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On heterogeneity in fluorescent few-atom silver nanoclusters

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Isabel Díez,†*[a] Robin H. A. Ras,[a] Mykola I. Kanyuk[b] and Alexander P. Demchenko*[b]

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Fluorescent clusters of several Ag atoms are fluorophores with a large set of attractive properties including subnanometer size, high fluorescence quantum yield and large Stokes shift. When formed on polymeric scaffolds they exhibit a broad range of heterogeneities in excitation and emission spectra. Addressing this issue we provide detailed spectroscopic studies of these clusters produced by photochemical reduction of silver salt on amphiphilic polystyrene-*block*-poly(methacrylic acid) block copolymer in *N*,*N*-dimethylformamide. Our results allow discriminating three types of emitters differing in positions of their excitation and emission bands. In addition, each band exhibits characteristic features of inhomogeneous broadening, such as strong dependences of excitation spectra on emission wavelength and of emission spectra on excitation wavelength in a mirror-image manner. The latter dependence does not appear on excitation at the 2nd band in the near-UV region. A qualitative model based on inhomogeneous broadening of spectra is suggested to explain these effects.

Introduction

Recently observed great interest in photophysics and spectroscopy of few-atom silver nanoclusters (AgNCs) is due to both their unique properties as fluorescence emitters and the broad range of their potential applications.[1–3] AgNCs can be easily produced by chemical or photochemical reduction of silver salts with the appearance of efficient visible light absorbance and bright emission. These fluorescent clusters being superior in brightness and photostability may substitute organic dyes.[4] They are good as reporters in fluorescence sensing[5–7] and biosensing including DNA hybridization assays[8,9] as well as for biological imaging,[10,11] and for single-molecule detection[4,12] that can be also provided with two-photon excitation.[13] AgNCs can be potentially used in optic and electronic devices on a single molecular level.[14]

With the aid of stabilizing agents and scaffolds they are usually produced in aqueous media,[15] but their photochemical formation and stabilization in a variety of organic solvents can be also realized.[16] In particular this can be achieved using an amphiphilic polystyrene-*block*-poly(methacrylic acid) block copolymer (PS-*b*-PMAA). The PMAA homopolymer was reported to be an excellent template for fluorescent silver clusters in aqueous medium,[17,18] whereas the PS block was selected to facilitate solubilization in polar and apolar organic solvents. We achieved photoreduction of silver ions in different organic solvents, including those of high and low polarity, demonstrating that the polymeric matrix has an important role in the stabilization of the clusters.

The spectroscopic heterogeneity in solutions of Ag clusters such as the presence of several bands in fluorescence emission spectra and the excitation wavelength dependence of positions of single bands was reported by many authors, see for example ref. 1, 18–20. These data obtained for cluster–scaffold composites in water demonstrated also unexpectedly large Stokes shifts (on the order of 2000 cm^{-1}). Strong light scattering was usually present in these samples. In our studies[16] the spectroscopic heterogeneity was manifested by a strong dependence of excitation spectra on emission wavelength (λ_{em}). Additionally, mirror-symmetric dependence of emission spectra on excitation wavelength (λ_{ex}) was observed with PS-*b*-PMAA scaffolds in solvents of different polarities. *N*,*N*-Dimethylformamide (DMF) proved to be the most attractive solvent as the medium for the formation and preservation of silver clusters. In this highly polar solvent the formed cluster–polymer composites are distinguished by bright and stable fluorescence and low levels of light scattering in the near-UV.

Here, we analyze in detail the spectroscopic heterogeneity of fluorescent silver nanoclusters produced in DMF hoping that this study will be a useful basis to interpret similar effects in other systems.

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[a] *Department of Applied Physics, Aalto University School of Science (previously Helsinki University of Technology), P.O. Box 15100, FIN-00076, Espoo, Finland*
[b] *Laboratory of Nanobiotechnology, Palladin Institute of Biochemistry of the National Academy of Sciences of Ukraine, 9 Leontovicha st., 01030 Kiev, Ukraine. E-mail: alexdem@ukr.net; Tel: +380 44 234 11 06*

† Present address: Departamento de Física de la Materia Condensada, ICMA-CSIC, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain. E-mail: isabeldiez@unizar.es; Tel: +34 976 76 1333.

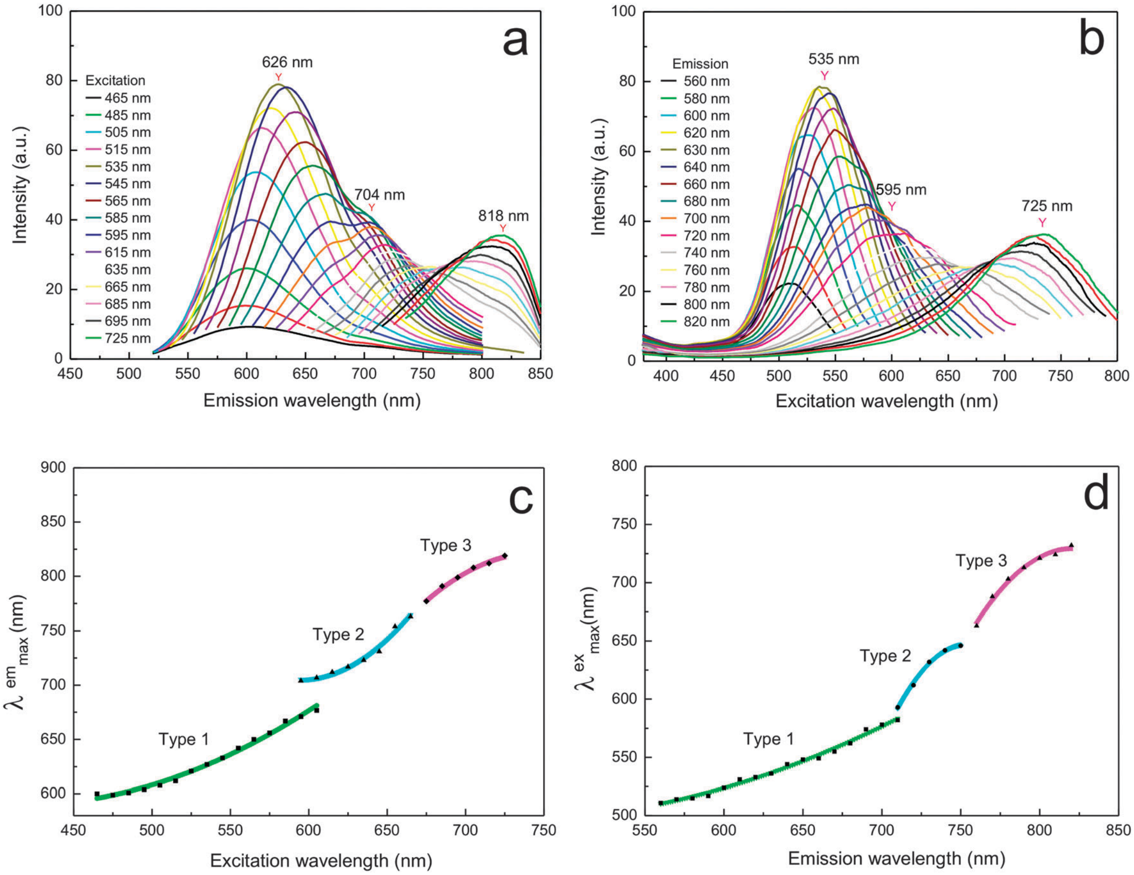

Fig. 1 AgNCs formed in DMF with an irradiation time of 9 h. (a) Fluorescence emission spectra as a function of excitation wavelength and (b) excitation spectra as a function of emission wavelength. (c) Representation of the positions of fluorescence emission spectra (λ^{em}_{max}) as a function of excitation wavelength (λ_{ex}) and (d) the positions of excitation spectra (λ^{ex}_{max}) as a function of emission wavelength (λ_{em}) in the visible range derived from the data of (a) and (b) respectively.

Experimental

A poly(styrene-*b*-methacrylic acid) (PS_{52}-$PMAA_{48}$) (M_n = 74 kDa) amphiphilic block copolymer was prepared by living anionic polymerization. $AgClO_4$ (anhydrous) was from Alfa Aesar and *N*,*N*-dimethylformamide from Sigma-Aldrich, 99.8%. All chemicals were used as received.

The amphiphilic polystyrene-*block*-poly(methacrylic acid) block copolymer (PS-*b*-PMAA) was used as a scaffold for the formation of silver clusters. The silver precursor was an organic-soluble salt, $AgClO_4$. The procedure was previously reported.[16] In short, a freshly prepared solution of silver salt was added to the block copolymer solution after it was fully dissolved in DMF. Then the mixture was irradiated with a desk-lamp (fluorescent light source, peak emission 366 nm, 11 W) until fluorescence appeared. Two samples (illumination time of 6 h and 9 h) were used in this study. The long-term stability of such clusters was excellent. The samples were stored at 4 °C in the dark for more than 10 months and no changes in their spectroscopic properties were noticed.

Recording of fluorescence spectra and analysis of excitation–emission functions were performed on a Cary Eclipse spectrofluorimeter in a standard cuvette at room temperature. The dependences of excitation spectra on emission wavelength and of emission spectra on excitation wavelength were obtained with intervals of 10 nm over the corresponding bands. Excitation and emission monochromator slits were 5 nm. For anisotropy studies the rotating film polarizers supplied with this instrument were used.

Results

An extremely broad spectral range of fluorescence emission is characteristic for different AgNCs formed in solutions irrespective of the nature of the support media. The spectroscopic heterogeneity can originate from the presence in studied systems of species of different structure and composition and also due to a variability of intermolecular interactions in which these species participate. With silver nanoclusters produced in DMF we performed four series of experiments. (1) Dependence of excitation spectra on emission wavelength (λ_{em}) with the steps of 10 nm in λ_{em} variation. (2) Dependence of emission spectra on excitation wavelength (λ_{ex}) within the long-wavelength band of absorption with the steps of 10 nm. (3) Excitation spectra at different λ_{em} and emission spectra at different λ_{ex} at excitations in the near-UV range of absorption. (4) In addition, we performed spectral anisotropy studies as a function of excitation and emission wavelengths.

Probing the structural and dynamic heterogeneity by stepwise shifts of excitation or emission wavelengths and recording the corresponding spectra is a frequently used tool with common application in the studies of polymers and biopolymers with intrinsic fluorophores and also with organic dyes introduced into the studied system.[21–24] Using the same approach, we observe that excitations and emissions of studied clusters demonstrate a remarkable broad heterogeneity that is extended over an extremely broad range of wavelengths. The data obtained for the excitation and emission bands in the visible part of the spectrum (Fig. 1a and b) reproduce our previous result[16] with extension of the range of excitation and emission wavelengths. This reveals two different ranges of heterogeneity. One is the presence of three types of species possessing partially resolvable distinct excitation and emission bands. From excitation–emission correlations their band maxima can be identified. The excitation ($\lambda^{\mathrm{ex}}_{\mathrm{max}}$) and emission ($\lambda^{\mathrm{em}}_{\mathrm{max}}$) band maxima are located correspondingly at 535 and 626 nm (type 1), 595 and 704 nm (type 2) and 725 and 818 nm (type 3). Comparing the samples obtained with different illumination times, of 6 h and 9 h, we do not observe any differences in the studied properties, but with one exception. Whereas the relative intensities of clusters of type 1 and 2 are essentially the same, the contribution of cluster type 3, which is strongly pronounced for the 9 h sample, in the 6 h sample is noticed only on a low level. Their identification based on the variation in λ_{ex} or λ_{em} is easy due to essential differences in both their excitation and emission spectra and the clear correspondence between these spectra.

For these three types of clusters the Stokes shifts are similar and very strong, 2700 cm^{-1} for type 1, 2600 cm^{-1} for type 2 and 1600 cm^{-1} for type 3, which suggests similar physical properties. It remains a question on what is the origin of relaxation processes leading to so strong Stokes shifts, which are also observed in other studies.

When we construct two-dimensional matrices (Fig. 1c and d) from the obtained excitation and emission data, we observe strong gradual variation in positions of these bands without detectable changes in their shapes that are roughly similar in all three emitters. Excitation bands shift strongly to longer wavelengths as a function of increasing emission wavelength and the emission spectra shift in the same direction and practically to the same extent as a function of excitation wavelength. This allows creating a series of mirror-like images (see Fig. 1a and b). This behaviour resembles the effect of "inhomogeneous broadening" that is well known in spectroscopy of organic dyes in rigid dielectric media.[21,25] In analogy with these results it can be suggested that a single type of cluster located in the environment with a broad variation in local electrostatic interactions forms a distribution of the excitation and emission energies. Thus manipulating with the wavelengths of excitation and emission one can photoselect the species having different interactions with the environment within the population of clusters of the same structure. Since the electronic transition energy varies within this population, the excitation with lower energy should result in lower energy of emission.

It was interesting to see if the differences in magnitude of the λ_{ex}-dependent shifts of emission spectra (the functions of $\lambda^{\mathrm{em}}_{\mathrm{max}}$ *vs.* λ_{ex}) are different for the three identified types of observed emission bands. The corresponding plot (Fig. 1c) shows that the shifts of emission bands are in fact very similar. This means the similarity of the effects of inhomogeneous broadening of spectra between three types of clusters and, therefore, similarity in distribution of their interaction energies with the environment. In a parallel way we analysed the dependence of excitation spectra on emission wavelength (the functions $\lambda^{\mathrm{ex}}_{\mathrm{max}}$ *vs.* λ_{em}) and observed analogous effects for these three types of clusters (Fig. 1d). As we will argue in the Discussion section, these facts indicate very important features of AgNCs that relate them with organic dyes: they should possess strong ground-state dipole moments and these dipole moments are of similar value for the three types of clusters.

Like in organic dyes, also in AgNCs there can be found high-energy excited states responsible for the UV absorption. Since these states should possess different distribution of electrons (and in organic dyes this distribution in the S_2 state located in the UV is commonly less polarized than in the S_1 state), the properties of fluorescence emission on UV excitation should be different. We identified the 2nd electronic transition in the near-UV range possessing an excitation band at 320–330 nm (Fig. 2a) and recorded the corresponding fluorescence emission spectrum at about 630 nm (Fig. 2b). According to the Kasha rule (which is the manifestation of a much faster rate of internal conversion to the emissive state than the rate of emission), the excitation to the 2nd excited state in the UV should result in the same fluorescence spectra in the visible as the excitation to the first state, which we actually observed. The UV-excited emission corresponds to the emission band of the most intensively fluorescent clusters of type 1, but in this case the excitation/emission dependences for this band are different. Thus, in a series of fluorescence spectra obtained by varying λ_{ex} over the UV excitation band we do not observe any significant dependence on excitation wavelength.

Fluorescence anisotropy was studied over the excitation and emission bands (Fig. 3). Its value at the main visible band is unexpectedly high, 0.35–0.36, which is close to the limiting value 0.4 for randomly oriented fluorophores in rigid environments and indicates the presence of strong transition dipole moments and the absence of rotation of photoselected clusters on the time scale of emission.[26] For achieving such high anisotropy values the absorption and emission dipoles must be collinear. In contrast, the anisotropy value at the UV absorption band is different being close to zero, which indicates a different electronic transition of the same major emitter.

High anisotropy of fluorescence emission is evidence for the restriction of rotational mobility of fluorophores during fluorescence lifetime, which can be provided by the rigid environment of the polymer matrix. Since these measurements are based on fluorophore photoselection by polarized excitation, we can combine them with photoselection by the wavelength of excitation light in order to obtain additional data on intra-band heterogeneity. The results are presented in Fig. 4.

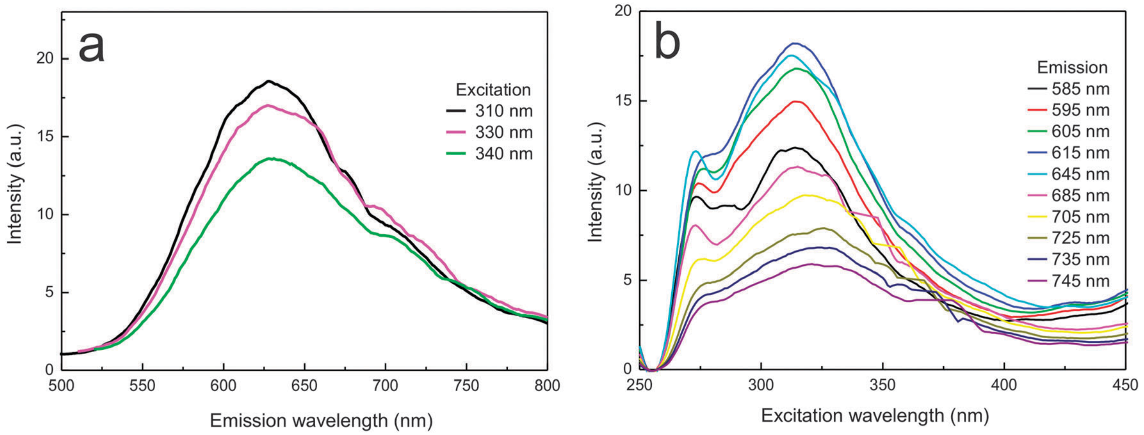

Fig. 2 Positions of fluorescence emission spectra (λ_{max}^{em}) as a function of excitation wavelength (λ_{ex}) (a) and the positions of excitation spectra (λ_{max}^{ex}) as a function of emission wavelength (λ_{em}) (b) in the near-UV range. Irradiation time = 6 h.

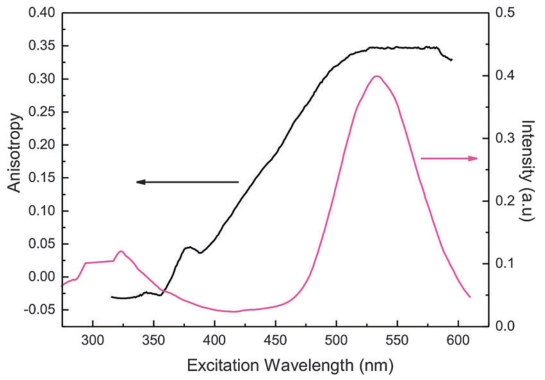

Fig. 3 Fluorescence anisotropy as a function of excitation wavelength in the extended UV-visible range of spectrum. Emission wavelength = 650 nm.

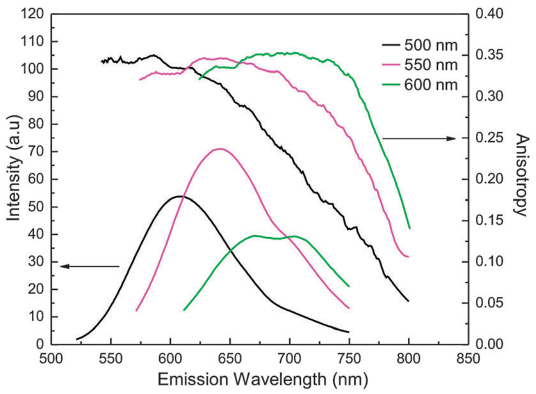

Fig. 4 Emission anisotropy and corresponding fluorescence spectra as a function of emission wavelength at excitations at 500, 550 and 600 nm.

It can be seen that high anisotropy values are characteristic for the species emitting at the wavelengths that correspond to the fluorescence emission band maximum and to its slope at shorter wavelengths. Meantime, a dramatic drop in anisotropy is observed at the long-wavelength slopes of the spectra. The variation in excitation wavelength allows demonstrating the fact that this feature is unrelated to wavelength-photoselection. In other words, the species excited at higher energies and at lower energies (500 and 600 nm in our case) behave in a similar way as when excited at the excitation band maximum (550 nm). Therefore we derive that the contour of emission spectrum of type 1 clusters is formed by the species with different rotational mobilities. The rotations of their major part are restricted, whereas there exist some part of them (possibly located at the periphery of polymer micelles) emitting at longer wavelengths than the mean, and they can rotate during the excited-state lifetime. The other possibility to explain these data is homo-FRET (the Förster resonance energy transfer between similar clusters). This mechanism requires strong overlap integral between absorption and emission spectra, which is not our case. Moreover, in inhomogeneously broadened systems homo-FRET always shows the characteristic differences in anisotropy for ''blue'' and ''red'' excitations,[23,24] which is not observed here. Therefore we consider the emissions of studied clusters to be well independent of each other.

Discussion

Despite the efforts of many research groups, the fundamental questions on the organization and stability of few-atom silver clusters formed in solutions and on correlation of their structures with spectroscopic properties remain unresolved. All the information that we presently know about these clusters conforms to a notion that for preventing their further growth the molecular scaffolds are absolutely needed. They always contain electron-rich atoms of sulphur, nitrogen or oxygen. It can be suggested therefore that these atoms play the role of electron donors in ligand-to-metal charge transfer (LMCT) complexes in which a fraction of electronic charge is transferred to the cluster of silver atoms. Several Ag atoms forming the cluster can be stabilized in these complexes by accepting and localizing the electron density, and the extent of this localization can determine the finite cluster size, prevent its continuing growth and induce electronic asymmetry. So, we postulate the formation of LMCT complexes that can be light absorbers and emitters. Such explanation is in line with that provided in comparative analysis of gold clusters formed with different electron-donating ligands.[27] In silver clusters, high electronic polarization within a system of coupled atoms was predicted in theoretical studies[28–31] and is in line with the results of recent experiments,[32] in which the clusters formed with the aid of low-molecular ligands were studied by time-resolved spectroscopy. They demonstrated strong dependence of the formation and decay rates of charge-separated states on solvent polarity. In our case we observe strongly dipolar behaviour of silver clusters that due to their interaction with the polar environment results in inhomogeneous broadening of their spectra. This leads to the formation of their symmetric excitation (gradually dependent on emission wavelength) and emission (gradually dependent on excitation wavelength) contours and to unexpectedly high and wavelength-dependent anisotropy of emission.

Being formed by a cluster of highly polarized atoms with asymmetric attachment of the ligand, the LMCT complexes should be asymmetric and possess high dipole moments that interact with surrounding dipoles. Those dipoles can be the fragments of a polymer chain but they can also be the DMF molecules that are known to possess strong dipole moments (3.86 D). Lacking ideal order, the dipoles interacting with the LMCT species perturb the energy of the ground state to a different extent forming the distribution of sites possessing different interaction energies. As it is stated elsewhere[24] the presence of this type of ground-state heterogeneity leads to monotonous shift of $\lambda_{\max}^{\mathrm{em}}$ as a function of λ_{ex} and of $\lambda_{\max}^{\mathrm{ex}}$ as a function of λ_{em} in a manner that we observe in the present experiment. It is known that when the dipole moment is low in the ground state and it is enhanced dramatically on excitation (which is the case of many "polarity sensing" organic dyes), the important contribution to spectral heterogeneity is only the excited-state distribution. It leads to a characteristic dependence of $\lambda_{\max}^{\mathrm{em}}$ on λ_{ex}, the so-called Red-Edge effect.[23,24] The present case is different, and, based on the observed symmetry in effects in the excitation and emission spectra, both the ground-state and the excited-state distributions are equally important in contributing to the spectral heterogeneity.

There are many possibilities for few-atom AgNCs to be heterogeneous in their spectroscopic properties. In addition to cluster size, there can also be variations in cluster geometry, ligation and oxidation/reduction states of constituting atoms. Potentially, all these factors could contribute to λ_{ex} and λ_{em} dependences observed in our experiment. It is essential therefore that the three types of emitters formed in DMF are easily recognized by their corresponding bands in excitation and emission spectra, so that the position of these bands and their widths are quite reproducible and do not depend on the duration of photoreduction. These properties are maintained for many days and even months when the clusters are kept in solution, without signatures of their oxidation or silver sediment formation. Such features manifest discrete character of cluster formation and organization.

At present we cannot determine the exact structure of these clusters due to the formation of multiple clusters on the same polymeric support. We can attribute tentatively these discrete spectroscopically distinguishable forms to AgNCs of different composition, regarding the number of Ag atoms, their oxidation state or their interaction with the matrix. A general rule that was well established for gold clusters[33] is probably valid also in this case: an increase in the number of atoms decreases the energy gap between ground and excited states resulting in the shifts of emission spectra to longer wavelengths (see also Table 2 in a recently published review[3]). It is notable that the Stokes shifts and the wavelength-dependent variations of spectra are very similar for the identified three types of clusters. Therefore it is reasonable to suggest that the difference is in the number of atoms in the clusters but not in their charge, which could dramatically change their dipole moments or LMTC behaviour in general.

Involvement of different types of heterogeneity besides the postulated inhomogeneous broadening cannot be ruled out, and therefore we tried to find additional supporting arguments for the suggested mechanism. We discovered the higher energy excitation band in the near-UV and noticed that there is a single (instead of three) corresponding band in emission that does not possess the excitation wavelength dependence. This fact can be interpreted in the following way. The electronic energy and electronic charge distribution within the LMCT complexes should be different for the 2nd excited state. Its effective dipole moment should also be different from that of the first state (in organic dyes it is usually differently oriented and smaller). Therefore it is natural to expect that the effects of inhomogeneous broadening in the case of UV excitation should vanish. A dramatic drop in anisotropy when the emission is excited at the UV excitation band is in line with this explanation.

Inhomogeneous broadening effects in spectra are strongly coupled with the dynamics of reorientation of dipoles surrounding the fluorophore (dielectric relaxations) in a sense that for the observation of these effects in steady-state spectra these dynamics should be slower than the fluorescence emission decay.[23–25] Therefore our results have to be analyzed with the account of data on the excited state lifetimes. Available literature data on different silver clusters formed and studied in solutions show that these lifetimes vary in a rather narrow range from several hundred picoseconds to several nanoseconds.[3,17,34–39] In our own studies on the clusters formed on a PMMA support in water[17] the fluorescence showed heterogeneous decay that could be deconvolved into 0.96 ns (82–88% of total emission) and 2.4–3.1 ns components. Thus, the characteristic time window for observing the fluorescence effects does not extend over several nanoseconds. On this scale most of the excited species (with the exception of those excited at longer wavelengths than the band maximum) do not rotate, which is evidenced by high anisotropy of fluorescence emission excited at the major part of the visible band. Moreover, double photoselection by polarization and energy of excitation light allows obtaining new evidence of site heterogeneity – the species emitting the quanta of lowest energies (at longest wavelengths) exhibit their ability for rotations.

They are probably located on a flexible polymer surface exposed to highly dielectric solvent, which also explains their long-wavelength shifted spectra.

Thus, we suggest the following model that explains our findings based on two mechanistically different types of heterogeneity (Fig. 5). The LMCT complexes, in which the electron-rich groups of ligands serve as the electron donors (D) and AgNCs as the electron acceptors, are formed in both ground and excited states. Three types of them differ probably by the number of silver atoms so that its increase shifts the spectra to longer wavelengths. Both the ground-state and excited-state energies of these complexes are distributed on their interaction with the environment forming the inhomogeneous contour in spectra.

Excitation and probing by monochromatic light selects the species of a particular cluster size. Their contours of fluorescence excitation and emission spectra are determined by the distributions of corresponding excitation and emission energies. The relaxations leading to strong Stokes shifts (shown in Fig. 5 as curving arrows) do not change this distribution, which is manifested by symmetry in wavelength-selective effects in excitation and emission spectra.

Notably, the strong Stokes shifts are characteristic for practically all silver nanoclusters studied in solutions by us and by many other authors.[1,11,40] Shifts of similar magnitude are observed in organic dyes with charge-transfer emission and usually are attributed to rapid dynamics of dielectric relaxations decreasing the energy of the fluorescent state.[25] Definitely, in the present case the mechanism of energy loss before the achievement of the emission state should be different. Such loss is observed even in cryogenic matrices of noble gases,[41] so new efforts are needed to understand its origin. Our finding that the Stokes shifts for the three types of clusters observed are similar in magnitude may be helpful for elucidating this mechanism.

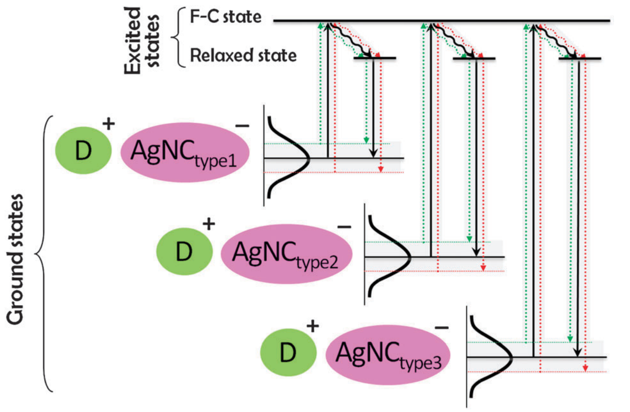

Fig. 5 Modified Jablonski diagram explaining the findings of this paper. Ground states are represented by LMCT complexes formed by the electron donors (D) and AgNCs as the electron acceptors (three types are shown, Ag_{type1}, Ag_{type2} and Ag_{type3}). The energy of each type of complex is distributed on their interaction energy with the environment, so that the energies of different cluster types can overlap. Electronic excitation by monochromatic light produces photoselection of species of a particular type and also within the distributions of every type. Excitation by selection within the mean of the distribution is depicted by black arrows, from high-energy edge – by green arrows and from low-energy edge – by red arrows. After excitation to the Franck–Condon (F–C) state (its distributions are not shown) fast relaxation occurs to the fluorescent state resulting in the large Stokes shift. If this relaxation does not involve configuration of surrounding dipoles, the fluorescence emissive transitions (depicted by downward arrows) lead to retention of original distributions demonstrating inhomogeneous broadening of both excitation and emission spectra.

Conclusions

In conclusion, we present the following model that illustrates our present findings (Fig. 5). There are three types of few-atom silver nanoclusters existing as LMCT complexes that, without exact knowledge of cluster composition, we can name Ag_{type1}, Ag_{type2} and Ag_{type3}. Their excitation and emission energies differ significantly. The origin of this difference is presently unclear but may involve the difference in composition of silver atoms, their oxidation state or their interaction with the matrix. Due to the charge-distributed nature of these complexes they interact strongly with heterogeneously distributed surrounding dipoles forming the broad distribution of ground-state energies. Electronic excitation with monochromatic light of variable wavelength provides the photoselection between these three species generating discrete bands in spectra. Photoselection is observed also within each type of clusters selecting the species possessing different interaction energies with their environment. This allows probing the distribution of interaction energies and observing that such distribution exists in both ground and excited states. Moreover, it does not change during the lifetime of the excited state, so that higher energy of excitation results in higher energy of emission, and a decrease in excitation energy results in a proportional decrease in the energy of emission. This can happen only if the cluster configuration and configuration of surrounding dipoles do not change during the lifetime of fluorescence emission. Involvement of this mechanism has to be taken into account in the analysis of spectroscopic heterogeneity of different metal clusters in solutions.

This work is hoped to stimulate active research on description and understanding of the mechanisms of light emission of few-atom clusters of noble metals. Definitely, these mechanisms are different from those of organic dyes, since their electronic polarization effects are different and must involve electronic coupling within the clusters and with their ligands.[28–31] Meantime we expect that the found regularities and their comparison with far more versatile and detailed literature on electronically polarisable organic dyes will be useful for future studies.

Acknowledgements

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