Separation of a homogeneous mixture of different components to reach an ordered out-of-equilibrium state in solution has attracted continuous attention. While this can be achieved using external chemical fuels or photo energy, an alternative energy source is heat. Here we realize a temperature-controlled cycle of transitions between ordered and disordered states based on a mixture of two kinds of building blocks that self-assemble into cubic structures (nanocubes). An almost statistical mixture of nanocubes (disordered state) is thermodynamically most stable at lower temperature (25 °C), while homoleptic assemblies composed of single components are preferentially produced at higher temperature (100 °C) followed by rapid cooling. The scrambling of the building blocks between the nanocubes takes place through the exchange of free building blocks dissociated from the nanocubes. Based on this mechanism, it is possible to accelerate, retard, and perfectly block the scrambling by the guest molecules encapsulated in the nanocubes.
two kinds of different gases put into a box spontaneously mix together to reach a homogeneous fluid in equilibrium. Such a disordered state is thermodynamically favored and entropy is the quantity that determines which direction a reaction spontaneously proceeds to. Thus, the separation of each component from a homogeneous mixture (towards ordered state) needs external energy or help of Maxwell’s demon if we want to realize the separation without any energy except for information\(^1\)\(^{-}\)\(^4\). The homogeneity of a mixture of gases in equilibrium derives from their negligibly weak interactions. Contrary to mixing of gases, molecular self-assembly of multiple components can spontaneously form homoleptic self-assemblies composed of single components through self-sorting under thermodynamic control with the aid of intermolecular interactions between well-designed molecular building blocks that discriminate between oneself and others\(^2\)\(^{-}\)\(^19\). Furthermore, in the case where a statistical mixture of components in molecular assemblies is thermodynamically preferred, recent progress on adaptive chemistry has realized the transition of such disordered states to an ordered out-of-equilibrium state by external photo or chemical energy\(^20\)\(^{-}\)\(^34\).

Here we present a simple example of a temperature-controlled reversible transition between ordered and disordered states consisting of a mixture of two kinds of molecular building blocks that self-assemble into hexameric cubic structures, i.e. nanocubes, with different thermal stabilities. Because of a structural similarity between the two components (A and B for example), scrambling of the building blocks between the nanocubes (A\(_6\) and B\(_6\)) spontaneously takes place at 25 °C to reach an almost statistical mixture of nanocubes composed of two kinds of building blocks, A\(_n\)B\(_{6-n}\) (n = 0–6), a disordered state. Then, a metastable ordered state (a mixture of homoleptic nanocubes composed of a single component, A\(_6\) and B\(_6\)) is spontaneously recovered by heating at 100 °C and subsequent rapid cooling. The reversible transition between the two states is realized by the change in the energy landscape of the system consisting of two kinds of building blocks in response to the temperature. It is also found that the scrambling is accelerated, retarded, or blocked by guest molecules encapsulated in the nanocubes, which enables us to lock and unlock a metastable state by the encapsulation and release of hydrophobic molecules in the nanocubes.

Results

Scrambling between nanocubes. Gear-shaped amphiphiles (GSA: 1-Cl\(_2\) and 2-Cl\(_2\)), which are C\(_{2v}\)-symmetric hexa-phenylbenzene (HPB) derivatives possessing three kinds of substituents on the periphery of HPB, self-assemble into a cube-shaped structure (nanocubes, 1\(_6\) and 2\(_6\)) in water driven by the hydrophobic effect and van der Waals (vdW) and cation–π interactions between GSA molecules (Fig. 1a)\(^{35\text{-}37\text{.}}\) Though the structures of 1 and 2 are very similar, 1\(_6\) is thermally more stable than 2\(_6\) because vdW interactions around p-tolyl methyl groups of 1\(_6\) significantly enhance its thermal stability (disassembly temperature (T\(_d\)) of 1\(_6\) is 130 °C, while that of 2\(_6\) is 65 °C). To investigate the relation between the thermal and kinetic stabilities of the nanocubes, scrambling of GSAs between nanocubes assembled from non-deuterated GSAs (1\(_6\) or 2\(_6\)) and from partially deuterated GSAs ((1D)\(_6\) or (2D)\(_6\)) was monitored by electrospray ionization-time-of-flight (ESI-TOF) mass spectrometry. When aqueous solutions of 1\(_6\) and (1D)\(_6\) were mixed at room temperature ([1] = [1D] = 0.025 mM), the scrambling was clearly monitored by change in the distribution of mass signals for 1\(_6\)(1D)\(_{6-x}\)(SO\(_4\))\(_{2-x}\)\(^{-}\) (x = 0–6), which captured two electrons during the ionization (an aqueous H\(_2\)SO\(_4\) solution was added just before the mass measurement in order to detect the nanocubes as negative ion species), and an almost statistical signal pattern was observed in 2 days (Fig. 2a). In contrast, the scrambling for a mixture of thermally less stable nanocubes, 2\(_6\) and (2D)\(_6\), finished just after the mixing of the two solutions (Fig. 2b), indicating that the rate of the scrambling is related to the thermal stability of the nanocubes. It was also found that the rate of the scrambling is dependent on the concentration; the scrambling took place faster at lower concentration of the nanocubes (Fig. 2a). This result indicates that the scrambling does not occur by the collision of the nanocubes but through the exchange of monomer GSAs dissociated from the nanocubes (Fig. 2d) even though the signals for free GSAs were not observed by 1H NMR spectroscopy.

Next, the scrambling between the two different nanocubes (1\(_6\) and 2\(_6\)) was monitored by ESI-TOF mass spectrometry (Fig. 2c). When 1\(_6\) and 2\(_6\) ([1] = [2] = 0.4 mM) were mixed at 25 °C, the signal for 2\(_6\) decreased faster than that for 1\(_6\), and finally reached an almost statistical compositional mixture of the nanocubes in 2 days. The scrambling in the same concentration of the nanocubes ([1] = [2] = 0.4 mM) was monitored by 1H NMR spectroscopy (Fig. 3a and Supplementary Fig. 3). The 1H NMR spectra of a 1:1 mixture of 1\(_6\) and 2\(_6\) at 25 °C changed for 2 days, which is consistent with the time taken for the convergence of mass signals of a mixture of 1\(_6\) and 2\(_6\). As observed by the mass measurements, the 1H NMR signals for 2\(_6\) decreased faster than those for 1\(_6\), indicating that the heteroleptic nanocubes, 1\(_2\)2\(_{4-x}\) (x = 1–5), tend to preferentially exchange GSAs with 2\(_6\) because the scrambling between less stable nanocubes takes place faster, which supports the idea that the scrambling takes place through the exchange of monomer GSAs dissociated from the nanocubes. The scrambling was accelerated by heating and reached convergence in 8 h at 50 °C.

Interconversion between ordered and disordered states. Considering the fact that 1\(_6\) (T\(_d\) = 130 °C) is thermally more stable than 2\(_6\) (T\(_d\) = 65 °C) due to the vdW interactions around p-tolyl methyl groups in 1, nanocubes composed of more 2 would be less stable than those composed of more 1. Hence, at higher temperature than T\(_d\) of 2\(_6\), the nanocubes composed of more 2 should be disassembled to lead to a mixture of monomer 2 and the nanocubes composed of more 1. Then rapid cooling of the mixture of the nanocubes (mainly 1\(_6\)) and free 2 thus obtained leads to a mixture mainly containing homooleptic nanocubes (1\(_6\) and 2\(_6\)) through faster self-assembly of monomer 2 into 2\(_6\) than the scrambling (Fig. 1b, c). As expected, heating of a mixture of 1\(_6\) and 2\(_6\) at 100 °C led to the homoleptic 1\(_6\) in 83% yield (Fig. 3c and Supplementary Fig. 5). Subsequent rapid cooling at 0 °C gave homoleptic nanocubes (ordered state) in 70.7 ± 0.7% yield (Fig. 3c and Supplementary Fig. 6). At 50 °C, this mixture was gradually converted into an almost statistical mixture of nanocubes 1\(_2\)2\(_{4-x}\) (x = 0–6) (disordered state), which is thermodynamically most stable at 50 °C. The interconversion between the ordered and disordered states is repeatable simply by changing the temperature of the solution without any degradation because the GSAs are completely stable even at 100 °C (Fig. 3b).

Guest effect on scrambling. As the nanocubes can encapsulate neutral and anionic species in their about-1-nm-sized hydrophobic inner space to lead to thermally more stable nanocubes\(^37\), the guest species would prevent the dissociation of the nanocubes into the monomers, thereby retarding the scrambling. When aqueous solutions of 1\(_6\) encapsulating two molecules of 1,3,5-tribromomesitylenes (TBM), TBM@1\(_6\) (T\(_d\) > 150 °C), and of 2\(_6\) (T\(_d\) = 65 °C) were mixed, nothing happened for 6 months (Supplementary Fig. 7); the scrambling of GSAs and the distribution of TBM molecules between the nanocubes were perfectly blocked.
The same result was found when aqueous solutions of TBM$_2@6$ ($T_d = 135 \degree C$) and 1$_6$ ($T_d = 130 \degree C$) were mixed (Supplementary Fig. 8). These results indicate that the encapsulated hydrophobic guest molecules stabilize the nanocubes to change the energy landscape, resulting in the suppression of the dissociation of free GSAs (Fig. 4d). Interestingly, when insoluble TBM existed in an aqueous solution of TBM$_2@6$ and 1$_6$, the scrambling took place slowly. (It took 26 days to reach equilibration, which is longer than the time for the scrambling between 1$_6$ and 2$_6$, 2 days.) (Supplementary Fig. 9). Insoluble TBM molecules were gradually encapsulated in 1$_6$, during which the structure of the 1$_6$ nanocube would partially be broken or free GSAs would be dissociated. Hence, these (partially) dissociated GSAs of 1 should promote the scrambling. On the other hand, no scrambling took place when insoluble TBM was present in a solution of TBM$_2@1$_6 and 2$_6$, though gradual encapsulation of TBM into 2$_6$ was observed (Supplementary Fig. 10). In this case, though the encapsulation of TBM into 2$_6$ caused the dissociation of monomer GSA 2, the dissociation of monomer GSA 1 was strongly prevented by the encapsulation of TBM into 1$_6$ ($T_d > 150 \degree C$), so the scrambling did not take place.

Fig. 1 A temperature-controlled cycle of transitions between ordered and disordered states in a mixture of nanocubes (1$_6$ and 2$_6$). a The chemical structures of GSAs used in this research. b A temperature-controlled cycle of the conversion between the ordered and disordered states. An almost statistical mixture of the nanocubes (disordered state) was produced at 25 or 50 °C, while a mixture of two kinds of nanocubes composed of single GSAs was preferentially produced by heating at 100 °C followed by rapid cooling at 0 °C. There are positional isomers for 1$_x2_{6-x}$ ($x = 2–4$). c A schematic representation of change in the energy landscape of a mixture of two kinds of GSAs, 1 and 2, in response to the temperature. An almost statistical mixture of nanocubes 1$_x2_{6-x}$ ($x = 0–6$) is thermodynamically most stable at 25 °C, while a mixture of 1$_6$ and monomer 2 is thermodynamically most stable at 100 °C because decomposition temperatures of the nanocubes composed of more GSAs 2 are lower than 100 °C.
These results indicate that whether the scrambling takes place or not is determined by the existence of monomer GSAs (1 and 2) and that in the case where the thermal stabilities of the two nanocubes are significantly different the rate-determining step of the scrambling is the dissociation of monomer GSAs from a thermally more stable nanocube.

Quite different results were observed when anionic species (NaPCCP: sodium pentacyanocyclopentadienide) was used as a guest molecule (Fig. 4b). When PCCP$_2@$1$_6$ and 2$_6$ were mixed together, the scrambling was significantly retarded (65% of PCCP$_2@$1$_6$ and 20% of 2$_6$ existed in the solution after 1 month) (Supplementary Fig. 11). Furthermore, the scrambling was...
perfectly blocked by the encapsulation of PCCP in both of the nanocubes (Supplementary Fig. 12). Surprisingly, the addition of 2 eq of PCCP in a 1:1 mixture of 16 and 26 accelerated the scrambling (the scrambling finished in 1 day, which is faster than that carried out in the absence of PCCP (2 days)) (Supplementary Fig. 13). Right after the addition of PCCP in a solution of 16 and 26, all PCCP molecules were selectively encapsulated in thermally less stable 26 under kinetic control. Then the exchange of PCCP between the nanocubes coincided with the scrambling of GSAs between the nanocubes. A simple mixing of 16 and PCCP2@26 also accelerated the scrambling (1 day) (Supplementary Fig. 14). The acceleration of the scrambling under this condition is ascribed to the dissociation of monomer 16 initiated by the transfer of PCCP encapsulated in 26 into 16 (PCCP2@26 + 16 → PCCP2@16 + 26).

Because of the lower stability of the ordered state at 25 °C, spontaneous scrambling takes place to reach the disordered state. To control the timing of the scrambling, a guest-encapsulation-release system was coupled with the cycle of transitions (Fig. 4c and Supplementary Fig. 15). After the formation of a mixture of homoleptic nanocubes from the disordered state, a hydrophobic guest molecule (Hex: n-hexane) was added in the mixture to form the nanocubes that encapsulate the guest molecules, Hex3@16 and Hex2@26. The scrambling of the GSAs between the two nanocubes was blocked for 7 days, indicating that the metastable ordered state was kinetically locked. The removal of the guest molecules by heating at 100 °C is the trigger to unlock the ordered state to lead to a mixture of guest-free homoleptic nanocubes, 16 and 26, which then was converted into the disordered state again.

Discussion
In conclusion, a temperature-controlled cycle of transitions that is fabricated from two kinds of building blocks that self-assemble into homoleptic and heteroleptic cubic assemblies (nanocubes) with different thermal stability was realized. The scrambling experiments (intermolecular exchange) of the building blocks (GSAs) between the nanocubes indicate that the kinetic stability of the nanocube is closely related to the thermal stability of the nanocubes; a thermally more stable nanocube is kinetically more inert. The concentration effect on the rate of the scrambling and the results obtained from the scrambling experiments in the presence of guest molecules indicate that the scrambling takes place through the exchange of free GSAs dissociated from the nanocubes and that the rate of the scrambling is determined by the dissociation of free GSAs provided from a thermally more stable nanocube. The interconversion between the metastable
ordered (a mixture of $1_6$ and $2_6$) and the thermodynamically most stable disordered states (an almost statistical mixture of $1_6$ and $2_6$) was realized simply by changing the temperature. The result that the induced-sorted state was preferred by heating at 100 °C and subsequent rapid cooling was realized because only the nanocubes composed of more $1_6$ can survive at this temperature. The rate of the scrambling can be controlled by anionic guest species. The blocking of the scrambling by the encapsulation of guest molecules would enable to kinetically capture a certain metastable species that is selected from a dynamic combinatorial library of compositional and positional isomers of nanocubes consisting of several kinds of GSAs in response to external stimuli.

**Methods**

**General.** $^1$H and $^{13}$C NMR spectra were recorded using a Bruker AV-500 (500 MHz) spectrometer. High-resolution mass spectra (HRMS) were obtained using a Waters Xevo G2-S QTOF mass spectrometer. 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. GSAs $1\cdot\text{Cl}_2$ and $2\cdot\text{Cl}_2$ and compounds $3$ and $4$ were synthesized according to...
previously reported procedures.35 See supplementary information for synthetic procedures, including Supplementary Figs. 16–19.

Host-guest complexation. The solutions of TBMe3@4, TBMe3@6 (TBMe3 indicates 1,3,5-trisubstituted benzene), PCCP@6 (PCCP indicates pentacyclicopentadentate) and Hex@6 (Hex indicates n-hexane) were prepared according to the literature36, 37. Hex (1 μL) was added by a syringe to a D2O solution of 2, (2 μL = 1.0 mM, 600 μL) in an NMR tube. The suspension was mixed by inverting the NMR tube four times and sonicated for 5 min to afford Hex@2 (Supplementary Fig. 1). The formation of PCCP@6@2 was confirmed by the titration experiments using the 1H NMR signals of the nanocube encapsulating PCCPs (Supplementary Fig. 2).

Monitoring of scrambling by ESI-TOF mass spectrometry. ESI-TOF mass spectra of the scrambling of the nanocubes in water were recorded on a SYNAPT G2-Si HDMS mass spectrometer (Waters, Massachusetts, Milford, USA) in negative ionization mode at 0.88 kV with a 0 V sampling cone voltage and source offset voltage. 4 V trap and 2 V transfer collision energy, and 1.5 mL/min trap gas flow. The scrambling experiment between 1 and 1D was presented as an example. Solutions of 1 and of 1D ([GSA] = 0.8 mM) in H2O were prepared separately. The solutions of 1 (150 μL) and of 1D (150 μL) were added to an Eppendorf microcentrifuge tube. Then, the concentration of GSAs was adjusted to be 0.4, 0.1, and 0.025 mM by addition of Milli-Q water. The scrambling of the GSAs was monitored by mass spectrometry. A portion of the mixture was taken. After addition of 1 mM H2SO4 aq., this solution was immediately injected into gold-microcentrifuge tube. Then, the concentration of GSAs was adjusted to 0.4, 0.1, and 0.025 mM in D2O. The scrambling of the GSAs was monitored at 25 °C by 1H NMR spectroscopy (Supplementary Fig. 2).

Interconversion between ordered and disordered states in a mixture of nanocubes. An almost statistical mixture of the nanocubes 1,2,6,8 (x = 0–6) was produced from a mixture of 1 and 2, (1) = (2) = 0.5 mM at 25 °C for 3 days or at 50 °C for 8 h. A mixture of 1 and 2 was preferentially produced by heating at 100 °C for 20 min followed by rapid cooling at 0 °C for 20 s. The induction of 1 and 2 was monitored by variable 1H NMR measurements (Supplementary Figs. 3, 4 and 7–14).

Kinetic lock and unlock of the induced-sorted state by the encapsulation and release of guest molecules. n-Hexane (Hex) (1 μL) was added via a syringe to a D2O solution of 1 and 2, (1) = (2) = 0.5 mM in an NMR tube. The suspension was mixed by shaking the NMR tube for 30 s to afford a D2O solution of Hex@1 and Hex@2. The encapsulated n-hexane was removed upon heating at 100 °C for 60 min and then a mixture of 1 and 2 was obtained by rapid cooling at 0 °C for 20 s (Supplementary Fig. 15).

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., 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. synthesized all the GSAs and carried out NMR measurements. K.I. and S.U. carried out mass measurements. Y.H. and H.M. synthesized NaPCCP.

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