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Resonance energy transfer reveals presence of multiple luminescence emission centers within a carbon nanodot

A. A. Astafiev[+1)], *A. M. Shakhov*[+], *V. A. Nadtochenko*[+*]

[+] *N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russia*

[*] *Chemistry Department, Moscow State University, 119991 Moscow, Russia*

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Luminescent carbonaceous nanoparticles or carbon nanodots (CNDs) are an emerging class of nanomaterials with unique and attractive properties for application in fluorescent bioimaging, fluorescence sensing, photocatalysis and light emitting devices [1, 2]. CNDs commonly exhibit visible photoluminescence (PL) attributed to small luminescent organic groups within their structure [3]. Due to heterogeneity of these emission centers CNDs frequently have excitation-dependent or even multicolor PL [4]. Knowing if a single nanoparticle can carry several emitters of the same or different colors is essential for understanding luminescence mechanism of CNDs and tailoring their emission properties. Usually this information is obscured by ensemble-averaged luminescence measurements. Detection of PL from a single nanodot using fluorescence microscopy can uncover distribution of emission centers of CNDs [5, 6], but is laborious and requires expensive and complicated equipment.

An alternative strategy for revealing localization of luminescence emitters of CND is based on nonradioactive resonance energy transfer (RET) between closely situated emitters [7]. RET affects emission anisotropy in case of homotransfer between fluorophores of the same type and also emission spectra and decay kinetics in case of heterotransfer between fluorophores of different emission colors (Fig. 1a). Here we employed measurements of luminescence anisotropy and photobleaching-induced changes in spectra and decay kinetics to study RET effects and uncover multiple emissions centers localized on the same nanoparticle.

Two types of carbon nanodots referred as *p*- and *b*-CNDs were produced by pulsed laser synthesis from liquid pyridine and benzene respectively [8]. Both samples consisted of nanometer-sized particles and exhibited visible PL with broad and excitation-dependent emission spectra. In order to reveal homo-RET effects we analyzed anisotropy decay of blue PL of CNDs at 450 nm emission wavelength as a function of solvent viscosity η. We show that a simple model of a cluster of several identical fluorophores in solution [9] predicts that the anisotropy decay rate is a linear function of inverse viscosity:

$$K = \alpha/\eta + K_0, \quad (1)$$

where α and K_0 are independent of viscosity and the first term corresponds to depolarization due to rotational diffusion of nanodots in solution and the second viscosity-independent term K_0 – to RET between fluorophores. Measurements of anisotropy decay kinetics of *p*- and *b*-CNDs under pulsed laser excitation in glycerol-ethanol mixtures confirmed that the anisotropy decay rate followed the linear dependence (1) (Fig. 1b). The homo-RET rate of *p*- and *b*-CNDs was found as an intercept on a linear fit of experimental $K(1/\eta)$ dependence and was equal to 0.17 and 0.22 ns^{-1} respectively. The homo-RET rate could be increased by photooxidation of CNDs, which produced additional luminescence groups and increased the average number of luminescence emitters per nanoparticle.

Presence of energy exchange between emission centers of CNDs was confirmed by measurement of anisotropy decay kinetics in pure glycerol, where rotational diffusion was arrested due to high solvent viscosity. Emission anisotropy of *p*- and *b*-CNDs in glycerol decayed as a single exponent and decay times – 7 and 4.5 ns respectively were in reasonable agreement with inverse of the homo-RET rate. Almost complete depolarization of PL at long time reveals that nanodots carry a large number of emission centers exchanging excitation energy – at least 10–15 per nanoparticle in average.

Steady-state emission anisotropy of *p*- and *b*-CNDs in glycerol strongly decreased with increase of the emis-

1)e-mail: astafiev.artyom@gmail.com

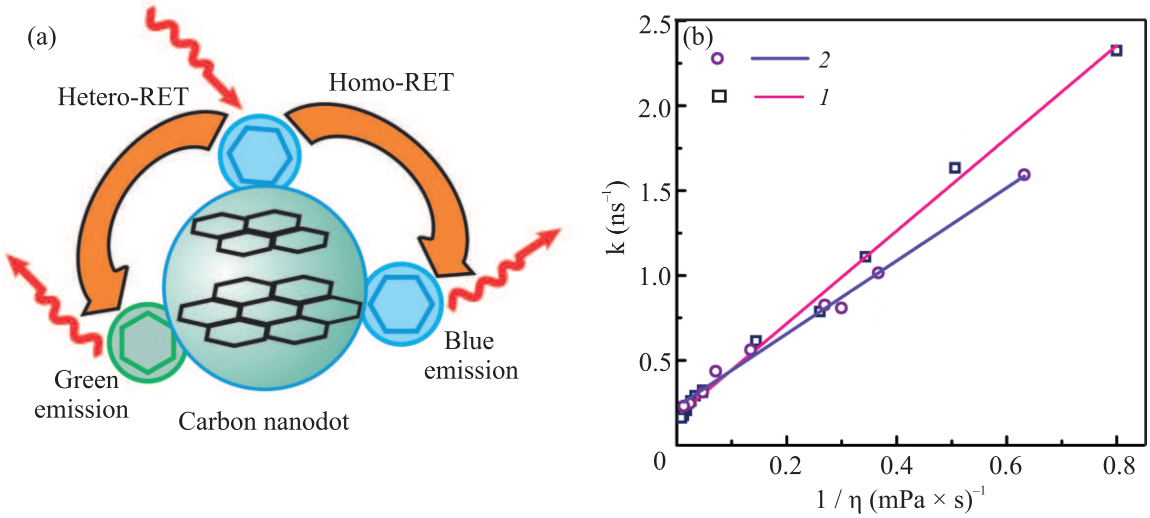

Fig. 1. (Color online) (a) – Scheme of homo- and hetero-RET between emitters localized on the same carbon nanodot. (b) – Anisotropy decay rate K of p-CNDs (*1*) and b-CNDs (*2*) at 450 nm emission wavelength as a function of solvent inverse viscosity, experimental data points and linear fit. Linear fit is expressed with the formula: $K = 2.73/\eta + 0.17$ (p-CNDs) and $K = 2.15/\eta + 0.23$ (b-CNDs)

sion wavelength. This fact suggests that green and yellow luminescence is excited by hetero-RET from blue emitters. Hetero-RET was further confirmed by photobleaching experiments, where CNDs solution was continuously irradiated with a blue diode at 450 nm wavelength. Irradiation resulted in bleaching of green PL, at the same time the intensity of blue PL of both samples increased by 20–25 % and the lifetime of blue PL became longer. These results are interpreted as dequenching of blue emitters (energy donors) upon bleaching of green emitters (acceptors). The average hetero-RET efficiency was estimated as 0.17 and 0.20 and heterotransfer rate as 0.17 and 0.33 ns^{-1} for p- and b-CNDs respectively.

In conclusion, we demonstrated homo- and hetero-RET within aromatic compounds–derived luminescent carbon nanodots, which revealed that a single nanodot can carry multiple luminescence emitters exchanging energy by nonradiative transfer. Resonance energy transfer influence luminescent properties of nanodots and should be considered in tailoring luminescent performance of CNDs and analysis of emission anisotropy. Experimental protocol described in the letter can be applied to other types of luminescent nanoparticles.

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