Luminescent Inclusion Crystals

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Guest-Responsive Fluorescence of Inclusion Crystals with π-Stacked Supramolecular Beads**

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Lattice inclusion host compounds entrap guest molecules of various sizes into their flexible cavities formed by the host framework.[1] The inclusion phenomena have been extensively investigated because of the potential application of these compounds in many fields such as separation,[2] storage,[3] catalysis,[4] and chemical sensing.[5] Considerable efforts have demonstrated that bulky and rigid molecules, or awkwardly shaped molecules, tend to include guest molecules because they do not pack easily without guests.[6] For example, crystals of anthracene derivatives bearing diphenylphosphanyl groups at the 9- and 10-positions include toluene molecules and show on/off fluorescence switching by absorption and desorption of the guest.[5a] Inclusion of various guests into fluorescent hosts will afford a multitude of fluorescent colors as if doping strongly affects the colors of jewels, as seen in sapphires and rubies. However, chemical affinity of their inclusion spaces often limits the appropriate guest molecules (i.e. polar or nonpolar molecules). Therefore, it still remains challenging to design new lattice host compounds that efficiently incorporate and respond to a wide range of guests.

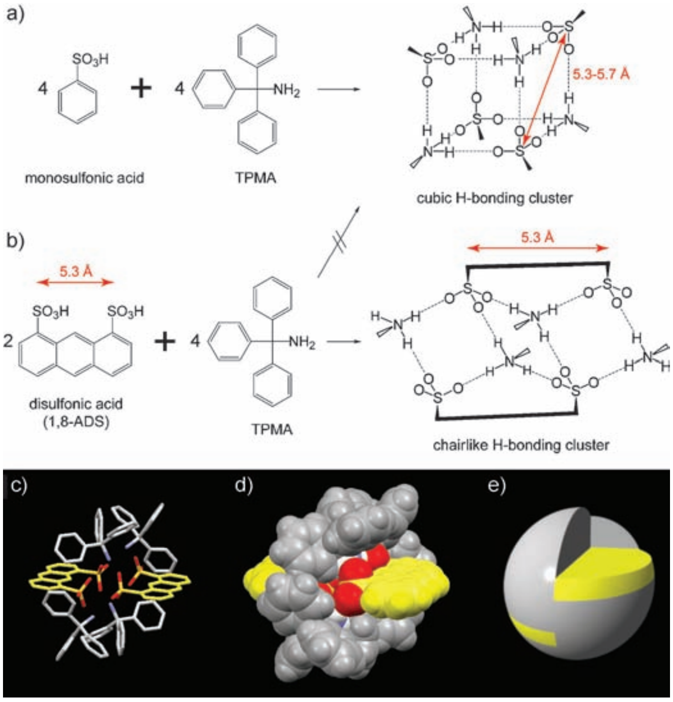

Figure 1. a) Supramolecular clusters with cubic H-bonding network comprising TPMA and a variety of monosulfonic acids such as benzenesulfonic acid. The shortest S–S distance is 5.3–5.7 Å. b) Novel supramolecular cluster with chairlike H-bonding network comprising TPMA and 1,8-ADS. The intramolecular S–S distance is 5.2–5.3 Å. This complex did not form cubic networks. c) The novel supramolecular cluster in crystals. d) Space-filling representation of the cluster. e) Schematic representation of the cluster. Yellow and gray represent anthracene and triphenylmethyl moieties, and blue, red, orange, and white represent N, O, S, and H atoms, respectively.

Previously, we readily prepared bulky and rigid supermolecules from simple molecules: triphenylmethylamine (TPMA) and a variety of sulfonic acids.[7] Four TPMA molecules and four monosulfonic acid molecules formed cubic hydrogen-bonding (H-bonding) networks completely covered with their substituents (Figure 1 a). Herein, in order to create fluorescent materials responsive to various guests, we have designed a new host supermolecule that possesses two aromatic fluorophores at the periphery. The fluorescent host forms one-dimensional (1D) π-stacked assemblies based on π–π stacking between the fluorophores. That is to say, the fluorophores serve as supramolecular glue as well as emitter.[8] The stacking geometry changes through crystallization with guest molecules, resulting in guest-responsive fluorescence.[5c,9] In that respect, we employed the supramolecular complex comprising TPAM and anthrace-1,8-disulfonic acid (1,8-ADS). This disulfonic acid has two sulfonate groups at a sulfur–sulfur (S–S) distance of approximately 5.3 Å, which corresponds to the typical nearest S–S distance in the cluster with a cubic H-bonding network (5.3–5.7 Å). Therefore, they should have formed cubic networks with two anthracene fluorophores at the peripheries of the resulting cluster. Surprisingly, however, this supramolecular complex formed not cubic H-bonding networks but topologically different, chairlike H-bonding networks (Figure 1 b). This topological difference led to a rather favorable supra-

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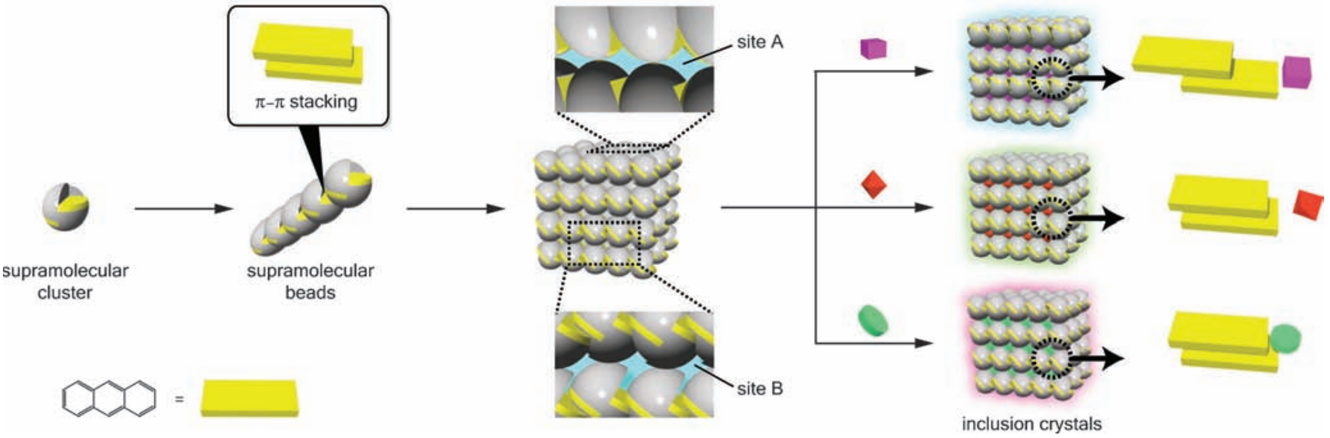


Figure 2. Schematic representation of the hierarchical construction of π-stacked inclusion assemblies with guest-dependent fluorescent properties from the ellipsoidal supramolecular cluster comprising TPMA and 1,8-ADS. Purple cube, red octahedron, and green disc represent guest (dopant) molecules.

molecular cluster, which was unusually shaped and exposed the anthracene fluorophores more. Consequently, the novel supramolecular clusters were robustly formed to construct π-stacked 1D assemblies that incorporate many kinds of nonpolar and even polar guest molecules. Their fluorescence colors widely changed depending on the included (doped) guests, thus behaving like "organic" jewels, suggesting their potential as chemo- and biosensors.

Recrystallization of the supramolecular complex of TPMA and 1,8-ADS from mixtures of methanol and a variety of organic solvents resulted in many kinds of crystal habits, depending on the solvents. X-ray crystallographic studies clearly demonstrated that these crystals included not only nonpolar solvents but also polar solvents.[10] In all of the crystal structures, two disulfonic acid molecules (four sulfonate groups) and four TPMA molecules robustly formed a discrete chairlike H-bonding network. Parallel orientation of the sulfonate groups in the 1,8-ADS molecule probably did not afford a stable cubic network. Alcohols such as methanol and 2-pentanol, which are often involved in H-bonding networks, were not incorporated but did not break such discrete networks upon crystallization. This observation indicates the high stability of this chairlike H-bonding network. The network was surrounded by anthracene backbones and triphenylmethyl groups, which led to ellipsoidal supramolecular clusters (major and minor axis are 23 Å and 18 Å, respectively; Figure 1 c–e). The clusters exposed two of the π planes of the anthracene moieties on the opposite sides of the ellipsoid. These clusters were hierarchically assembled into inclusion crystals (Figure 2). Each cluster was linked by face-to-face π–π interactions between the anthracene moieties to give beadlike π-stacked motifs. These supramolecular beads were bundled by CH–π interactions between triphenylmethyl groups, leaving two kinds of inclusion spaces depending on the guest molecules. 1,2-Dichloroethane, 1-bromobutane, and 1,3-diiodopropane were incorporated into the gaps between both sides of the ellipsoids (site A in Figure 2), whereas acetonitrile, ethyl acetate, and acetone were entrapped into the gaps between top and bottom of the ellipsoids (site B in Figure 2). Toluene and 1,4-dioxane were incorporated into both sites. The precise geometry of π–π stacking and relative positions between the beads slightly changed so as to pack efficiently with the guests (Figure 2 and Figure 3, and Table 1). Nevertheless, assembly manners of the clusters and the beads are basically similar in any crystals.

The versatile inclusion ability of these clusters seems to be attributed to the presence of accessible oxygen atoms of the sulfonate groups as well as the shape of the resulting supramolecular beads (Figure 1 d). The ellipsoidal clusters exposed their sulfonate groups on the edge of the chair, though the cubic H-bonding networks in our previous cluster were efficiently covered by their substituents. Without interrupting formation of the H-bonding core, these accessible oxygen atoms captured alkyl halides, 1,4-dioxane, and toluene in site A by CH–O interactions with CH at α position or of phenyl groups of the guests. In other words, the oxygen atoms serve not only as structural elements in forming the H-bonding cores but also function as receptors for molecules having weak acidic protons. On the other hand, other guests were incorporated into site B without CH–O interactions. In these inclusion crystals, the guests adequately filled the gaps between the beads. The accessible oxygen atoms caught the neighboring beads instead of the guests. This observation suggests that both the receptor oxygen atoms and the awkward shape of the supramolecular beads contribute to incorporating various guest molecules. Interestingly, despite their awkward shape, they are also able to crystallize without guest molecules from methanol and 2-pentanol; in the guest-free crystal, two non-equivalent beads coexisted in the same lattice to complement each awkward shape as if beads themselves are hosts and guests.

The guest molecules are located above or beside the anthracene moieties either within the sum of the van der Waals radii or within 0.2 Å over this value (Figures 3 and S2). Therefore, the included guest molecules must have an influence on the fluorescence properties. In fact, these crystals displayed a wide range of emission colors from blue to orange-yellow depending on the included guests under UV

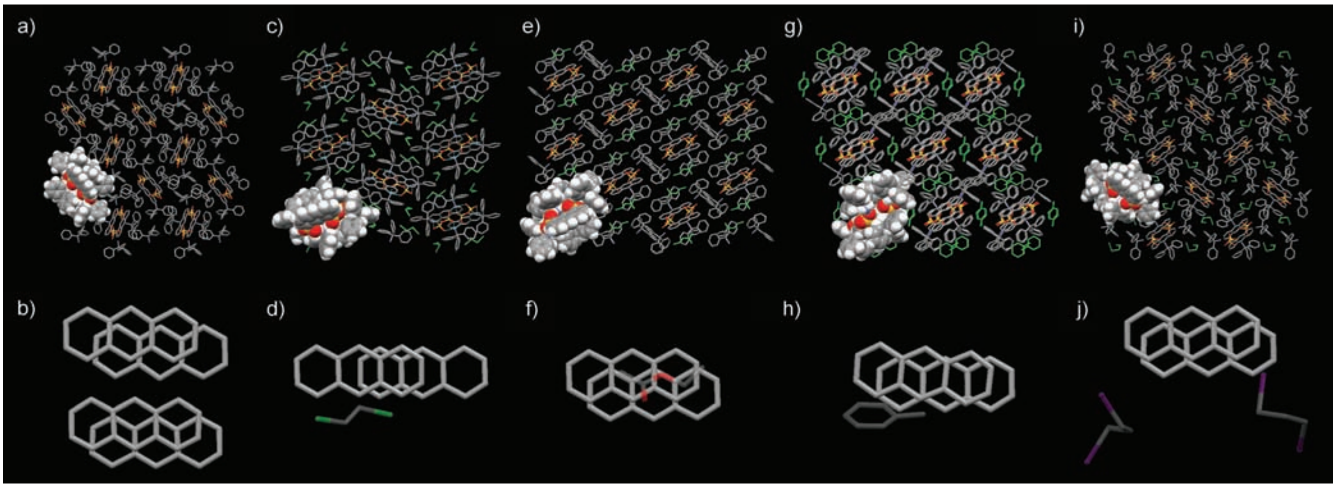
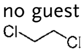
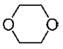
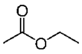
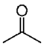
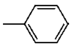
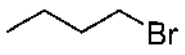


Figure 3. Crystal structures of the supramolecular clusters a) without guests, c) with 1,2-dichloroethane, e) ethyl acetate, g) toluene, and i) 1,3-diiodopropane. The clusters stack perpendicularly to form supramolecular beads. The π-stacking geometries within the beads depend on the guests (b, d, f, h, and j). Two types of stacking geometry coexist in the guest-free crystal. Guest molecules are represented by green sticks in (a), (c), (e), (g), and (i), and those near the fluorophores are represented by transparent sticks in (b), (d), (f), (h), and (j). Hydrogen atoms and minor components of disordered 1,2-dichloroethane and toluene molecules are omitted for clarity.

Table 1: Structural and spectral properties of the crystals comprising 1,8-ADS and TPMA with various guests.

Guests	λ_{em} [nm][a]	λ_{ex} [nm][b]	$d_{\pi-\pi}$ [Å][c]	Overlap [%][d]
no guest	473	409	3.25, 3.34	43, 40
	452	418	3.44	41
	537	420	3.40	51
—CN	537	428	3.32	38
	544	419	3.30	41
	546	421	3.32	39
	554	421	3.40	62
	564	420	3.32	54
	570	402	3.33	51

[a] Maximum wavelength of emission spectra of the inclusion crystals excited at 340 nm. [b] Maximum wavelength of excitation spectra monitored at their respective emission bands. [c] Interplane distances between the anthracene planes of dimer pairs. In guest-free crystals, two non-equivalent dimer pairs coexist in the same lattice. [d] The ratio of the area of overlapped moieties of anthracene aromatic rings in the crystal structures calculated as the overlapped area divided by the whole area of the anthracene ring in Figure 3 b,d,f,h, and j, and Figure S1b, d, f, and h.

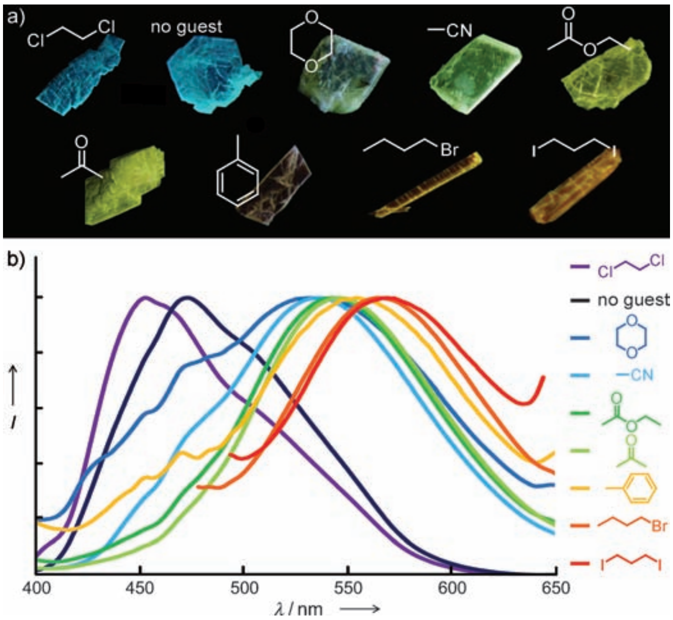


Figure 4. a) Photographs of guest-free and inclusion crystals of supramolecular complexes of 1,8-ADS and TPMA with various guest molecules under UV irradiation ($\lambda = 365$ nm). b) Normalized fluorescence spectra of the guest-free and inclusion crystals excited at 340 nm.

irradiation (Figure 4a). Figure 4b shows the fluorescence spectra of the inclusion crystals excited at 340 nm. The maximum wavelength of the fluorescence emission spectra (λ_{em}) widely shifted from 452 nm to 570 nm. Guest-free crystals showed a broad emission profile around 470 nm. This result is in contrast to the dilute solution of anthracene and 1,8-ADS, the fluorescence spectra of which have vibrational structures with λ_{em} of approximately 400 nm. Such large red-shifts and broadenings of fluorescence spectra are characteristics for excimer or dimer fluorescence. The π-stacked geometry of anthracene dimers in these crystals probably allowed the formation of ground-state dimers to emit red-shifted fluorescence.

Inclusion of guest molecules into the lattice caused larger red-shifts of λ_{em} by 60–100 nm compared to the guest-free crystal but only 1,2-dichloroethane did blue-shift the emission. In both cases, the maximum wavelength of the excitation spectra (λ_{ex}) are red-shifted from guest-free crystals by 10-20 nm. These phenomena imply that the red-shifts of λ_{em} and λ_{ex} in the inclusion crystals are caused by large stabilization of excited states or destabilization of ground states by lattice guests. On the other hand, the blue-shift of λ_{em} is attributed to its unique geometry of π-stacked anthracene dimers. That is, an inclusion crystal with 1,2-dichloroethane showed a parallel slipped stacked geometry (Figure 3 d), whereas the other inclusion crystals displayed common offset (centre-to-edge) stacked geometry (Figure 3 b,f,h,j). Such obvious differences in stacking geometry of fluorophores has a significant influence on the formation of their excited complexes. It was reported that anthracenophane as a model of anthracene dimers shows a blue-shift in fluorescence with slipping the stacking geometry along its long axis.[11] Interestingly, inclusion of 1,3-diiodopropane rather induced a blue-shift of λ_{ex} in spite of the largest red-shift of λ_{em}. This uncommon behavior is not observed for the inclusion crystal with 1-bromobutane, the crystal structure of which is quite similar to that of 1,3-diiodopropane in the guest locations and the π-stacked geometry. This inclusion crystal possibly responded to the unique properties of iodine compounds. These results indicate that both the stacking geometry and the host–guest interactions are responsible for the guest-dependent fluorescence in these inclusion crystals.

In summary, we hierarchically constructed 1D π-stacked assemblies of organic fluorescent supramolecular clusters with remarkable inclusion ability. TPMA and 1,8-ADS formed ellipsoidal cluster with two anthracene fluorophores at their periphery based on a chairlike H-bonding network. The disubstituted clusters afforded supramolecular beads by linking the anthracene moieties through π–π interactions. Both the receptor oxygen atoms and the awkward shape of the supramolecular beads enhanced the inclusion ability of the supermolecule. Resulting inclusion crystals modulated their fluorescence maximum wavelength from 452 nm to 570 nm, depending on the guests. The construction of such π-stacked supramolecular beads is a novel approach to produce lattice inclusion hosts and/or solid-state sensors. Solid sensor systems based on the supramolecular bead should respond to a wide range of polar and nonpolar solvents. The dynamic change of fluorescence in this inclusion system upon external stimuli is currently under investigation.

Experimental Section

Single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-RAPID imaging-plate diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54187$ Å). Solid-state fluorescence spectroscopy was carried out with a FP-6500 spectrofluorometer (JASCO). The crystals that were used for the spectroscopy were ground to crystalline powder. See the Supporting Information for more experimental details.

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[10] CCDC 848993, 848994, 848995, 848996, 848997, 848998, 848999, 849000, 849001 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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