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Supramolecular fluorescence sensor for liquefied petroleum gas

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Sensing systems of nonpolar gas molecules without functional groups such as natural gas and liquefied petroleum gas (LPG) remain difficult to develop because of lacking selective detection of such molecules over other gas molecules. Here we report a supramolecular fluorescence sensor for LPG using a 2-nm-sized cube-shaped molecular container i.e. a nanocube self-assembled from six molecules of gear-shaped amphiphiles (GSA) in water. The nanocube selectively encapsulates LPG, while it does not bind other gas molecules. Upon encapsulation of LPG in the nanocube, the fluorescence from the nanocube is enhanced by 3.9 times, which is caused by the restricted motion of the aromatic rings of GSA in the nanocube based on aggregation-induced emission. Besides the high selectivity, high sensitivity, quick response, high stability of the nanocube for LPG, and easy preparation of GSA satisfy the requirement for its practical use for an LPG sensor.

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Liquefied petroleum gas (LPG), which is mainly propane or butane or both, has been one of widely used fuels in daily life (cooking and automobile) and industry for a century all over the world. Recent increase in the use of LPG for refrigerant and aerosol spray has made LPG more familiar in our life unwittingly. As LPG is liquefied under pressure of ca. 1 MPa at room temperature, which is much lower than the required pressure for compressed natural gas (20–32 MPa), LPG has a great advantage in terms of transportation compared with other fuel gases¹. However, its low explosive limit (~0.2 vol%) has often caused accidents and harm². Thus, an LPG sensor that can selectively respond to LPG at low concentration has been awaited. Most of the LPG sensors reported are composed of metal oxides^{3–7} or their composites with conductive polymers^{8–10}. On the surface of these solid materials, LPG is oxidized by O[–] or O^{2–} to CO₂ to co-produce electrons, which enhance the electric conductance of the materials, as is basically the same as conventional semiconductor sensors. A main drawback of this type of sensors is low selectivity for LPG over other gaseous molecules¹¹.

Here we report a supramolecular sensor for LPG that can selectively respond to LPG and output enhanced fluorescence in visible region. The supramolecular sensor is a 2-nm-sized cube-shaped assembly i.e. nanocube consisting of six molecules of gear-shaped amphiphiles (GSAs), which tightly mesh with each other¹². The nanocube has an ~1-nm-sized hydrophobic inner cavity, where several hydrophobic and anionic species are encapsulated to alter the size of the nanocube in an induced-fit manner¹³. It was found that the self-assembly of the nanocube caused a blue fluorescence from hexaphenylbenzene moieties in GSAs at ~450 nm through aggregation-induced emission (AIE)¹⁴ and that the fluorescence intensity was enhanced upon encapsulation of hydrophobic guest molecules by a balance between AIE and aggregation-caused quenching (ACQ)¹⁵ of the GSAs. As far as gas molecules are concerned, the nanocube selectively encapsulates LPG molecules to increase its fluorescence intensity, indicating a great response to LPG. The fluorescence intensity quickly changed depending on the concentration of LPG (response and recovery times are 15 and 6 s, respectively) without any decomposition of the nanocube. This high selectivity, sensitivity, response, and stability of the nanocube for LPG enable us to fabricate a simple sensing system for LPG, whose working principle is different from conventional gas sensors.

Results

Fluorescence of the nanocube. The GSA used in this research is a C_{2v}-symmetric hexaphenylbenzene (HPB) derivative, **1-Cl₂** (Fig. 1a), six molecules of which assemble into a nanocube, [**1₆**]Cl₁₂, in water, while **1-Cl₂** retains its monomer state in methanol¹². Absorption and emission spectra of [**1₆**]Cl₁₂ and of **1-Cl₂** were measured in water and in methanol, respectively. Although the absorption spectra of the monomer GSA (**1-Cl₂**) and the nanocube ([**1₆**]Cl₁₂) are similar, their fluorescence spectra are quite different; the nanocube showed a strong blue fluorescence band at ~450 nm, while the fluorescence of the monomer was very weak (Fig. 2a). The decay of the fluorescence for the monomer and the nanocube contains two exponentials (Supplementary Figs. 1 and 2). Fluorescence lifetimes of the nanocube, 9.5 ± 0.5 ns and 38.9 ± 0.8 ns (Supplementary Fig. 1) in water, are significantly longer than those of the monomer, 1.3 ± 0.06 ns and 8.2 ± 0.5 ns in methanol (Supplementary Fig. 2), suggesting that most of the excited energy in the monomer was lost by non-radiative processes. This fluorescence from the nanocube would be due to the restricted motion of the aromatic rings of the HPB core (colored in red in Fig. 1a) that tightly mesh with each other in the nanocube (AIE mechanism)¹⁴ (Fig. 1b). The quantum yield

of the fluorescence of the nanocube is 5.4%, which is lower than those reported in other AIE systems. This is partly due to the stretching vibrational motion of the nanocube along its S₆-axis¹⁶ and to ACQ arising from π-stacking of the outer aromatic rings (phenyl and pyridinium groups colored in purple and cyan, respectively, in Fig. 1a, b) in the nanocube.

Similar absorption spectra of the monomer and the nanocube (Fig. 2a) indicate that the first excitation state in the nanocube is similar to that of the monomer. A large Stokes shift for the nanocube suggests that the first excitation state ([**1^{*}**]₅)¹²⁺, which resembles to the excited monomer state (**1^{*}**)²⁺, is converted into energetically stabilized emissive states. The observation of two emission bands at 450 and 470 nm suggests the formation of two kinds of vibrational structures. To elucidate the emissive states of the nanocube, time-dependent fluorescence anisotropy measurement for [**1₆**]Cl₁₂ was carried out (Fig. 2c). When the excitation and emission dipoles are non-degenerate and parallel to each other, fluorescence anisotropy shows the maximum value of 0.4. This situation is often realized right after the excitation of molecules. However, the fluorescence anisotropy for monomer **1-Cl₂** decreased from 0.14 (Fig. 2c), which suggests a faster energy-migration process than the rotation of the excited **1²⁺**^{17,18}. This is probably due to the *ipso*-conjugation in the HPB core^{19–22} of **1-Cl₂**. Similarly, the decay of the fluorescence anisotropy of the nanocube started from 0.16. The relaxation time for the nanocube (0.12 ns) is shorter than that for the monomer (0.20 ns), which indicates that a very fast process except that caused by the *ipso*-conjugation occurred in the nanocube. This would be attributed to the energy migration between the GSAs in the nanocube to produce the emissive state, [**1₆^{*}**]¹²⁺, where the excited energy is delocalized in the nanocube (Fig. 2b). There is a possibility that the initial anisotropy values smaller than 0.4 represent the fast delocalization of the electronic excitation among degenerate electronic states rather than non-degenerate states. It is not possible, however, to distinguish the difference by the current time-resolved fluorescence anisotropy measurements.

Effect of guest molecules on fluorescence. The effect of the encapsulation of guest molecules on the fluorescence property of the nanocube was investigated. The encapsulation of *n*-alkanes from *n*-propane to *n*-decane in the nanocube¹³ brought about the increase in the fluorescence intensity without changing the fluorescence wavelength (Fig. 2d). The fluorescence lifetime for the nanocube encapsulating two *n*-decane molecules (8.0 ± 0.6 and 39.4 ± 0.4 ns) is slightly shorter than that of the free nanocube (Supplementary Fig. 1). To exclude the possibility of the vaporization of the guest molecules encapsulated in the nanocube, *n*-decane was used as a guest in this measurement. The decay of the fluorescence anisotropy was also not affected by the encapsulation of the guest molecules (Fig. 2c). These results indicate that the guest molecules in the nanocube do not affect the emissive states except the fluorescence intensity. Among *n*-alkanes tested, *n*-butane led to the highest fluorescence intensity and the increase in the fluorescence intensity gradually decreased with increase in the total volume of the *n*-alkanes encapsulated larger than 300 Å³ (Fig. 2e). This would be because AIE is diminished by weaker molecular meshing between the GSAs in the nanocube encapsulating *n*-alkanes whose total volume are larger than 300 Å³. On the other hand, when the nanocube contracted by the encapsulation of anionic species (Na₂[¹⁰B₁₂H₁₂]) (Supplementary Fig. 3), which is induced by the electrostatic attraction between the cationic nanocube ([**1₆**]¹²⁺) and the anionic guest, the fluorescence intensity decreased by ~39%. This is probably due to stronger ACQ caused by π-stacking of the outer aromatic rings

Fig. 1 Formation of the nanocube complex by the encapsulation of liquefied petroleum gas (LPG). **a** A chemical structure of gear-shaped amphiphile (GSA) **1-Cl₂**, whose fluorescence is negligibly small. **b** A proposed change in the fluorescence intensity of the nanocube composed of six GSAs, **[1₆]Cl₁₂**. Upon self-assembly of the GSA, the motion of the benzene rings in the hexaphenylbenzene parts is restricted to cause aggregation-induced emission (AIE), while π -stacking of the outer aromatic rings causes aggregation-caused quenching (ACQ). Thus, the fluorescence intensity of the nanocube is determined by the conflicting effects of AIE and ACQ. **c** Fluorescence property of the nanocube (**[1₆]Cl₁₂**). Upon UV-irradiation, the nanocube emits in visible region (450 nm). When LPG molecules are encapsulated in the nanocube, the fluorescence intensity from the nanocube is enhanced. **d** ^1H NMR spectra (500 MHz, D_2O , 298 K, **[1²⁺]** = 1 mM) of the nanocube (upper) before and (lower) after the encapsulation of LPG (a mixture of *n*-butane (60 vol%), *i*-butane (39 vol%), and propane (1 vol%)). Asterisk indicates free *i*-butane dissolved in D_2O . The assignment of the signals is shown in the Supplementary Figs. 13–16

(colored in cyan and purple in Fig. 1b) than AIE mainly caused by the restricted motion of the aromatic rings in the HPB core (colored in red in Fig. 1b) upon the contraction of the nanocube.

Sensing of LPG by the nanocube. The performance of the supramolecular sensor for LPG was evaluated. LPG was injected in a solution of the nanocube and the fluorescence intensity at 450 nm was monitored (Fig. 3a). Surprisingly, the nanocube selectively responded to LPG (a mixture of *n*-butane (60 vol%), *i*-butane (39 vol%), and propane (1 vol%)) with the highest fluorescence intensity (3.9 times at 450 nm), which is ~ 1.5 times higher than that observed when pure propane or *n*-butane was encapsulated in the nanocube (Fig. 2d). Thus, the encapsulation of LPG in the nanocube can clearly be visualized by UV-irradiation (Fig. 3b). The quantum yield of the fluorescence also increased to be 16.5% upon encapsulation of LPG. When *i*-butane

molecules are encapsulated, the fluorescence intensity increased by 3.5 times. This result indicates that the shape of guest molecules affects the fluorescence efficiency. Other gas molecules shown in Fig. 3c were not encapsulated in the nanocube, which was confirmed by ^1H NMR spectroscopy (Supplementary Figs. 4–9), so only negligibly small change in the fluorescence intensity of the nanocube was observed for these gas molecules (Supplementary Fig. 12). The reason why smaller alkanes than propane (methane and ethane) cannot be trapped in the nanocube¹³ 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.

The ^1H NMR spectrum of the nanocube encapsulating LPG showed a simple signal pattern with only three *p*-tolyl methyl signals (H^i) and two *N*-methyl signals (H^j) of **1-Cl₂** (Fig. 1d), which indicates the formation of a single species. However, this

Fig. 2 Photophysical property of the nanocube. **a** Steady-state absorption and emission spectra ($\lambda_{\text{ex}} = 305$ nm) of the monomer GSA ($\mathbf{1}\text{-Cl}_2$) in CH_3OH and of the nanocube $[\mathbf{1}_6]\text{Cl}_{12}$ in H_2O ($[\mathbf{1}^{2+}] = 0.09$ mM and 2.25 μM for absorption and fluorescence spectroscopy, respectively). **b** A proposed energy diagram for the emission of the nanocube ($[\mathbf{1}_6]\text{Cl}_{12}$). The first excited state ($[\mathbf{1}^*\mathbf{1}_6]^{12+}$) produced by UV-irradiation is quickly converted into the stable excited state ($[\mathbf{1}_6^*]^{12+}$), where the excited energy is migrated in the nanocube. The observation of the two fluorescence bands at 450 and 470 nm is due to two different vibrational structures. **c** The change in the fluorescence anisotropy of the excited nanocubes, $\mathbf{1}\text{-Cl}_2$, $[\mathbf{1}_6]\text{Cl}_{12}$, and (*n*-decane)₂@ $[\mathbf{1}_6]\text{Cl}_{12}$ ($\lambda_{\text{ex}} = 305$ nm, $[\mathbf{1}^{2+}] = 2.25$ μM). **d** Steady-state fluorescence spectra of the nanocubes that encapsulate different guest molecules (G@ $[\mathbf{1}_6]\text{Cl}_{12}$) ($\lambda_{\text{ex}} = 305$ nm, $[\mathbf{1}^{2+}] = 2.25$ μM). G indicates the guest molecules encapsulated. **e** The change in the fluorescence intensity of the nanocube with the total volume of the guest molecules encapsulated

spectrum is different from those of propane₃@ $[\mathbf{1}_6]\text{Cl}_{12}$ ¹³, (*n*-butane)₃@ $[\mathbf{1}_6]\text{Cl}_{12}$ (Supplementary Figs. 10 and 17), and (*i*-butane)_x@ $[\mathbf{1}_6]\text{Cl}_{12}$ ($x = 3$ or 4) (Supplementary Figs. 11 and 18). According to the integration of the signals for the encapsulated *n*-butane and *i*-butane, *n*-butane and *i*-butane were found to be encapsulated in the nanocube in a 2:1 ratio, indicating that (*n*-butane)₂(*i*-butane)@ $[\mathbf{1}_6]\text{Cl}_{12}$ was selectively produced²³. In contrast, when *i*-butane molecules were encapsulated, two sets of *p*-tolyl methyl signals of the nanocube were observed in a 1:2 ratio, suggesting the formation of two kinds of nanocubes where the number of the encapsulated *i*-butane molecules is different. The integration of the signals of the encapsulated *i*-butane indicated that (*i*-butane)₃@ $[\mathbf{1}_6]\text{Cl}_{12}$ and (*i*-butane)₄@ $[\mathbf{1}_6]\text{Cl}_{12}$ were equilibrated in a 2:1 ratio. The total volume of two molecules of *n*-butane and one molecule of *i*-butane (285 Å³) is almost the same as that of three molecules of *n*-butane or *i*-butane (285 Å³). Thus, the selective formation of (*n*-butane)₂(*i*-butane)@ $[\mathbf{1}_6]\text{Cl}_{12}$ should be due to high shape complementarity between the cube-shaped inner space of the nanocube and a cluster of two molecules of *n*-butane and one molecule of *i*-butane. However, no desymmetrization of the $[\mathbf{1}_6]\text{Cl}_{12}$ nanocube by the guest molecules indicates that tumbling motion of the guests in the nanocube is faster than the NMR time scale. Higher fluorescence intensity of (*n*-butane)₂(*i*-butane)@ $[\mathbf{1}_6]\text{Cl}_{12}$ is also due to the high shape complementarity, which strongly reduces the motion of the aromatic rings in the hexaphenylbenzene core.

The LPG concentration dependence of the fluorescence intensity of the nanocube was investigated. It was found that

the fluorescence intensity linearly increased against the logarithm of the concentration of LPG ranging from 0.1 to 100 vol% (Fig. 3d and Supplementary Fig. 21). This result indicates that the nanocube can detect LPG whose concentration is lower than the low explosive limit (0.2 vol%) and that the concentration of LPG in the sample air can be determined by the fluorescence intensity of the nanocube, so 3.9 times increase in the fluorescence intensity by the encapsulation of 100 vol% LPG is high enough to sense as low concentration of LPG as can be detected by previously reported LPG sensors (Supplementary Table 1).

The encapsulation and release of LPG under sensing condition (bubbling of sample gas with different concentration of LPG) do not exactly take place under equilibrium, but it is worth discussing the performance of the supramolecular sensor based on its binding constant. Considering that the binding constant (K_b) relates to the rate constants of binding (k_{on}) and release (k_{off}), $K_b = k_{\text{on}}/k_{\text{off}}$, when $k_{\text{on}} \gg k_{\text{off}}$, the sensitivity of the sensor is high and the recovery time would be long. Thus, in general, the sensitivity to the target, which is mainly determined by K_b , and the recovery efficiency, which relates to k_{off} , compete with each other. With this in mind, supramolecular sensors that realize real-time monitoring need as large k_{off} as enables the sensor to release the target molecule(s) quickly upon decreasing their concentration. The nanocube does not disassemble at all even at 100 °C and the inner space of the nanocube is surrounded by six GSAs, which made one worry if the encapsulation and release of the target molecules in and from the nanocube were difficult; k_{on}

Fig. 3 Performance of the nanocube as a supramolecular sensor for LPG. **a** Schematic illustration of a supramolecular sensor system for LPG. Sample gas is loaded into an aqueous solution of the supramolecular sensor. When sample gas contains LPG, the fluorescence of the supramolecular sensor that binds LPG molecules (at 450 nm) increases. **b** Photographs of solutions of the nanocube before and after the encapsulation of LPG ($\lambda_{ex} = 356$ nm). **c** Selectivity of the nanocube for gas molecules ($\lambda_{ex} = 305$ nm). **d** The change in the relative fluorescence intensity of the nanocube with the concentration of LPG in air after convergence ($\lambda_{ex} = 305$ nm, $[1^{2+}] = 2.25$ μ M). **e** The response and recovery times of the nanocube for LPG ($\lambda_{ex} = 305$ nm, $[1^{2+}] = 2.25$ μ M). Flow rate of 0.2 vol% LPG and air is 0.5 L min⁻¹. Error bars indicate the standard errors of the means of the fluorescence intensity. The experiments were carried out three times. **f** Recycle use of the supramolecular sensor for the sensing of LPG ($\lambda_{ex} = 305$ nm, $[1^{2+}] = 22.5$ μ M).

and k_{off} would be very small. The rates of exchange ($k_{ex} = k_{on} + k_{off}$) of butanes between in and out of the nanocube were determined by exchange spectroscopy (EXSY) measurement (Supplementary Figs. 19 and 20). The exchange rates for *n*-butane (2.65 s⁻¹) and for *i*-butane (0.153 s⁻¹) are much faster than expected from the fact that there exist only very small holes in the nanocube. As the GSAs in the nanocube only mesh with each other without strong chemical bonds, the encapsulation and release of the guest molecules would take place by partial opening of a GSA. The result that k_{ex} for *i*-butane is smaller than that for *n*-butane indicates that *i*-butanes are more strongly

bound in the nanocube, which is consistent with the higher shape complementarity between *i*-butanes and the nanocube expected by the stronger fluorescence intensity upon the encapsulation of *i*-butanes.

The response and recovery times, which are defined as the time required to reach 90% of the change in the fluorescence intensity compared to the converged states (LPG-bound and free states), were determined using 0.2 vol% LPG and air with a flow rate of 0.5 L min⁻¹. As expected, the response time of 15 s and the recovery time of 6 s are fast enough for us to apply this supramolecular LPG sensor to practical use (Fig. 3e).

The recycle use of the supramolecular sensor was tested by alternate injection of LPG and air in an aqueous solution of $[1_6]^{12+}$ (Fig. 3f). The nanocube could respond to LPG at least five times, though the fluorescence intensity of the free nanocube gradually increased with cycles. The reason for the increase in the fluorescence intensity is unclear. The ^1H NMR spectra of the solution after the injection of air perfectly recovered to the original one (Supplementary Fig. 22), indicating that all the LPG molecules encapsulated in the nanocube were removed by bubbling of air. The encapsulation of CO_3^{2-} and HCO_3^- in the nanocube during the injection of air containing CO_2 was excluded by the result that CO_3^{2-} and HCO_3^- were not encapsulated in the nanocube and by that the same slight increase was observed by injection of N_2 gas.

Discussion

Unlike conventional gas sensors based on semiconductors or others, this supramolecular sensor exhibits extremely high selectivity for LPG over other gas molecules, which is reasonable because the supramolecular sensor, $[1_6]\text{Cl}_{12}$, possesses a 1-nm-sized hydrophobic inner space suitable for the accommodation of several LPG molecules. This supramolecular sensor works at room temperature, while many semiconductor gas sensors require high temperature of 200–500 °C, indicating that the supramolecular sensor operates with lower power consumption. Molecular hosts that can bind gas molecules^{23–37} have been developed so far. A main difference between the nanocube and other molecular hosts is that the nanocube finely responds to the guest molecules and outputs a strong fluorescence signal. This high responding property of the nanocube arises from its precise induced-fit ability¹³, which causes slight change in the molecular meshing between the GSAs in the nanocube to modulate AIE and ACQ. As the GSA (1-Cl_2) can easily be synthesized in a large scale³⁸, the supramolecular LPG sensor can be fabricated from inexpensive materials (1-Cl_2 and water) and several commercial devices (UV lamp, detector, and monitor) shown in Fig. 3a.

Methods

General. All NMR spectra were recorded using a Bruker AV-500 (500 MHz) spectrometer. UV-vis absorption measurements were performed using JASCO V-670. Steady-state fluorescence spectra were obtained using a FP-6500. Quantum yields were measured using Quantaaurus-QY. Time-resolved fluorescence spectra were recorded by a laboratory-built time-resolved fluorescence spectrometer. Unless otherwise noted, all reagents were obtained from commercial suppliers (TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO Chemical Co., Inc., and Sigma-Aldrich Co.) and were used as received. Gaseous methane, ethane, and propane were obtained from GL Sciences Co. Liquefied petroleum gas (LPG), which contains a mixture of 60 vol% *n*-butane, 39 vol% *i*-butane, and 1 vol% propane is obtained from Nichiren Co., Ltd. $\text{Na}_2[^{10}\text{B}_{12}\text{H}_{12}]$ was provided by Stella Chemifa Co. 1-Cl_2 was prepared according to the literature³⁸.

Time-resolved fluorescence spectroscopy. Time-resolved fluorescence spectra were recorded by a laboratory-built time-resolved fluorescence spectrometer. The output from a Ti:sapphire regenerative amplifier (Micra/Legend Elite-HE, Coherent; 800 nm, 1 kHz, ~3.0 W, 40 fs) was converted to 305 nm pulses by an optical parametric amplifier (OPERA Solo, Coherent). The 305 nm radiation was used for fluorescence excitation. The 305 nm pump pulses were focused on the sample solution in a quartz cell while it was stirred by a magnetic stirrer. The pump pulse energy on the sample position was 0.1–0.03 μJ . The fluorescence signal was focused into a spectrograph (Acton SpectraPro SP-2300, Princeton Instruments) through a polarizer, a polarization scrambler and UV cut filters. Two-dimensional spectral and time profiles of the fluorescence signals were obtained by a streak camera (CI0627, Hamamatsu). The fluorescence component polarized at 54.7° with respect to the pump pulse polarization was corrected for recording the excited-state decay kinetics. The fluorescence decay curve $I(t)$ was obtained by adding the fluorescence intensities $I(\lambda, t)$ on each time delay t for a window wavelength range,

$$I(t) = \sum_{\lambda} I(\lambda, t) \quad (1)$$

The fluorescence lifetime was calculated by least-squares analysis, with a model

function of double exponential function convoluted with a Gaussian response function.

For measuring fluorescence anisotropy, we measured the fluorescence signals at time delay t , polarized at parallel and perpendicular directions to the pump polarization, $I_{\parallel}(t)$ and $I_{\perp}(t)$. The fluorescence anisotropy at t , $r(t)$, was then calculated as

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (2)$$

Each of the observed fluorescence anisotropy decay curves was fitted by an exponential function

$$r(t) = r(0) \exp\left(-\frac{t}{\tau}\right) \quad (3)$$

where τ is the time constant of the anisotropy decay. The anisotropy value $r(0)$ corresponds to an angle θ between the absorption and fluorescence transitional moments when they are non-degenerate.

$$r(0) = \frac{1}{5} (3 \cos^2 \theta - 1) \quad (4)$$

The anisotropy becomes 0.4 when the two transition moments are parallel with each other. It is -0.2 when they are perpendicular.

Water was deionized and distilled before it was used for the spectroscopic measurements. Methanol (HPLC grade) was purchased from Wako Pure Chemical Industries and used as received. All measurements were performed at 25.0 °C.

Host-guest complexation between $[1_6]\text{Cl}_{12}$ and guest molecules. Gaseous molecules were introduced through bubbling into a D_2O solution of $[1_6]\text{Cl}_{12}$ ($[1^{2+}] = 1.0 \text{ mM}$) and a Milli-Q water solution of $[1_6]\text{Cl}_{12}$ ($[1^{2+}] = 2.25 \mu\text{M}$) for NMR measurements and fluorescence measurements, respectively. The stoichiometry between $[1_6]\text{Cl}_{12}$ and the guests were determined by the integrals of the ^1H NMR signals of the encapsulated guest. As to $\text{Na}_2[^{10}\text{B}_{12}\text{H}_{12}]$, the stoichiometry between $[1_6]\text{Cl}_{12}$ and the encapsulated $^{10}\text{B}_{12}\text{H}_{12}^{2-}$ was determined by titration experiment using the ^1H NMR signals for the nanocube encapsulating $^{10}\text{B}_{12}\text{H}_{12}^{2-}$. After addition of $\text{Na}_2[^{10}\text{B}_{12}\text{H}_{12}]$ to an aqueous solution of $[1_6]^{12+}$, the solution was heated at 60 °C for 30 min to complete the encapsulation. Complexes between $[1_6]^{12+}$ and liquid alkane molecules were prepared according to the literature¹³.

Preparation of the gaseous mixtures of LPG with different concentrations in air. LPG and air were introduced to a balloon, in which the residual air was removed by vacuum before use, sequentially to prepare 0.1, 0.2, 0.5, 1.0, 5, 10, 30, and 50 vol% LPG with air.

Data availability

The authors declare that all the other data supporting the findings of this study are available within the article and its supplementary information files and from the corresponding author upon request.

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Author contributions

Y.-Y.Z., J.L., T.K., S.T. and S.H. conceived the project. S.H. prepared the manuscript and all the authors discussed the results and commented on the manuscript. Y.-Y.Z. and J.L. synthesized the GSAs and carried out ¹H NMR measurements, steady-state absorption, and fluorescence measurements of the nanocube in the presence and absence of guest molecules. M.K., T.T. and K.I. performed time-resolved fluorescence and fluorescence anisotropy measurements.

Additional information

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