Near-Field Scattering Enhancement of Perylene Based Aggregates for Random Lasing

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Strong near-field scattering enhancement (NFSE) of polyhedral oligomeric silsesquioxanes (POSS) nanoparticles (NPs) aggregates is found through physical simulation. An aggregation of \(N,N'\)-di-[3-(isobutyl polyhedral oligomeric silsesquioxanes) propyl] perylene diimide (DPP) which possesses POSS as scatteres experimentally performs strong NFSE, which conforms the physical simulation results. Moreover, coherent random laser is triggered from the DPP aggregates in carbon disulfide. It is the NFSE of POSS NPs connected to both ends of DPP through covalent bonds and the NFSE of their aggregation thanks to DPP’s aggregation that is responsible for the coherent random laser. So, this work develops a method to improve weak scattering of system through construction of molecules, and opens a road to a variety of novel interdisciplinary investigations, involving molecular designing for disordered photonics.

Key words: Isolated particles, Aggregates, DPP, Near-field scattering enhancement, Random Laser

I. INTRODUCTION

Light scattering in disordered materials has attracted much interest recently. And the light scattering by groups of particles has important applications in light detection and ranging (LiDAR) experiments [1] and astrophysics [2] through its multiple scattering effects, such as enhanced backscattering [3, 4] and negative polarization branches [5], and so forth. In particle groups, according to the distance between the particles (\(d\)), multiple scattering is divided into three categories [3, 6]: near-field scattering (\(d<\lambda\)), transition-field scattering and far-field scattering (\(d>\lambda\)). Besides, near-field scattering enhancement (NFSE) is discovered in some recent researches about near-field scattering [7–11], and it is mainly applied to the Raman scattering, infrared absorption and fluorescence emission of the reinforced materials, and there are few reports about its application to random laser (RL).

It is well known that the occurrence of RL in disordered medium requires a gain medium and a scattering medium. The gain medium can be a fluorescent dye, a quantum dot and so on. Perylene diimide (PDI) is a kind of fluorescent dye which has high quantum yield in dilute solutions (close to 100%) [12] and excellent performance such as high molar absorptivity, and optical, chemical and thermal stability [13]. Up to now, PDI has been widely used in the field of liquid crystal display [14] and fluorescent sensor [15].

Strong enough scattering from scatterers is another element for pumping RL. The scatterer can be divided into strong scatterer, such as ZnO [16], and weak scatterer, like polyhedral oligomeric silsesquioxanes (POSS) nanoparticles (NPs). Due to weak scattering, POSS NPs’ application is limited to some extent. For obtaining RL, some researches [17, 18] need the help of waveguide effect of a fiber. In our recent work, POSS units were chemically bonded with PDI to fabricate a hybrid molecule, i.e. \(N,N'\)-di-[3-(isobutyl polyhedral oligomeric silsesquioxanes) propyl] perylene diimide (DPP). POSS units in the hybrid molecule not only act as steric hindrance groups to reduce fluorescence quenching resulting from aggregation, but also as

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weak scatterers [19].

In this work, enhancement in the near-field scattering of POSS units in DPP single molecule and aggregates in CS2 is investigated in detail through physical simulation and experiments. Firstly, the scattering cross-section (SCS) of two isolated adjacent dielectric spherical NPs within 100 nm much smaller than emitting wavelength 582 nm (near-field distance) and their aggregates is theoretically calculated utilizing a physical stimulate model. According to the result, we fabricate the DPP. And then we note that, in the single molecule state, the fluorescence intensity of DPP solution is slightly larger than that of reference solution DCP&2POSS under different pumping powers. While in the case of aggregation, the fluorescence intensity of aggregated DPP is much larger than that of aggregated DCP&2POSS. Additionally, with the degree of DPP’s aggregation rising, the fluorescence intensity grows up greatly. Results indicate that NFSE of POSS units in DPP is responsible for the phenomenon above. Finally, the aggregated DPP can be used to trigger RL thanks to the NFSE.

II. EXPERIMENTS

The commercial aminopropylisobutyl POSS was obtained by Hybrid Plastics. CS2 was purchased and used as solvent in all samples without further purification. Ultraviolet visible (UV-Vis) absorption spectra were measured on a UV-2550 PC spectrophotometer (Shimadzu). A Q-switched neodymium-doped yttrium aluminium garnet (Nd:YAG) laser (pulse duration 10 ns, repetition rate 10 Hz) with an output of 532 nm was used to pump the sample, with a focus lens of f=10 cm. Pump pulse energy was controlled by using a Glan prism. The sample was located on a three-dimensional mobile station. Emitted light was collected by using a QE65 Pro fiber spectrometer (Ocean Optics, FL, USA; resolution of 0.4 nm, integration time of 100 ms), which is shown in FIG. 1(b).

Active hybrid molecules (DPP) were synthesized with POSS connected to both ends of PDI by covalent bond. DPP, DCP and POSS molecular structures are shown in FIG. 1(a), and synthesis process of DPP and DCP referred to previous relevant reports [12]. DPP was dissolved in CS2 solvent and prepared in series of concentrations (10⁻¹⁷−10⁻⁴ mol/L), which acts as sample 1. Simultaneously, two reference samples were prepared as well, called sample 2 and sample 3, respectively. Sample 2 is a mixture of DCP and POSS NPs (DCP&2POSS NPs) with a ratio of 1:2, (DCP of 10⁻¹⁷−10⁻⁴ mol/L and POSS NPs of 2×10⁻⁷−2×10⁻⁴ mol/L); sample 3 contains only DCP (10⁻⁷−10⁻⁴ mol/L). And both samples are also dissolved in CS2.

III. RESULTS AND DISCUSSION

A. Physical model of near-field scattering

According to physical model in Ref.[20] which can be exerted to study our issue, a similar double-particle model is depicted in FIG. 2 (b) and (c). In FIG. 2(b), it is shown that two adjacent dielectric spherical nanoparticles are symmetrical along the y axis with the same radius a=0.27 nm (a radius size of POSS NPs). The scatterers are illuminated by the monochromatic z-polarized plane wave, whose wave vector is in the x-y plane with the azimuth angle φ to x axis. Therefore, when φ=π/2, the light is incident along the axis of the two spheres (y axis). FIG. 2(c) is similar to FIG. 2(b), this is a simplified system about aggregated spheres based on the upper right inset: molecular modelling configurations of two aggregated DPP [12]. As we know, the extinction cross section signifies the gross loss of the incident field energy which also can be written as the sum of the SCS and absorption cross section [21].

Given the Eq.(1) [22], a z-polarized plane wave with propagating direction k can be gained by taking the dot product of \(\mathbf{T}^k\mathbf{e}^{i\mathbf{k}\cdot\mathbf{r}}\) with the polarization vector of incident electric field. Here \(\mathbf{T}\) is unit dyadic. \(C_{mn}(\mathbf{k})\), \(B_{mn}(\mathbf{k})\) are vector spherical harmonics. Given the expansion coefficients of the incident field and the scattered field about the sphere origin is as follow

\[
\mathbf{T}^k\mathbf{e}^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{m,n} (-1)^m \frac{2n+1}{n(n+1)} j^{2m} \left( C_{-mn}(\mathbf{k}) F_{1mn}^{(1)}(kr) + i B_{-mn}(\mathbf{k}) F_{2mn}^{(1)}(kr) \right)
\]

\[
E_x(r,\omega) = \sum_{m,n} \left[ f_{mn}^{(1)} F_{1mn}^{(1)}(kr) + g_{mn}^{(1)} F_{2mn}^{(1)}(kr) \right]
\]

\[
E_y(r,\omega) = \sum_{m,n} \left[ p_{mn}^{(1)} F_{1mn}^{(1)}(kr) + q_{mn}^{(1)} F_{2mn}^{(1)}(kr) \right]
\]

The total extinction cross section of the cluster is [26]:

\[
C_{ext}=4\pi \sum \frac{N_s}{k^2} \left( \sum_{m,n} E_{mn} \left( f_{mn}^* p_{mn} + g_{mn}^* q_{mn} \right) \right)
\]

The total absorption cross section is [26]

\[
C_{abs}=4\pi \sum \frac{N_s}{k^2} \left( \sum_{m,n} E_{mn} \left( d_n^i |g_{mn}|^2 + c_n^i |f_{mn}|^2 \right) \right)
\]

\[
d_n^i = j \frac{\phi_n^i (m^i x^i) \phi_n^i (m^i x^i) m^i}{|m^i \phi_n^i (m^i x^i) \phi_n^i (x^i) - \phi_n^i (x^i) \phi_n^i (m^i x^i)|^2}
\]

\[
c_n^i = j \frac{\phi_n^i (m^i x^i) \phi_n^i (x^i) m^i}{|\phi_n^i (m^i x^i) \phi_n^i (x^i) - m^i \phi_n^i (x^i) \phi_n^i (m^i x^i)|^2}
\]

\[
E_{mn} = \frac{n(n+1)(n+m)!}{(2n+1)(n-m)!}
\]

\[
\phi_n^i(x) = x_i^n(x)
\]

\(N_s\) is the number of spheres, \(m^i\) is the complex refractive index of sphere \(i\), and \(x^i=ka^i\) is the size parameter.
and the SCS is $C_{\text{sca}} = C_{\text{ext}} - C_{\text{abs}}$. According to Ref. [20], the SCS area of the mere two isolated POSS particles (system 1) at any distances and aggregated POSS particles (multiple spheres) (system 2) will be obtained if the relevant parameters (like radii, refractive index, incident wavelength, and the number of aggregated POSS particles) in the scattering matrix [20] are fixed.

B. Properties of the physical model

Here, with the assistance of Eqs. (1−7), the effects of the distance (0−100 nm) between two isolated POSS NPs (system 1) and the number of aggregated POSS NPs in aggregate (system 2) on SCS.
NPs in aggregates (system 2) on SCS are shown in FIG. 3 (a) and (b), respectively. And here fixed radius $a$ is 0.27 nm, incident wavelength is 582 nm. From FIG. 3(a), interestingly we find that the SCS of two isolated POSS nanoparticles grows up as their approaching to each other within the distance of 0–100 nm. The curve in FIG. 3(b) shows that the SCS of aggregates increases with the number of the nanoparticles in aggregates increasing. Two results above give a clue that with nanoparticles approaching to each other or aggregating, they may lead to an NFSE, which can intensify the scattering of POSS NPs.

Inspired by the physical simulation results, DPP was fabricated, and a series of active DPP solutions were designed to explore NFSE. DPP contains both of fluorescent dye (PDI) and scattering groups (POSS), and has different aggregation extent at different concentrations in CS$_2$ solution. In experiments, DCP, one fluorescent dye similar to DPP in chemical structure (shown in FIG. 1) without scattering groups, was also synthesized to prepare two samples: DCP solution in CS$_2$, and a mixture solution of DCP and POSS in CS$_2$.

C. Structure results and discussion

UV-Vis absorption of DPP, DCP&2POSS, and DCP is shown in FIG. 4 (a), (b), and (c) respectively. Taking the UV-Vis absorption of DPP for an example, the perylene imide molecule has three characteristic peaks between 400 and 600 nm (531, 492, and 462 nm) from right to left corresponding to 0-0, 0-1, 0-2 electronic transitions [25–27] of PDI respectively. To explain the physical meaning of 0-2, 0-1, 0-0, we have supplied the energy level configuration for electron transition of perylene imide molecules in FIG. 5 from which we can see the 0-0 electron transition in the absorption spectra represents the transition from the 0 energy level of the ground state to the 0 energy level of the first electron excited state, the 0-1 represents the transition...
from the 0 energy level of the ground state to the 1 energy level of the first electron excited state, and 0-2 represents the transition from the 0 energy level of the ground state to the 2 energy level of the first electron excited state, which have been marked with three upward black arrows. And 0-1 and 0-2 transitions are affected by the aggregation state \([25, 28]\), and the 0-0 electronic transition is not. With the increase of the concentration of DPP and DCP, DPP and DCP will aggregate, which leads to the change of the absorption peak intensity corresponding to the 0-1 electron transition different from that of 0-0, so \(\varepsilon_{0-1}/\varepsilon_{0-0}\) \([19]\) is used as a quantity for characterizing the aggregation extent of molecules containing PDI groups. \(\varepsilon_{0-1}\) and \(\varepsilon_{0-0}\) are the extinction coefficients of the absorption peak corresponding to 0-1, 0-0, and the extinction coefficient is proportional to the peak intensity.) As the concentration increases, the change of \(\varepsilon_{0-1}/\varepsilon_{0-0}\) of DPP, DCP&2POSS and DCP is described in FIG. 4(d), which is experimental data. It can be easily seen that with the concentration of DPP below \(10^{-5}\) mol/L, \(\varepsilon_{0-1}/\varepsilon_{0-0}\) is almost unchanged, indicating that the DPP exists in single molecules in CS\(_2\) solvent. However, with the concentration of DPP above \(10^{-5}\) mol/L, \(\varepsilon_{0-1}/\varepsilon_{0-0}\) rises rapidly, manifesting that DPP molecules are aggregated \([28]\).

Similarly, it is seen from FIG. 4(d) that DCP molecules also aggregate above \(10^{-5}\) mol/L concentration in both the DCP&2POSS and the DCP solution. To confirm the occurrence of aggregation in above solutions, the fluorescence spectra of them at various concentrations are measured and shown in FIG. S1 (a, b, c) in supplementary materials, respectively, from which fluorescence quenching phenomenon can be clearly seen with the concentration above \(10^{-5}\) mol/L. It is well known that fluorescence quenching takes place when the distance between fluorescent molecules are within 10 nm because Förster resonance energy transfer typically occurs over distance up to 100 \(\AA\). From above experimental observation and absorption spectra analysis, it is concluded that the distance of POSS within aggregates is from 0.5 nm to 10 nm, far smaller than the wavelength of the emission from DPP above 500 nm.

In order to investigate the effect of pump energies on fluorescence, a pulsed laser with an output of 532 nm was used to pump samples with and without aggregation. All tests are performed in a 10 mm cuvette where the concentrations of DPP are \(10^{-5}\) and \(10^{-4}\) mol/L. Results are shown in FIG. 6 (a) and (b), respectively. FIG. 6(a) shows three fluorescence peaks at 541.42, 582, 632.46 nm respectively and the main peak appears at
541.42 nm. Three fluorescence peaks in FIG. 6(b) are at 548.1, 582.14, 631.43 nm, the main peak position is at 582.14 nm. The comparison of fluorescence intensities of three samples are also investigated, and the dye concentrations are $10^{-5}$ and $10^{-4}$ mol/L in FIG. 6 (c) and (d), respectively. When the concentration of dye is $10^{-3}$ mol/L (FIG. 6(c)), three samples are not aggregated, so the fluorescence quantum yields of them are nearly the same about 100%, thus if there are changes in fluorescence intensity of the three samples, the intensity of scattering is responsible for them. The fluorescence intensities of DCP solution where there is no POSS NP and DCP&2POSS solution are basically the same at different pumping energies as shown in FIG. 6(c), implying the scattering of POSS NPs in DCP&2POSS solution has no effect on the fluorescence intensity at various pumping energy. However, when there are POSS NPs in solution, fluorescence intensities of DPP solution under various pump energies are slightly stronger than that of DCP&2POSS solution at the same pumping power, as shown in FIG. 6(c). This difference lies in the distance of POSS NPs. In DPP solutions, POSS is chemically bonded at two ends of PDI, and the distance is about 1.2 nm by simple calculation from its chemical structure, which can be seen from the molecular structure of DPP. While in DCP&2POSS solution, POSS NPs are freely dispersed in the $10^{-5}$ mol/L solution, with the distance about 43.36 nm (shown in Table S1 in supplementary materials) which is greatly larger than 1.2 nm. So this experimental result demonstrates that POSS NPs can display scattering enhancement if the distance is quite small. Therefore, our experiment agrees well with the physical simulation (FIG. 3(a)) that the enhancement in near-field scattering rises up with the decreasing distance.

When the dye’s concentration is $10^{-4}$ mol/L (FIG. 6(d)), three samples are aggregated. To begin with, the intensities of DCP&2POSS and DCP are always the same although $10^{-4}$ mol/L DCP&2POSS possesses larger concentration of POSS NPs compared to $10^{-5}$ mol/L DCP&2POSS solution, which again illustrates that POSS’s scattering is fairly weak. Moreover, it is notable that at a low pump energy, like 10 µJ, fluorescence intensities of DPP and DCP&2POSS are almost the same, which means that fluorescence quantum yields are similar, so is the degree of fluorescence quenching caused by aggregation. Yet there still is a small difference in intensities at 10 µJ mainly caused by NFSE of POSS fixed at the ends of DPP. At a high pumping power, such as 90 µJ, the fluorescence intensity of DPP solution is fairly stronger than that of DCP&2POSS solution. Compared with the fluorescence intensity difference in the single molecule state, the fluorescence intensity difference in the aggregated state is much more obvious. The reasons are as follows: the dye molecules emit fluorescence after absorbing photons matching the energy level, and the fluorescence photons scatter when they encounter the scattering medium. The stronger the scattering of the system is, the more time the photons before leaving the system is, the longer the time they spend in the gain medium is, and the greater the fluorescence intensity is. Owing to nearly same fluorescence quantum efficiency, the obvious difference in fluorescence intensity is attributed to strong NFSE from the aggregation of DPP. Besides, the comparison of fluorescence intensities of $10^{-5}$ (marked as a), $10^{-4}$ (marked as b) and $10^{-3}$ mol/L (marked as c) DPP solution (which are under different aggregation degree) are investigated and displayed in FIG. 7. From this picture, firstly we observe that the intensities start from the same point, and their rates of growth are ordered by $c>b>a$, which demonstrates the NFSE is stronger under lager pump energy. Secondly, at every pump energy, the intensities are also ordered by $c>b>a$, which points out with the degree of aggregation increasing the NFSE grows up greatly as well. This is rightly consistent with previous physical simulation result depicted in FIG. 3(b), which also illustrates DPP molecules do have the properties we want, such as strong NFSE in the aggregated state. So, they are really the ideal molecules for the investigation of random lasers.

The mechanism of the population inversion for stimulated emission of random laser is different from the traditional one, which is shown in FIG. 8(a). And the mechanism of RL is as follows. When the gain medium (or dye) is pumped by the laser, fluorescence will be emitted, and the emitted light photons will scatter in the disordered scattering medium. When the scattering is strong, a loop will be formed in which the photons will be localized. In this process, the gain medium will absorb the photons continuously and emit fluorescence, and more photons will be localized in this loop. Only when the light intensity reaches a certain intensity will they be emitted, thus completing the inversion of particle number and stimulated emission. The RL phenomena of DPP and DCP&2POSS in Cs2 are investigated. The samples are obtained by encapsulating the...
solution in a glass tube with an inner diameter of 300 μm. From experimental observation shown in FIG. S4 in supplementary materials, it is seen that no RL phenomenon but only fluorescence peaks appear in 10^{-5}, 10^{-4}, and 10^{-3} mol/L DCP&2POSS solution at 700 μJ pump energy. While in DPP solution, when its concentration over 10^{-5} mol/L, multiple sharp peaks appear (each peak corresponds to a loop, which is randomly formed and changes at all times, so the position and intensity of RL peak also changes at all the time) and the evolution of emission spectra of 10^{-3} and 10^{-4} mol/L DPP in CS_{2} solution at different pump energies are displayed in FIG. 8 (d) and (c). Moreover the dependence of the intensity and linewidth of the main peaks of the emission spectra of 10^{-4} and 10^{-3} mol/L PPP in CS_{2} solution on different pump energies are shown in FIG. S3 (a), (b) and (c) of Supplementary materials respectively, from which we can see the abrupt change of the intensity and the linewidth of main peaks that is one of the typical features of stimulated emission. So we think coherent RL [29–32] is detected from 10^{-4} and 10^{-3} mol/L PPP solution. And in 10^{-5} mol/L DPP solution, no RL is shown in FIG. 8(b). All these reveal that stronger NFSE from aggregated DPP is responsible for the generation of RL thanks to the special chemical structure of DPP.

IV. CONCLUSION

To summarize, in this work, through physical simulation it is found that strong NFSE exists in POSS NPs aggregates. To verify physical simulation result, we have investigated the NFSE phenomenon in aggregated DPP solution with the concentration over 10^{-5} mol/L, from which we have observed strong NFSE. Besides, we obtain coherent RL from the solution above. Strong NFSE of POSS NPs owing to the aggregation is responsible for the RL in the aggregated DPP solution.

Supplementary materials: Fluorescence emission spectra of DPP, DCP&2POSS and DCP at different concentrations are provided, demonstrating that the three samples aggregate at concentrations above 10^{-5} mol/L. And distance between POSS nanoparticles in DCP&2POSS solutions at different concentrations is offered. Besides emission spectra of 10^{-5} mol/L DCP&2POSS and 10^{-4} mol/L DCP&2POSS in CS_{2} solvent at various pump energy, and emission spectra of 10^{-5} mol/L DCP and 10^{-4} mol/L DCP in CS_{2} sol-
vent at various pump energy are also supplied. Dependence of the intensity and linewidth of the main peaks of the emission spectra of $5 \times 10^{-5}$, $10^{-4}$, and $10^{-3}$ mol/L DPP on different pump energies is added to verify the generation of random lasers. At last, emission spectra of $10^{-3}$, $10^{-4}$, and $10^{-5}$ mol/L DCP&2POSS in CS$_2$ solvent at a pump energy of 700 μJ are provided to demonstrate that random lasers can not be pumped from above DCP&2POSS samples.

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