# Radiative Rate Modulation Reveals Near-Unity Quantum Yield of Graphene Quantum Dots

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A fundamental but difficult to assess photophysical property of quantum emitters is their fluorescence quantum yield. It describes how efficiently a fluorophore converts absorbed light into fluorescence. Conventional measurements of quantum yield are prone to errors when the sample contains also absorbing but non-luminescent species. This is, however, commonly encountered in complex systems such as graphene quantum dots that are either optically inactive themselves or contain impurities formed during nanoparticle synthesis. Their presence can lead to a gross underestimation of the quantum yield of the luminescent species. Here, a plasmonic nanocavity-based method is used to measure absolute quantum yields of graphene quantum dots by modulating their radiative rate. This method is insensitive to the presence of non-luminescent species and allows to measure absolute values of quantum yield of the luminescent nanoparticles. The determined quantum yields of nearly 100% significantly exceed previously reported values. By comparing these values with those obtained with a comparative method, the average size and relative concentration of the nonluminescent particles is determined. Thus, this nanocavity-based method offers a new way for not only measuring absolute values of quantum yield, but also for assessing the fraction of optically inactive species within a sample.

# 1. Introduction

Graphene quantum dots (GQDs) are nanoparticles that consist of one or few layers of graphene and have a lateral size

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of a few tens of nanometers.<sup>[1]</sup> Although their intriguing chemical and physical properties have been the focus of many recent studies, exact values of some of them are only poorly known.<sup>[2]</sup> One of the main but hard to measure photophysical properties is the fluorescence quantum yield (QY) that is defined as the ratio of the number of photons emitted by a fluorophore to the number of photons absorbed by that fluorophore. It determines the fluorophore's brightness (number of fluorescence photons per time at a given excitation intensity) and hence its suitability for all applications where its ability to emit light is vital. Although standard methods such as the integrating sphere or the comparison to a reference sample allow for the reliable measurement of QY values of many types of fluorophores, they are prone to considerable errors when the photo-physical properties of a sample are non-uniform or when a sample contains a fraction of nonluminescent but light-absorbing species.<sup>[3]</sup> Their light absorption and subsequent non-radiative de-excitation reduces the

apparent QY of a sample, in proportion to the relative amount of the non-luminescent impurities. Despite a few reports on the synthesis of chemically identical GQDs using a bottomup approach,<sup>[4]</sup> most of the methods that are based on a topdown approach result in non-uniform optical properties and the presence of non-luminescent impurities.<sup>[5]</sup> As a result, the reported QY values of GQDs with similar spectral properties differ widely from publication to publication, within the range of 0.03–0.53.<sup>[6]</sup>

An elegant way of measuring absolute QY values of luminescent particles is by using the Purcell effect, that is, by modulating their radiative rate of emission by placing them into a non-uniform environment.<sup>[7]</sup> This approach does not require optical absorption measurements and thus excludes the influence of non-luminescent species within the sample. Modulation of the de-excitation rate has been demonstrated for immobilized fluorophores placed close to a dielectric interface,<sup>[8]</sup> a sharp tip of a scanning probe microscope,<sup>[9]</sup> a metallic mirror,<sup>[10]</sup> a metallic nanoparticle,<sup>[11]</sup> between two gold nanoparticles,<sup>[12]</sup> or between the mirrors of a nanocavity.<sup>[13]</sup> The latter can also be used to modulate the radiative rate of an ensemble of fluorophores freely diffusing in solution. Changing the size of the nanocavity (distance between the two metallic mirrors)<sup>[14]</sup>

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modulates the mode structure of the vacuum electromagnetic field, which changes the de-excitation rate of a fluorophore inside the cavity. This effect forms the basis of the recently developed nanocavity-based method for absolute QY measurements of dye molecules,<sup>[15]</sup> semiconductor nanocrystals,<sup>[16]</sup> fluorescent proteins<sup>[17]</sup> as well as such complex systems as mixtures of different types of quantum emitters<sup>[18]</sup> or molecules embedded into a lipid bilayer.<sup>[19]</sup>

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In the present paper, we apply the tunable nanocavity method for measuring QY values of GQDs. The core advantage is that this method is completely insensitive to the presence of non-luminescent particles or impurities. We compare our nanocavity results with values obtained by using a conventional method. We demonstrate that nanocavity-based measurements of non-purified and purified samples yield nearly equal values, while the conventional method of comparing against a fluorescence standard results in lower QY values depending on the sample purity.

# 2. Results and Discussion

To demonstrate that the nanocavity-based method is applicable for GQDs fluorescing in different spectral ranges, we used blue-, cyan- and green-emitting nanoparticles (Sigma-Aldrich, product numbers 900 708, 900 707, and 900 712, respectively) synthesized from graphite using a top-down electrochemical method described in ref. [20]. The samples show bright luminescence with maxima at 448, 473, and 520 nm (black dotted curves in Figure 1). Recent single particle measurements of the GQDs showed that their emission stems from surface emission cites<sup>[2c]</sup> that were recently identified also by other research groups.<sup>[21]</sup> To measure the average size of luminescent nanoparticles, we performed fluorescence correlation spectroscopy (FCS) measurements of GQDs in aqueous solution that allowed us to unambiguously link their size with luminescence.<sup>[22]</sup> FCS measurements on aqueous solutions of GQDs could be well fitted with two diffusion components that



Figure 1. Absorption, excitation, and emission spectra of an ensemble of unfiltered and filtered graphene quantum dots and of dye molecules in aqueous solution.

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**Figure 2.** Fluorescence correlation spectroscopy measurements of graphene quantum dots in water. Open circles are experimental data; solid curves are theoretical fits. The green and red curves correspond to two diffusion components that correspond to few nanometer-sized particles and to large aggregates, respectively. *<D>* is the average diameter of luminescent particles as deduced from the diffusion-related correlation decay shown in green.

we attribute to two different populations of particles with different average sizes (**Figure 2**).<sup>[23]</sup> When using an oblate spheroid model for the shape of a graphene nanoparticle, we find for the green curves in Figure 2a lateral diameter in the range from 4.9 to 6.5 nm when assuming that one particle consists of only one single graphene layer. The red curves in Figure 2a,b reveal significantly slower diffusion values that correspond to dimensions of at least several tens of nanometers. This component is attributed to large single particles or aggregates. The FCS curve of the green-emitting sample (Figure 2c) does not show the presence of a slow-diffusing component. This suggests a higher mono-dispersity of green GQDs and the absence of large aggregates.

Extensive FCS studies of fluorescence dynamics of dye molecules showed that signal fluctuations on a sub-microsecond time scale can be attributed to rotational diffusion of the anisotropic emitters and/or their rapid blinking.<sup>[22,23]</sup> Recent studies of fluorescence blinking of carbon dots for which fluorescence emission does also originate from surface states did show that fluorescence fluctuations in the range from  $10^{-7}$ – $10^{-5}$  s have the same origin.<sup>[24]</sup> Therefore, for all three samples, we attribute the sub-microsecond FCS decay to rotational diffusion or triplet state photophysics. Further details on FCS measurements can be found in the Supporting Information (Section S1, Supporting Information).

For the referential QY measurement based on comparing against a fluorescence standard, we used the dyes Alexa 350, Atto 390, and Atto 488 as references (Section S2, Supporting Information). All three dyes absorb and emit light in the same spectral ranges as the blue, cyan, and green GQDs, respectively (shaded areas in Figure 1).

GQD purification was done using an extruder (Avanti Mini Extruder, Avanti Polar Lipids) and by passing the aqueous GQD-containing solution through a polycarbonate membrane with a pore diameter of 50 nm (polycarbonate membrane 0.05  $\mu$ m 19 mm, Avanti Polar Lipids). While purification did not lead to any significant changes in the emission (red vs black dotted curves in Figure 1) and excitation (red vs black dashed curves in Figure 1) spectra of nanoparticles, the absorption spectra exhibited a certain redistribution of spectral bands. This suggests that the purification did not change the population of luminescent GQDs with dimensions on the order of several nanometers, but reduced the presence of larger non-luminescent species that contribute only to the absorption spectrum.

Nanocavity-based QY measurements were performed using a confocal microscope that was equipped with a pulsed excitation laser and a single photon avalanche diode with time-correlated single photon counting electronics for luminescence lifetime measurements (Figure 3). The plasmonic nanocavity consists of two silver layers that were deposited by vapor deposition onto the surfaces of a glass cover slide (30 nm, bottom mirror) and a plano-convex lens (60 nm, upper mirror), respectively. Prior to silver deposition, glass substrates were coated with a 2 nm thick titanium layer for better adhesion of silver. The thicker upper mirror maximized the collection efficiency of the fluorescence that was mostly transmitted through the bottom mirror toward the high numerical aperture objective lens. The spherical shape of the upper mirror allows for easy modulation of the cavity length by laterally moving the cavity with respect to the excitation focus with a piezo scan stage. For a given lateral laser focus position, the exact distance between the cavity mirrors was determined by measuring a white light transmission spectrum, using a broad-band halogen lamp as





**Figure 3.** Schematic of the confocal scanning microscope and the plasmonic nanocavity that were used for measuring absolute quantum yields of graphene quantum dots. The inset shows the white light transmission pattern around the center of the nanocavity. The first color ring corresponds to the  $\lambda/2$  region of the cavity.

excitation source. For the excited state lifetime measurements, a droplet of aqueous solution of GQDs was placed between the cavity mirrors. The lifetime measurements were done across the first interference ring ( $\lambda/2$  region) of the cavity that can be seen in the white light transmission pattern as the first color ring around the center of the cavity (inset in Figure 3), a region where the lifetime modulation of a fluorophore is maximized. The measurements of the blue and cyan samples were done using a diode UV laser emitting at 378 nm; the measurements of the green GQDs were performed using the 485 nm light of a supercontinuum laser. Further details of the experimental setup can be found in the Supporting Information (Section S3, Supporting Information).

Open circles in **Figure 4** show results for the excited state lifetime measurements of GQDs at different cavity lengths. For each data point, both the fluorescence decay and the white light transmission spectrum were measured. The obtained curve was fitted with a theoretical model that takes into account all the parameters of the optical system and the electrodynamic coupling of a quantum emitter to a planar metallic nanocavity. Since the particles studied have fixed linear emission and excitation transition dipole moments (see ref. [2c] for more details), the model explicitly takes into account the orientation-dependent interaction of GQDs with the cavity.<sup>[15a]</sup> The only free parameters of this model are the QY and the free-space (out-of-cavity) lifetime values. A complete description of the model can be found in ref. [15b]. Comparison of the free-space lifetime



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**Figure 4.** Excited state lifetime of graphene quantum dots as a function of the cavity length. Open black and red circles are data that were measured from unfiltered and filtered samples, respectively. The fit parameters are the fluorescence quantum yield and the excited state lifetime in the absence of the cavity.

as calculated from the nanocavity measurements with a value measured in a droplet of solution placed on a clean glass cover slide allows us to estimate the reliability of the obtained QY value.

**Table 1** (column  $\Phi_{cavity}$ ) shows the determined QY and lifetime values of the GQDs. For all the three types of GQDs, both filtered and unfiltered samples showed identical QY values within measurement error margins. The difference between the calculated and measured free-space lifetimes for all the GQDs samples did not exceed 3%, confirming reliability of the calculated QY values. Furthermore, the identity of QY values for the unfiltered and filtered samples suggests that the population of the luminescent particles did not change during purification.

Since not all QY values of the dyes that were selected as reference for the comparative QY determination were known from literature, we measured all three reference samples also using

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Fluorophore	$\Phi_{cavity}$	$ au_{0\_cavity} [ns]$	$ au_{0\_meas}$ [ns]	$arPsi_{comp}$
Alexa 350	$\textbf{0.91} \pm \textbf{0.01}$	$4.7\pm0.1$	$4.6\pm0.05$	-
Atto 390	$\textbf{0.96} \pm \textbf{0.01}$	$5.0\pm0.1$	$5.0\pm0.05$	-
Atto 488	$\textbf{0.83}\pm\textbf{0.01}$	$4.2\pm0.1$	$4.2\pm0.05$	-
Blue GQDs unfiltered	$\textbf{0.95} \pm \textbf{0.01}$	$14.0\pm0.3$	$13.7\pm0.05$	0.63
Blue GQDs filtered	$\textbf{0.98} \pm \textbf{0.01}$	$14.0\pm0.2$	$14.0\pm0.05$	0.67
Cyan GQDs unfiltered	$\textbf{0.90} \pm \textbf{0.01}$	$4.7\pm0.1$	$4.7\pm0.05$	0.36
Cyan GQDs filtered	$\textbf{0.89} \pm \textbf{0.01}$	$4.8\pm0.1$	$4.6\pm0.05$	0.53
Green GQDs unfiltered	$\textbf{0.80} \pm \textbf{0.01}$	$4.0\pm0.1$	$4.1\pm0.05$	0.15
Green GQDs filtered	$\textbf{0.82}\pm\textbf{0.01}$	$3.9\pm0.1$	$4.1\pm0.05$	0.14

 Table 1. Results of the quantum yield and excited state lifetime measurements of dye molecules and graphene quantum dots. Comparative quantum yield values for the dye molecules are not provided because they served as reference.

the nanocavity-based method as described above (see Table 1, column  $\Phi_{\text{cavity}}$ ). This allowed us to obtain absolute QY values using the same technique for all the three dyes that is an essential prerequisite for a consistent comparison of all results. The experimental data and fits for the nanocavity-based QY measurements of the dyes can be found in the Supporting Information (Section S4, Supporting Information).

To determine reliable QY values of GQDs by comparing against the reference dyes, fluorescence intensities of reference and test samples were measured over a range of fluorophore concentrations corresponding to five different extinction values at the excitation wavelength. This allowed us to minimize inaccuracies of the QY determination due to errors in the optical absorption measurements. Sample concentrations were chosen in such a way that the maximum extinction did not exceed 0.1, so that non-linear (re-absorption) processes can be neglected. A detailed description of the complete QY measurement procedure is given in the Supporting Information (Section S5, Supporting Information).

The GQD QY values that were obtained by referencing against the dye solutions (Table 1, column  $\Phi_{\text{comp}}$ ) are significantly lower than those obtained with the nanocavity. This suggests that all measured samples contain non-luminescent but light-absorbing contaminations. Their presence leads to a systematic underestimation of the average QY when using the comparative method, while the nanocavity-based measurements deliver absolute unbiased QY values. Since we detected no signs of other fluorophores than GQDs in our samples, we attribute the non-luminescent species to GQDs without luminescent centers. The top-down synthesis leads to non-uniformity of nanoparticle structure and diversity of surface group types.<sup>[2c]</sup> Such surface state diversity has been observed before for carbon dots<sup>[25]</sup> or SiO<sub>2</sub> nanoparticles.<sup>[26]</sup> A further analysis of the obtained values reveals more details about the character of the non-luminescent species and their relative amount for each of the GQD types.

The nearly identical values obtained using the comparative method for the unfiltered and filtered green GQDs and the significantly higher values determined using the nanocavity-based method suggest that the sample contains a large fraction of non-luminescent particles whose population was not changed during purification. Hence, their dimensions and absorption cross-section are comparable to those of the luminescent GQDs. This conclusion is also supported by the FCS measurements (Figure 2c) that show that, in contrast to cyan or blue GQDs, the green sample has no particles or aggregates that are larger than a few tens of nanometers. These results suggest that for the green GQD sample, the ratio of the concentrations of luminescent and non-luminescent particles is comparable to the ratio of quantum yields that was obtained using the nanocavity (0.82) and the comparative (0.14) methods, respectively.

In contrast to the green GQDs, the blue and cyan samples showed an increase of the QY value as measured with the comparative method during purification. This suggests that both unfiltered samples contained a fraction of large non-luminescent particles or aggregates with sizes larger than filter pores. This conclusion agrees also with the FCS measurements that show the presence of particles or aggregates that have dimensions of hundreds of nanometers. However, the significant difference between the QY values of the filtered samples obtained with the nanocavity and with the dye references suggest that small non-luminescent particles that passed the purification were also present in the cyan and blue samples. While it is hard to make precise estimations of the absorption cross-sections of larger aggregates and thus their amount, a comparison of the OY values of the filtered cyan (0.89 and 0.53) and blue (0.98 and 0.67) samples as measured with the two methods suggests that the concentrations of the optically active and inactive particles in both samples are similar.

# 3. Conclusions

In summary, by measuring QY values of different types of GQDs using the nanocavity-based and the comparative methods, we showed that all samples contain a significant fraction of non-luminescent but optically absorbing species. Their presence leads to a gross underestimation of the QY values of light-emitting particles as measured by referencing against a dye solution. Comparison of QY values for the unfiltered and filtered samples obtained with the two fundamentally different techniques (referencing or nanocavity) allows one to quantify the average size and relative concentration of the non-luminescent particles. The nanocavity-based method is applicable to all types of quantum emitters, including such complex samples as semiconductor nanocrystals, carbon dots, SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

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or fluorescent proteins. Therefore, we envision that the experimental approach suggested in this work will be useful not only for measuring absolute QY values of luminescent nanostructures in various complex systems, but can also help to estimate properties of non-emitting but optically absorbing species.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### **Keywords**

graphene quantum dots, nanocavities, optical microscopy, plasmonics, quantum yield

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- a) K. Müllen, ACS Nano 2014, 8, 6531; b) S. Zhu, Y. Song, J. Wang, H. Wan, Y. Zhang, Y. Ning, B. Yang, Nano Today 2017, 13, 10.
- [2] a) J. Lee, D. Wong, J. VelascoJr., J. F. Rodriguez-Nieva, S. Kahn, H.-Z. Tsai, T. Taniguchi, K. Watanabe, A. Zettl, F. Wang, L. S. Levitov, M. F. Crommie, Nat. Phys. 2016, 12, 1032; b) S. Zhao, J. Lavie, L. Rondin, L. Orcin-Chaix, C. Diederichs, P. Roussignol, Y. Chassagneux, C. Voisin, K. Müllen, A. Narita, S. Campidelli, J.-S. Lauret, Nat. Commun. 2018, 9, 3470; c) S. Ghosh, N. Oleksiievets, J. Enderlein, A. I. Chizhik, J. Phys. Chem. Lett. 2020, 11, 7356; d) N. Suzuki, Y. Wang, P. Elvati, Z.-B. Qu, K. Kim, S. Jiang, E. Baumeister, J. Lee, B. Yeom, J. H. Bahng, J. Lee, A. Violi, N. A. Kotov, ACS Nano 2016, 10, 1744; e) Z. Gan, H. Xu, Y. Hao, Nanoscale 2016, 8, 7794.
- [3] a) C. Würth, M. Grabolle, J. Pauli, M. Spieles, U. Resch-Genger, Nat. Protoc. 2013, 8, 1535; b) K. Rurack, in Standardization and Quality Assurance in Fluorescence Measurements I: Techniques,

(Ed: U. Resch-Genger), Springer, Berlin, Heidelberg **2008**, pp. 101–145; c) M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller, U. Resch-Genger, *Anal. Chem.* **2009**, *81*, 6285.

- [4] R. Liu, D. Wu, X. Feng, K. Müllen, J. Am. Chem. Soc. 2011, 133, 15221.
- [5] a) L.-s. Li, X. Yan, J. Phys. Chem. Lett. 2010, 1, 2572; b) Q. Li,
   B. W. Noffke, Y. Liu, L.-s. Li, Curr. Opin. Colloid Interface Sci. 2015, 20, 346.
- [6] a) Y. R. Kumar, K. Deshmukh, K. K. Sadasivuni, S. K. K. Pasha, RSC Adv. 2020, 10, 23861; b) L. Li, G. Wu, G. Yang, J. Peng, J. Zhao, J.-J. Zhu, Nanoscale 2013, 5, 4015; c) P. R. Kharangarh, S. Umapathy, G. Singh, Appl. Surf. Sci. 2018, 449, 363; d) P. R. Kharangarh, S. Umapathy, G. Singh, ECS J. Solid State Sci. Technol. 2018, 7, M29; e) P. R. Kharangarh, S. Umapathy, G. Singh, J. Appl. Phys. 2017, 122, 145107; f) P. R. Kharangarh, S. Umapathy, G. Singh, Integr. Ferroelectr. 2017, 184, 114.
- [7] E. M. Purcell, Phys. Rev. 1946, 69, 37.
- [8] a) X. Brokmann, L. Coolen, M. Dahan, J. P. Hermier, *Phys. Rev. Lett.* 2004, *93*, 107403; b) J. J. Macklin, J. K. Trautman, T. D. Harris, L. E. Brus, *Science* 1996, *272*, 255.
- [9] W. P. Ambrose, P. M. Goodwin, R. A. Keller, J. C. Martin, Science 1994, 265, 364.
- a) K. H. Drexhage, in *Progress in Optics* (Ed: E. Wolf), Vol. 12, Elsevier, New York 1974, pp. 163–232; b) B. C. Buchler, T. Kalkbrenner, C. Hettich, V. Sandoghdar, *Phys. Rev. Lett.* 2005, *95*, 063003.
- [11] a) P. Holzmeister, E. Pibiri, J. J. Schmied, T. Sen, G. P. Acuna, P. Tinnefeld, *Nat. Commun.* 2014, *5*, 5356; b) J. C. Prangsma, R. Molenaar, L. van Weeren, D. S. Bindels, L. Haarbosch, J. Stouthamer, T. W. J. Gadella, V. Subramaniam, W. L. Vos, C. Blum, *J. Phys. Chem. B* 2020, *124*, 1383.
- [12] M. Ringler, A. Schwemer, M. Wunderlich, A. Nichtl, K. Kürzinger, T. A. Klar, J. Feldmann, *Phys. Rev. Lett.* 2008, 100, 203002.
- [13] A. I. Chizhik, A. M. Chizhik, D. Khoptyar, S. Bär, A. J. Meixner, J. Enderlein, *Nano Lett.* **2011**, *11*, 1700.
- [14] K. J. Vahala, Nature 2003, 424, 839.
- [15] a) A. I. Chizhik, I. Gregor, F. Schleifenbaum, C. B. Müller, C. Röling, A. J. Meixner, J. Enderlein, *Phys. Rev. Lett.* 2012, 108, 163002;
  b) A. I. Chizhik, I. Gregor, B. Ernst, J. Enderlein, *ChemPhysChem* 2013, 14, 505.
- [16] A. I. Chizhik, I. Gregor, J. Enderlein, Nano Lett. 2013, 13, 1348.
- [17] D. Ruhlandt, M. Andresen, N. Jensen, I. Gregor, S. Jakobs, J. Enderlein, A. I. Chizhik, *Commun. Biol.* 2020, 3, 627.
- [18] N. Karedla, J. Enderlein, I. Gregor, A. I. Chizhik, J. Phys. Chem. Lett. 2014, 5, 1198.
- [19] F. Schneider, D. Ruhlandt, I. Gregor, J. Enderlein, A. I. Chizhik, J. Phys. Chem. Lett. 2017, 8, 1472.
- [20] a) Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou, L. Qu, Adv. Mater. 2011, 23, 776; b) J. Shen, Y. Zhu, X. Yang, C. Li, Chem. Commun. 2012, 48, 3686.
- [21] a) J. Lu, P. S. E. Yeo, C. K. Gan, P. Wu, K. P. Loh, *Nat. Nano-technol.* **2011**, *6*, 247; b) G. Eda, Y.-Y. Lin, C. Mattevi, H. Yamaguchi, H.-A. Chen, I.-S. Chen, C.-W. Chen, M. Chhowalla, *Adv. Mater.* **2010**, *22*, 505; c) Q. Fang, Y. Dong, Y. Chen, C.-H. Lu, Y. Chi, H.-H. Yang, T. Yu, *Carbon* **2017**, *118*, 319.
- [22] J. Enderlein, I. Gregor, D. Patra, T. Dertinger, U. B. Kaupp, ChemPhysChem 2005, 6, 2324.
- [23] K. Goossens, M. Prior, V. Pacheco, D. Willbold, K. Müllen, J. Enderlein, J. Hofkens, I. Gregor, ACS Nano 2015, 9, 7360.
- [24] S. Khan, W. Li, N. Karedla, J. Thiart, I. Gregor, A. M. Chizhik, J. Enderlein, C. K. Nandi, A. I. Chizhik, J. Phys. Chem. Lett. 2017, 8, 5751.
- [25] A. M. Chizhik, S. Stein, M. O. Dekaliuk, C. Battle, W. Li, A. Huss, M. Platen, I. A. T. Schaap, I. Gregor, A. P. Demchenko, C. F. Schmidt, J. Enderlein, A. I. Chizhik, *Nano Lett.* **2016**, *16*, 237.
- [26] L. Tarpani, D. Ruhlandt, L. Latterini, D. Haehnel, I. Gregor, J. Enderlein, A. I. Chizhik, *Nano Lett.* 2016, 16, 4312.