:

The authors claimed that the fluorescence of the nanocube was due to the AIE mechanism (the restricted motion of the aromatic rings). Further experiments need to be done to prove this speculation.

Response to the reviewer

In this paper, we discuss the mechanism of the fluorescence from the nanocube by fluorescence lifetime, quantum yield, and fluorescence anisotropy measurements. Based on these results, a proposed fluorescence mechanism in the nanocube is shown in Figure 2. Most of the papers concerning AIE do not discuss the mechanism in detail, only showing the finding that molecular aggregation caused the enhancement of the fluorescence intensity. Tang *et al.* reported a AIE system where hexaphenylsilole, whose chemical structure is similar to GSA, aggregates in a mixed solvent of THF and H_2O with higher content of H_2O to increase the fluorescence intensity (*Adv. Mater.* **26**, 5429 (2014) [DOI: 10.1002/adma.201401356]. Thus, the discussion based on our results besides a

similarity of the chemical structure between GSA and Tang's molecule indicates that AIE is the main reason for the increase in the fluorescence intensity of GSA in the assembled state.

Comment 4:

The detailed analysis/discussion about the mechanism of the fluorescence enhancement with the liquefied petroleum gas molecule inside of the cavity is needed.

Response to the reviewer

According to X-ray analysis of the nanocube whose structure is very similar to that of $[\mathbf{1}_6]^{12+}$, the benzene rings in the hexaphenylbenzene (HPB) core tightly mesh each other, while the outer aromatic rings are stacked. This result has already been discussed in our previous paper (*Commun. Chem.* **1**, 14 (2018). DOI: 10.1038/s42004-018-0014-2). Thus, it is suggested that the self-assembly of the nanocube induces AIE on the HPB parts and ACQ (aggregation-caused quenching) on the outer aromatic rings. This suggests that the fluorescence intensity of the GSAs in the nanocube is determined by the balance between the AIE and the ACQ. Upon encapsulation of LPG molecules in the nanocube, the size of the nanocube becomes large, which is confirmed downfield shift of the three *p*-tolyl methyl signals. The relation between the chemical shift value of the *p*-tolyl methyl signals in the nanocube and the size of the nanocube has already been discussed in our previous paper (*Nat. Commun.* **9**, 4530 (2018) [DOI: 10.1038/s41467-018-06874-y]). The encapsulation does not change the fluorescence wavelength, only affecting the fluorescence intensity, which suggests that the same excited state is produced regardless whether guest molecules are encapsulated or not. Thus, the fluorescence intensity of the nanocube is dependent on the efficiency of emission and the non-radiative decay from the excited state. As the size of the nanocube with LPG molecules is larger than that of the free nanocube, the GSAs in the nanocube with LPG molecules mesh more loosely with each other, which allows the benzene rings in the GSAs to move more freely. The fluorescence intensity of the nanocube with LPG molecules is higher than that of the free nanocube, which is explained by weaker suppression of the AIE from the HPB core than the suppression of the ACQ. This idea is supported by the result that the contraction of the nanocube by the encapsulation of $^{10}B_{12}H_{12}$ diminished the fluorescence intensity of the nanocube and that the fluorescence intensity became weaker by the encapsulation of guest molecules whose volume is larger than that of LPG molecules. It was also found that the encapsulation of LPG molecules (two molecules of *n*-butane and one molecule of *i*-butane) in the nanocube caused dramatic increase in the fluorescence intensity compared when only *n*-butane molecules are encapsulated in the nanocube. This result and the selective encapsulation of two molecules of *n*-butane and one molecule of *i*-butane in the nanocube suggest that a high shape complementarity between the cavity of the nanocube and a cluster of LPG molecules. These discussions have been described in the main text.

Comment 5:

Longer linear alkanes caused the decrease of the fluorescence. ^{1}H NMR experiment should tell the encapsulation mode and the content.

Response to the reviewer

As the reviewer pointed out, it is interesting to discuss the conformation of longer liner alkanes encapsulated in the nanocube, whose inner space is about 1 nm in diameter when the guest molecules are not encapsulated. This point was discussed in our previous paper (*Nat. Commun.* **9**, 4530 (2018) [DOI: 10.1038/s41467-018-06874-y]). Contrary to the result reported by Rebek Jr. that long linear alkanes adopt helical conformation in their supramolecular host, the nanocube does not induce the helical conformation of long linear alkanes. This would be due to high flexibility of the

nanocube, so the nanocube can change its structure so as to fit the shape of the guest molecule. Because we have already discussed this in our previous paper, we think that the same discussion should not be repeated in this paper, only citing the reference.

Comment 6:

It doesn't seem appropriate to call 3.9 times enhancement "high sensitivity".

Response to the reviewer

As the reviewer pointed out, the description that 3.9 times enhancement of the fluorescence indicates high sensitivity is subjective; whether 3.9 times enhancement is high sensitivity or not depends on the system of interest. In this case, the nanocube can detect LPG in the concentration ranging from 0.1 vol% to 100 vol%, showing the linear relationship between the fluorescence intensity of the nanocube and the logarithm of the concentration of LPG. 0.1 vol% of LPG is the lower than the low explosive limit of LPG (0.2 vol%). Compared with previously reported LPG sensors (the lowest LPG concentrations detected are summarized in Supplementary Table 1 in the revised SI), the nanocube indicates high enough sensitivity to detect LPG in a wide range of concentration. The description in the main text is edited to clearly show why we call the 3.9 times enhancement of the fluorescence of the nanocube high sensitivity.

Comment 7:

The authors claimed that the "*nanocube can detect LPG whose concentration is lower than the low explosive limit and that the concentration of LPG in the sample air can be determined by the fluorescence intensity of the nanocube.*" Direct experimental evidence is needed, instead of the analysis of the concentration dependence of the fluorescence intensity.

Response to the reviewer

It is said that the low explosive limit of LPG is 0.2 vol%. It was found that the nanocube can detect LPG whose concentration of higher than 0.1 vol% (Figure 3c) and that the change in the fluorescence intensity linearly correlates to the logarithm of the concentration of LPG. We have clearly emphasized the low explosive limit of LPG (0.2 v%) in the revised manuscript. Although the reviewer requested some other experimental evidence, this study is as basic research as was submitted to *Communications Chemistry*, and we believe that our current results are sufficient to lead this conclusion. If the reviewer kindly recommends a concrete experiment, we would like to conduct as long as it is reasonable and required in this paper.

To reviewer 3

We are grateful for your careful review and valuable comments. Our response is as follows. Thank you again for your time in advance.

Reviewer 3's comments and our response

Reviewer's Comment

In this manuscript, the authors developed a supramolecular fluorescence sensor for LPG using a nanocube self-assembled from six molecules of gear-shaped amphiphiles in water. And this supramolecular fluorescence sensor exhibited high selectivity, high sensitivity, quick response and high stability for LPG. In general, this work is very interesting. All characterizations were performed very carefully and the results described here are very reasonable. I would recommend this paper to publish in Communications Chemistry with the following suggestions.

1. The length of the manuscript is a little bit long. Some overdetailed descriptions and discussions, even explanations should be simplified appropriately.

1) For example, this part of content "It was found that…without any decomposition of the nanocube." in the second paragraph of the Introduction section should be simplified and should not involve too many experimental details.

2) In the results section, the first three paragraphs were concentrated on the mechanism discussions of different fluorescent observations. I think these results should not be the focus of the present work and should be simplified appropriately.

2. According to the content of the main text, the detection of LPG and the corresponding potential used as commercial device were mentioned until the end of the manuscript, so Figure 1 should be divided properly and represented to well match the content described in the text.

3. Regarding the fluorescence changes encapsulated different guest molecules, the authors mentioned that "linear alkanes from n-propane to *n*-decane in the nanocube brought about the increase in the fluorescence intensity from the nanocube", while the authors then also claimed that "those longer than *n*-butane the fluorescence intensity of the nanocube decreased with increase in the total volume of the linear". These results are confusing and should be re-described clearly. In addition, the authors claimed that "the reason why smaller alkanes than propane (methane and ethane) cannot be trapped in the nanocube would be due to entropic disadvantage arising from that more methane or ethane molecules should be needed to properly fill the inner space of the nanocube". This explanation is not convincing enough. It is likely that there exists a dynamic balance between their complexation and dissociation, which ultimately results in an unchanged fluorescence intensity.

4. For the quenched fluorescence when encapsulated anionic species ($Na_2[^{10}B_{12}H_{12}]$), the authors deemed that it was due to the stronger ACQ caused by π-stacking. However, the above anionic species should not bring any significant impact on the intermolecular π-stackings.

Comment 1:

The length of the manuscript is a little bit long. Some overdetailed descriptions and discussions, even explanations should be simplified appropriately.

1) For example, this part of content “It was found that…without any decomposition of the nanocube.” in the second paragraph of the Introduction section should be simplified and should not involve too many experimental details.

2) In the results section, the first three paragraphs were concentrated on the mechanism discussions of different fluorescent observations. I think these results should not be the focus of the present work and should be simplified appropriately.

Response to the reviewer

According to the reviewer’s kind suggestion, the descriptions in the introduction section and the first three paragraphs in the results section are slightly simplified.

Comment 2:

According to the content of the main text, the detection of LPG and the corresponding potential used as commercial device were mentioned until the end of the manuscript, so Figure 1 should be divided properly and represented to well match the content described in the text.

Response to the reviewer

As the reviewer pointed out, Figure 1 is cited in the end of the manuscript. Thus according to the reviewer’s suggestion, this figure is separated from Figure 1 and is assigned as Figure 3a in the revised manuscript. Then the discussion on the practical use of the nanocube for gas sensing is described in the final paragraph in the results section, citing Figure 3a.

Comment 3:

Regarding the fluorescence changes encapsulated different guest molecules, the authors mentioned that “linear alkanes from *n*-propane to *n*-decane in the nanocube brought about the increase in the fluorescence intensity from the nanocube”, while the authors then also claimed that “those longer than *n*-butane the fluorescence intensity of the nanocube decreased with increase in the total volume of the linear”. These results are confusing and should be re-described clearly. In addition, the authors claimed that “the reason why smaller alkanes than propane (methane and ethane) cannot be trapped in the nanocube would be due to entropic disadvantage arising from that more methane or ethane molecules should be needed to properly fill the inner space of the nanocube”. This explanation is not convincing enough. It is likely that there exists a dynamic balance between their complexation and dissociation, which ultimately results in an unchanged fluorescence intensity.

Response to the reviewer

As to the discussion on the effect of the length of *n*-alkanes on the fluorescence intensity of the nanocube in this paragraph (Figure 2e), we found two experimental results: (1) When *n*-alkanes are encapsulated in the nanocube, the fluorescence intensities of the nanocube are higher than that of the free nanocube. (2) The highest fluorescence intensity was found when *n*-butanes are encapsulated in the nanocube. According to the reviewer’s suggestion, the descriptions are edited to avoid confusion.

As to the reason why smaller alkanes than propane are not encapsulated in the nanocube, the reviewer’s idea would be that the rate constant of the encapsulation (k_{on}) is much smaller than that of the release (k_{off}) to lead to very small binding constants for these alkanes based on the relation between the binding constant (K) and the rate constants, $K = k_{on}/k_{off}$. This is true to explain the result from a kinetic point of view. Our idea is based on a thermodynamic point of view. Very small K value indicates that ΔG value for the encapsulation is close to zero or positive. The encapsulation of hydrophobic alkanes in the nanocube is due to (1) the hydrophobic effect and to (2) the attractive

intermolecular interactions between the alkanes and the cavity of the nanocube (mainly van der Waals (vdW) interactions). In addition, as the size and shape of the nanocube slightly change upon the encapsulation, the interactions between the GSAs in the nanocube also change. The expansion of the nanocube by the encapsulation of neutral guest molecules causes weaker molecular meshing between the GSAs to lead to the destabilization of the nanocube. However, when the former two factors overcome this destabilization, the guest molecules can be encapsulated in the nanocube. The hydrophobic effect is related to the number of desolvated water molecules upon the encapsulation. If all the water molecules trapped in the free nanocube are released in a bulk by the encapsulation of the guest molecules, the number of water molecules are the same regardless of the guest molecule, so the difference in the hydrophobic effect by the guest molecules depends on the total desolvation surface area of the guest molecules. As to the attractive intermolecular interactions between the guest molecules and the cavity of the nanocube, considering a very similar chemical nature between *n*-propane and methane or ethane, it is reasonable to consider that the same intermolecular interactions work between the smaller alkanes and the cavity of the nanocube. Considering that three molecules of *n*-propane are filled in the nanocube, smaller methane or ethane would also properly be filled in the cavity of the nanocube. But, more molecules are needed to fill the inner space of the cavity, which is entropically unfavorable. As three molecules of longer *n*-alkanes than propane (*n*-butane, *n*-pentane, and *n*-hexane) are encapsulated in the nanocube, the number of molecules trapped in the nanocube is not determined by the total volume of the guest molecules, suggesting that the entropic factor is important for the stability of the host-guest complex.

Comment 4:

For the quenched fluorescence when encapsulated anionic species ($Na_2[^{10}B_{12}H_{12}]$), the authors deemed that it was due to the stronger ACQ caused by π-stacking. However, the above anionic species should not bring any significant impact on the intermolecular π-stackings.

Response to the reviewer

As the reviewer pointed out, $^{10}B_{12}H_{12}^-$ would not directly interact with the π-stackings in the nanocube. The mechanism to enhance ACQ by the encapsulation of the anionic guest is based on the contraction of the nanocube induced by the anionic guest. The contraction of the nanocube causes the tighter molecular meshing between the GSAs in the nanocube. This leads to enhance both AIE and ACQ. The decrease in the fluorescence intensity by the encapsulation of $^{10}B_{12}H_{12}^-$ indicates that ACQ is more preferentially enhanced by the contraction than AIE. This is probably because the motion of the benzene rings in the hexaphenylbenzene moiety has already been well restricted in the free nanocube, so further AIE cannot be induced by the contraction of the nanocube.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

This revised manuscript can be published as it is now.

Reviewer #3 (Remarks to the Author):

The authors have adequately addressed my previous comments and suggestions. The revisions are satisfactory and the changes are acceptable. The quality of the manuscript has been improved after revision. I do not have further criticism of the work.