Self-Assembly

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Spontaneous Generation of Highly Emissive RGB Organic Nanospheres**

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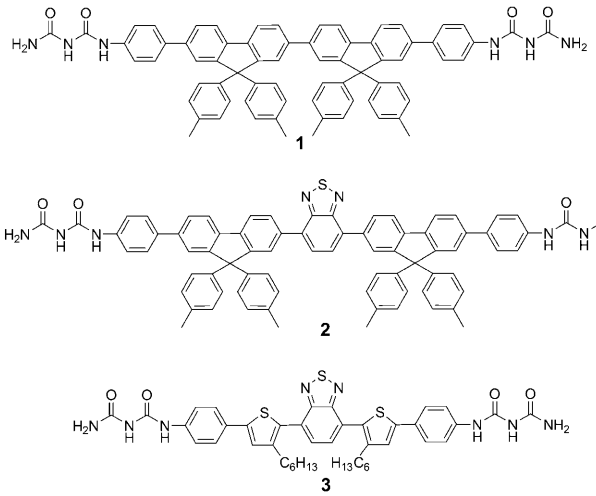
The rational design of mesoscopic structures endowed with tunable electronic properties is a milestone towards bridging the bottom-up and top-down approach to molecule-based electronics that could herald an important step forward in attaining the levels of miniaturization needed for future generations of electronic devices. Aggregation can be induced by the interplay of hydrophobic forces and offers access to a variety of well-defined architectures that span multiple orders of scale in size, from a few nanometers (e.g. micelles), to hundreds of microns (e.g. giant vesicles, lamellar assemblies, or fibers) into which photo- or electroactive functionalities can be incorporated.[1] Numerous examples of luminescent fibrillar aggregates in which the color of the emitted light is controlled by the energy gap of the material have been reported. Further tuning of the emission envelope, particularly important for white-light emission, can be achieved through Förster resonant energy transfer by incorporating luminescent guests whose absorption spectrum overlaps with the emission spectrum of the material.[2] On the other hand, the size and shape of spherical aggregates make them attractive candidates for the fabrication of soft light-emitting devices in which the size of the luminophore is determined by the self-assembly properties of the molecular constituent. These can be one or more orders of magnitude smaller than current printable domains and would be valuable as point light sources and in high-resolution displays. However, the spontaneous self-assembly of nanometer-sized spherical aggregates larger than micelles is uncommon.[3]

A limited number of luminescent vesicles based on conjugated organic chromophores and polymers have been reported to date, obtained either by dispersion of an organic solution of the material in water or by cooling in a hydrocarbon solvent. The formation of spherical aggregates is driven by the presence of long hydrocarbon or ethylene-oxide chains and can be sensitive to minor variations in structure.[2b,4] Furthermore, such vesicles are generally obtained as aqueous suspensions[5] that are not ideal for incorporation into electronic devices, for which anhydrous conditions are preferred. We now report a series of intensely fluorescent compounds that spontaneously generate vesicle-like nanospheres (200–600 nm in diameter) when dropcast from an anhydrous organic solvent. The compounds are neutral, relying on the presence of self-complementary hydrogen bonding (H-B) rather than hydrocarbon chains to drive the self-assembly process. Their color can be tuned from blue to red by adjusting the energy of the singlet excited state, and the compounds can be mixed in varying proportions without affecting aggregate morphology. Because the system allows blending of not just two, but all three primary colors, a large spectrum (including pure white) is readily available by simply mixing the compounds. The palette of colors each individual aggregate can generate is unprecedented and covers more than 75% of the gamut of current liquid crystalline displays (LCDs).

Compounds **1**–**3** (Scheme 1) are composed of a π-conjugated core appended with self-complementary H-B biuret groups at the extremities and were synthesized by Suzuki coupling of the corresponding aryl bromide and a phenylboronic biuret derivative.[6] These compounds are not amphiphilic, and appear freely soluble in common organic solvents such as chloroform and THF. While investigating the self-



Scheme 1. Structures of compounds **1**–**3**.

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assembly of **1**, we discovered that it spontaneously lead to the deposition of hollow spheres when dropcast from dilute (10^{-4} M) THF solutions. The aggregates range in size from approximately 200 nm to 0.5 μm and are similar in morphology to previously reported artificial vesicles, as evidenced by scanning electron microscopy (SEM, Figure 1). Evidence for

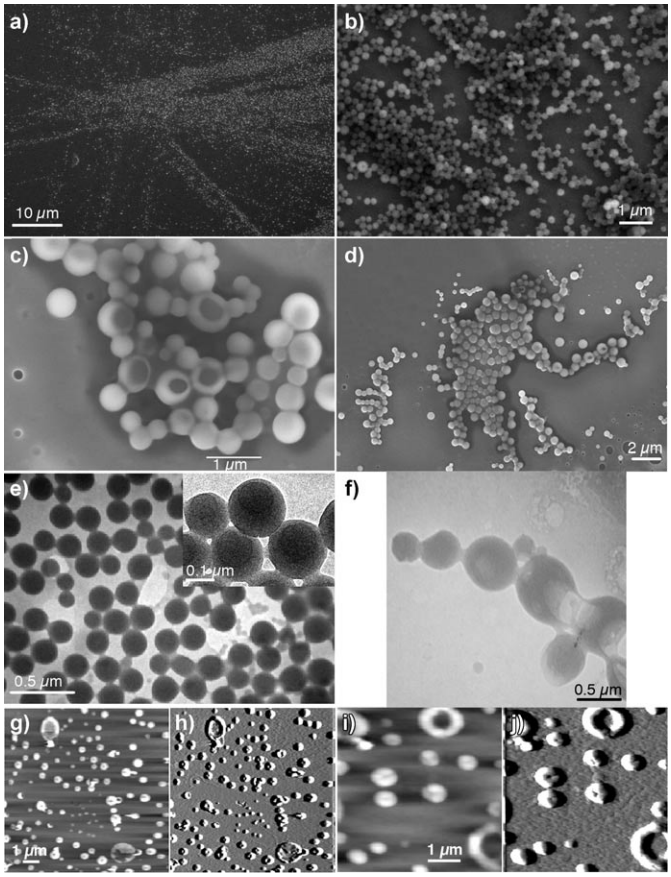

Figure 1. SEM images of the spherical aggregates formed by compound **1** upon dropcasting from dilute anhydrous THF solution ([**1**] = 0.1 mM) onto SiO_2 substrates at various magnification ratios (a–d). In (b), water (30%) was intentionally added to the solution prior to deposition. The presence of holes in some of the aggregates (c, d) is indicative of their hollow nature, which is further confirmed by TEM (e, f). Tapping mode AFM images of the aggregates on SiO_2 substrates ((g), (i): height; (h), (j): phase) shows the presence of flattened or partially collapsed aggregates.

the hollow nature of the aggregates is provided by the identification of pores or holes in which some of the material was lost during sample preparation, and from TEM and AFM studies (see below). The formation of these aggregates is independent of the nature of the substrate, whether semiconducting (silicon), insulating (SiO_2), or conducting transparent metal oxide (ITO).[7]

Anticipating that the combination of a rigid core and the presence of the strong self-complementary H-B motifs is responsible for the spontaneous generation of spherical aggregates, we proceeded to prepare compounds **2** and **3**, in which a benzothiadiazole moiety or the juxtaposition of electron donor–acceptor units is used to tailor the S_1–S_0 energy gap. Compared to the highly fluorescent bisfluorene **1**, which emits in the blue region of the visible spectrum, compounds **2** and **3** respectively cover the green-yellow and red regions of the spectrum (Figure 2). The photoluminescence efficiencies of all three compounds in THF solutions are high, with $\Phi_F = 0.96$, 0.85, and 0.64 for compounds **1**, **2**, and **3**, respectively.[8] More importantly, both **2** and **3** share the ability of compound **1** to spontaneously generate hollow spheres when dropcast from dilute THF solutions.[7]

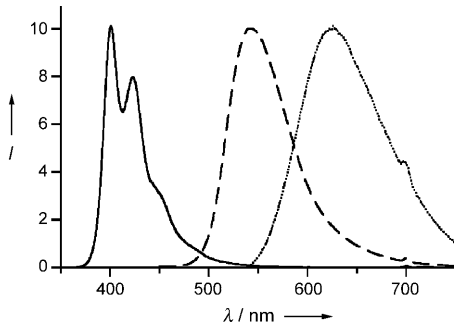

Figure 2. Normalized fluorescence spectra (1 μM solutions, $\lambda_{ex} = 350$ nm) of **1** (——), **2** (-----), and **3** (•••••) in THF.

We observe that the vesicle-like aggregates are obtained from THF solutions regardless of the absence of water (THF dried by refluxing over Na/benzophenone), or if water is intentionally added to the solution prior to deposition (see Figure 1 b and S2). Therefore, the process does not appear to be driven by the presence of nonmiscible solvent mixtures. No heating or sonication is required to obtain clear solutions of **1**, **2**, or **3** in THF at concentrations up to 1 mM. However, dynamic light scattering (DLS) analysis of THF solutions of **1**, **2**, or **3** revealed that, even at 10^{-4} M, aggregates whose average hydrodynamic radius is 250 nm are present.[7] Although DLS does not provide direct information on their morphology, this value is very close to the typical diameter of the vesicles that are deposited and suggests that aggregates commensurate in size are present prior to deposition. In agreement with the hypothesis that H-B interactions are important for aggregation, replacing THF by DMSO, a solvent known to break up H-B interactions, leads to the disappearance of the DLS signal.

The morphology of the aggregates was characterized by environmental SEM, TEM, and AFM, and proved independent of the substrate onto which the aggregates are deposited (SiO_2, Si, or ITO).[7] We found that the presence of solvent vapors in the SEM chamber reduced the proportion of ruptured aggregates, in contrast to TEM images, which showed a large percentage of fractured aggregates and that the shell is very thin (ca. 5-10 nm, Figure 1 f). AFM microscopy revealed that the aggregates collapse to flat discs or doughnuts upon evaporation of the solvent (Figure 1 g–j). The discs present an indentation of varying depth and size, indicating they are being deformed by the pressure exerted by the AFM tip, as already observed in artificial vesicles assembled from polymers[9] or from discotic liquid crystalline molecules.[4b]

The luminescence properties of individual aggregates deposited on SiO_2 substrates were investigated using confocal fluorescence microscopy. Although their size is near the diffraction limit, the aggregates are clearly identifiable as they are relatively dispersed and highly luminescent. The results, summarized in Figure 3, indicate that the emission collected

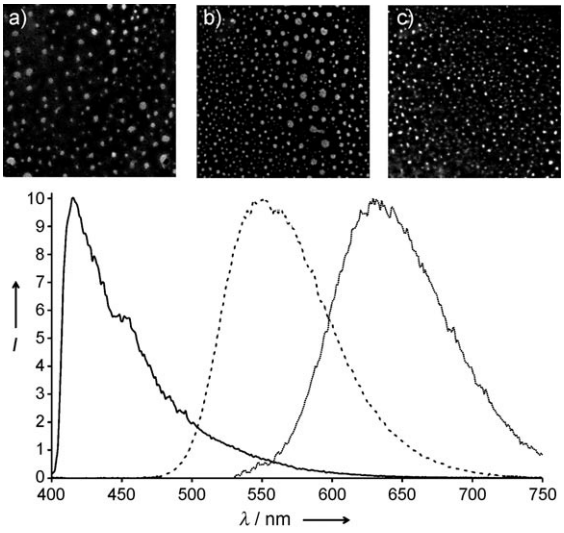

Figure 3. Confocal fluorescence microscopy images (40×40 μm, $\lambda_{ex}=385$ nm) and averaged corrected fluorescence spectra from these areas of aggregates of **1** ((a), solid line), **2** ((b), dashed line), and **3** ((c), dotted line). The emission of compound **1** is cut off below 410 nm by a long-pass filter. See Figure S14 for corresponding fluorescence lifetime images.

from each single vesicle-like aggregate is only slightly bathochromically shifted (by <10 nm) with respect to the emission from THF solution, and that it varies minimally between aggregates. The emission spectra of the vesicle-like aggregates of **1**, **2**, and **3** on SiO_2 correspond to the blue, yellow-green, and red colors of the CIE plot, respectively, and form a triangle that defines the possible colors (gamut) that can be generated from a combination of the emission of the pure compounds.

Energy transfer processes are known to be efficient in artificial vesicles because of fast exciton migration and proximity of the chromophores.[4a] The S_1–S_0 energy gaps of compounds **2** and **3** overlap well with the emission spectrum of **1** and are thus well-suited for this purpose. Together, compounds **1**–**3** can potentially generate single aggregates the emission of which can be tuned over the entire visible spectrum. Given that the compounds form aggregates even in relatively dilute solutions, we may expect static fluorescence quenching behavior. This is indeed the case, and emission of **1** (10^{-4} M solution in THF) is efficiently quenched by the addition of micromolar amounts of **2** or **3** (Figure 4 and S9). At these quencher concentrations, the Stern–Volmer plots show only minimal curvature and give values of $K_{SV}=2.2\times10^5$ or $1.0\times10^5\,M^{-1}$ for the quenching of **1** by **2** or **3**, respectively. Because the excited state lifetime of **1** is short (0.75 ns),[7] such large values of K_{SV} are incompatible with a diffusion-limited quenching process and indicate static

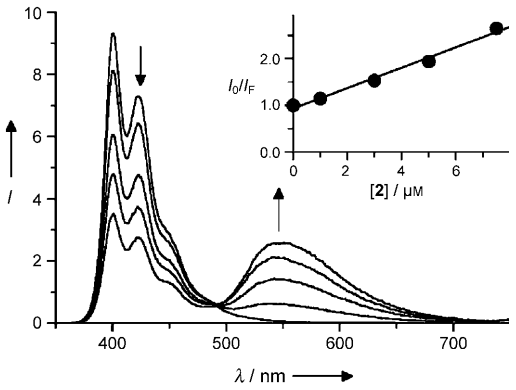

Figure 4. Fluorescence quenching of the emission of **1** (0.1 mM in THF, $\lambda_{ex}=350$ nm) by **2** and corresponding Stern–Volmer analysis ($\lambda_{em}=420$ nm, $K_{SV}=2.2\times10^5\,L\,mol^{-1}$, see inset). It is calculated that at the highest concentration of the acceptor used (7.5 μM), less than 5% of the light is directly absorbed by **2**.

quenching behavior characteristic of aggregation in solution. The quenching process is assigned to singlet energy transfer on the basis of the favorable overlap between the emission spectrum of **1** and the absorption shell of **2** or **3**, and the presence of electronic transitions of **1** in the excitation spectrum of **2** or **3** acquired at a wavelength at which **1** does not emit.[7]

Along similar lines, we found it possible to tune the emission spectrum of the individual vesicle-like aggregates by adjusting the composition of the solution from which they are drop-cast. To demonstrate this, the color coordinates of a series of samples in which the proportion of **1**, **2**, and **3** are varied were measured, and the vesicle-like aggregates thus formed gave the expected progression of colors from blue to yellow (Figure 5).[10] Thanks to the possibility of combining three different colors, the gamut obtainable is very large: as shown in Figure 5, the overlap between the gamut of colors covered by our system overlaps substantially ($>75\%$) with that of a standardized red-green-blue (RGB) color display. In fact, a very good match would be obtained by blue-shifting the emission of **2** by 10 nm (less than 0.04 eV). A special case is obtained when a THF solution composed of 10^{-4} M of **1**, 0.2 μM (0.20 mol%) of **2**, and 0.25 μM (0.25 mol%) of **3** is used, as it gives rise to vesicles that emit a very clean white light that corresponds precisely to the D65 standard when excited at 385 nm (Figure 5). Other shades of white (D50 and warm white) were also obtained by slightly adjusting the proportions of **2** and **3**. From the relative molar extinction coefficients, it can be calculated that $>99.85\%$ of the incident radiation is absorbed by **1** at these concentrations. However, the observed emission corresponds to a composite of **1** (84.5%), **2** (5.0%), and **3** (10.5%), in agreement with energy transfer within each aggregate from excited **1** to **2** or **3**. This result is further supported by time-resolved confocal microscopy fluorescence measurements: in the blue spectral region, the average decay time of **1** in the aggregates decreases upon addition of **2** (0.2 mol%) or **2** and **3** (0.2 and 0.4 mol%, respectively) from 0.7 ns to 0.6 and 0.5 ns, respectively. Simultaneously, the average decay times of the emission

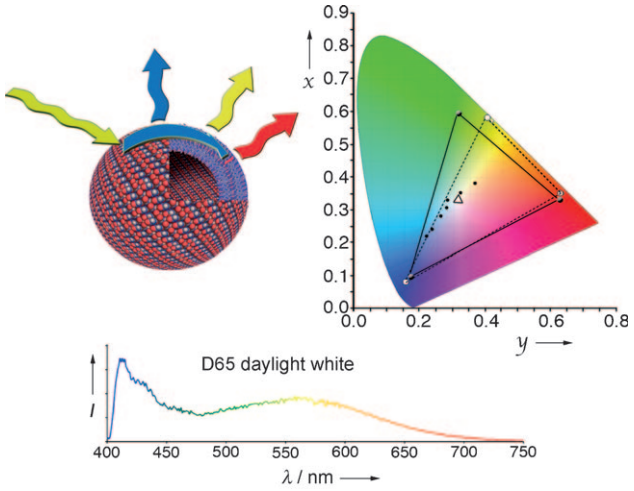

Figure 5. Energy migration in tricomponent spherical aggregates allows a large portion of the visible spectrum to be covered. Open circles correspond to the chromatic coordinates of the emission from aggregates of **1**, **2**, or **3** and define a gamut (dashed line) of available colors. Filled circles represent the color obtained by doping aggregates of **1** with varying proportions of **2** and **3**. For comparison, the gamut of a standard RGB display is also shown (solid lines). Bottom: Emission spectrum of a single vesicle-like aggregate emitting D65 white light. Its position on the chromatic diagram is indicated by the white triangle, ($x = 0.313$, $y = 0.331$).

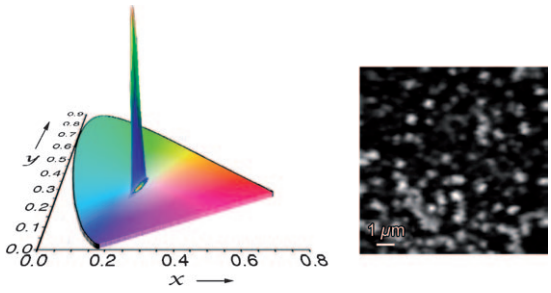

Figure 6. Dispersion of colors obtained by analyzing 10^4 spectra from the 10×10 μm image shown on the right. The composition of the solution used for depositing the aggregates was 0.1 mM in **1**, 0.2 μM in **2**, and 0.25 μM in **3** (in THF).

above 605 nm exhibits long-lived components (4.0 and 4.8 ns, respectively) that are similar to the average decay times of **2** and **3**.[11] The observed decrease in the average decay time of **1** is attributed to the presence of a distribution of distances that separate the quencher molecules from the excited donor at such low quencher concentrations, as has been previously observed in doped fluorescent fibers.[2e] The effectiveness of such low dopant levels to quench the emission of the donor indicates that energy transfer is highly efficient. In this respect, the lack of bulky hydrocarbon chains generally used to promote aggregation may contribute to enhancing the packing density of the chromophores in the aggregates.

Because the emission of composite colors (including white) involves multiple energy transfer processes between identical (exciton hopping) as well as between different chromophores, we may expect that the emission spectrum may vary from one aggregate to another. To assess this point, we investigated the distribution of colors from a 10×10 μm area containing approximately 200 vesicle-like aggregates (10^4 spectra). The results are shown graphically in Figure 6, giving the standard deviation of the x and y chromatic coordinates of a population of individual objects to be $\sigma_x = 0.008$ and $\sigma_y = 0.011$. Furthermore, for each compound, the corrected emission spectra from individual aggregates of different sizes were collected and compared. In all cases, the differences in the emission spectra between the aggregates were minimal (see Figure S12).[7] It is also interesting to note that, whereas the emission spectra of compounds **2** and **3** are unchanged when they are included as dopants in aggregates of **1** or **2**, respectively, the emission of **3** is shifted hypsochromically when included in aggregates of **1**.

Under the experimental conditions used for the confocal microscopy studies, we find the emission from the deposited vesicle-like aggregates to be very stable. For example, under an argon blanket, the emission from a single aggregate composed of **1** doped with **2** and **3** was found to decrease with a half-life of 260 s under pulsed picosecond laser illumination.[7] The estimated energy at the focal point is approximately 1.6×10^{-17} J per pulse, which corresponds to an average excitation irradiance of approximately 0.24 W cm^{-2}. During this time, we observe a shift of the color towards the blue, in agreement with the loss of the red component from the composite emission. The preferential bleach of the lowest-energy acceptor is in agreement with its enhanced excitation by the light-harvesting donor component through energy transfer.[4a] Aggregates prepared using a single component, either compound **1**, **2**, or **3**, are even less susceptible to photobleaching and required higher laser powers (3 W cm^{-2}) to show a significant decline in emission intensity (see Figure S13).

The system described herein offers an unprecedented combination of high photostability, with the spontaneous formation of spherical aggregates that can incorporate up to three different chromophores giving access to a large spectrum of colors. Furthermore, the possibility of depositing mixed-component vesicles on a variety of insulating or conducting substrates makes this system very promising for the in-depth study of energy-transfer processes in organic vesicle-like aggregates and for the development of nanometer-sized point sources for light-emitting devices covering the visible spectrum. Elucidation of the mechanism responsible for the spontaneous formation of spherical aggregates and their inclusion into organic electroluminescent devices are underway.

Experimental Section

Preparation of vesicles. Solutions of compounds **1**, **2**, or **3** were prepared by adding the appropriate volume of THF (dried over Na/benzophenone and distilled prior to use) to a glass vial containing a solid sample of the compound to produce a 0.1 mM solution. Dissolution was achieved by gentle shaking of the vial. For mixed-color vesicles, to a sample of **1** in THF (0.5 mL, 0.1 mM) was added an aliquot (1–5 μL) of a solution of **2** or **3** (0.1 mM in THF), and the solution was homogenized by gentle swirling. The solutions were

dropcast onto the substrates using a syringe to deposit approximately 5 μL of solution, and the solvent was allowed to evaporate in air.

Scanning electron microscopy. Samples were prepared by dropcasting a THF solution of **1** (0.1 mM) onto a flat SiO_2/Si substrate as described above. The samples were imaged using a FEI Nova NanoSEM 200 in low-vacuum mode with no conductive overcoat. The chamber pressure was maintained at 0.45 Torr water or THF vapor using a differential pumping system. An immersion lens was employed and the secondary electrons amplified by gas vapor and collected by an electrode mounted on the pole piece.

TEM. Samples were dropcast onto a 200 mesh copper grid coated with formvar film stabilized with vacuum-evaporated carbon and dried under air. The samples were examined in electron microscopes operating at 75 kv (Hitachi H-7650) and at 200 kv (JEOL JEM-2100).

AFM. Samples were prepared by dropcasting a THF solution of **1** (0.1 mM) onto a flat SiO_2/Si substrate a described above. The samples were imaged using an Autoprobe CP-Research (SPI) instrument equipped with a PP FMR tip operated in intermittent (tapping) mode ($\nu = 75090$ Hz).

Confocal fluorescence microscopy. Measurements were performed on a Picoquant Microtime 200 inverted confocal microscope, using a PicoHarp 300 multichannel single photon counter and two MPD SPADs. The excitation originates from a frequency doubled Ti-Sa laser (Coherent) tuned at 385 nm with picosecond pulses (6 ps) at 4.76 MHz repetition rate. Average powers of typically 0.24 $W\,cm^{-2}$ (peak power of ca. 16 $kW\,cm^{-2}$), and up to 24 $W\,cm^{-2}$, have been used for image and spectra acquisition. The laser beam is injected by 90° reflection on a 80%T/20%R spectrally flat beam splitter into the microscope objective (100× UPLSAPO, N.A. 1.4). The emission is collected by transmission through the same beam splitter and a suitable interferential filter before being focused on a 50 μm pinhole. After the pinhole, light can be diverted into an Andor SR300i spectrometer equipped with a Newton EM-CCD for spectroscopy measurements. All spectra are QE corrected. All decays obtained using the confocal setup were tail-fitted as the emission is accumulated on a broad spectral range and the instrument response function (IRF) is wavelength dependent. The fit is done according to $I(t) = \Sigma A_i e(-t/\tau_i)$ and the average decay times are defined as $\Sigma A_i\tau_i^2/\Sigma A_i\tau_i$.

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[10] The formation of nanospheres was confirmed by SEM and confocal fluorescence microscopy was used to determine the emission spectrum of individual objects.

[11] The average luminescence decay times from vesicle-like aggregates composed of pure **2** or **3** were determined to be 3.2 and 5.3 ns, respectively.

