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ARTICLE TYPE

Polyol-mediated C-Dot Formation showing Efficient Tb^{3+}/Eu^{3+} Emission

Hailong Dong[a], Ana Kuzmanoski[a], Dorothee M. Gößl[a], Radian Popescu[b], Dagmar Gerthsen[b], and Claus Feldmann*[a]

C-dots (3–5 nm in diameter) obtained by most simple refluxing of polyols (glycerol, diethylene glycol, PEG 400) show intense blue and green emission (50 % quantum yield). Upon modification with TbCl$_3$/EuCl$_3$, energy transfer from 10 **the C-dots to the rare-earth metal results in line-type Tb^{3+} (green)/Eu^{3+} (red) emission with quantum yields up to 85 %.**

Carbon dots (C-dots) recently have attracted much attention owing to their fascinating physical properties and their wide range of potential applications,[1] including bioimaging,[2] 15 optoelectronics,[2b,3] and catalysis.[2b,4] In contrast to heavy-metal-based quantum dots (Q-dots),[5] C-dots offer the advantages of absence of toxic heavy-metal elements, high chemical stability, high water dispersibility, and absence of blinking. In contrast to molecular fluorescent dyes, they show broader excitation spectra 20 and low photobleaching. They consist of graphitic carbon with quasi-spherical structure.[6] The associated photoluminescence is still not completely understood but attributed to surface-allocated trapping sites.[6a,7] High crystallinity of graphitic carbon layers, doping with heteroatoms, and surface passivation with poly- 25 ethylene glycol or long-chained amines have been reported as being essential for high emission intensities and quantum yields.[8]

Since their discovery, carbon sources such as hot-pressed graphite, coal, carbon from arc-discharge and laser ablation, graphene and graphene oxide, soot from plasma and candles as 30 well as carbonization of carbohydrates, polymers or amino acids have been established as access to C-dots, partly with excellent quantum yields (up to 80 %).[1,2b,6a] Although widely applied, these methods involve complex, partly less controllable synthesis conditions and/or expensive starting materials and equipment. 35 Alternatively, microwave- and solvothermal-based liquid-phase carbonization of carbohydrates (including multivalent alcohols, saccharides),[3b,9] or other molecular species (e.g., CCl$_4$/NaNH$_2$, citric acid/ethylene diamine, sodium citrate/urea, amino acids)[2b,6a,10] came into focus. These liquid-phase methods yet 40 result in significantly lower quantum yields (< 40 %). Red emitting C-dots, in general, are with the lowest quantum yield due to weak and broad emission. Efficient red emission, however, is highly relevant for medical application in view of penetration depth and autofluorescence of tissue as well as for efficient 45 multicolour light emission of optoelectronic devices.[1,2b,8b]

Here, we use straightforward refluxing of polyols, such as glycerol (GLY), diethylene glycol (DEG) and polyethylene glycol with a molecular weight of 400 (PEG400) for C-dot formation (Fig. 1). GLY and DEG are widely used for the polyol- 50 mediated synthesis of nanoparticles.[11] PEG400 is representative for the widely used class of PEG-type stabilizers.[8a,9b,c,e] Handling of low viscous PEG400, however, is more straightforward as compared to the highly viscous, if not solid PEGs with molecular weights ≥500. In view of the formation and photoluminescence of 55 C-dots, we have studied: (*i*) simple heating of GLY, DEG and PEG400; (*ii*) the influence of different metal ions; (*iii*) the duration of heating; and (*iv*) the fluorescence transfer to line-emitting Tb^{3+} and Eu^{3+}.
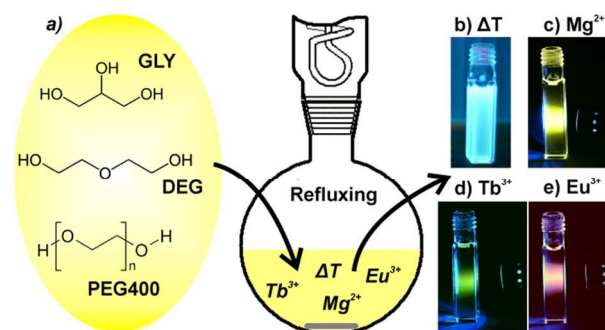

60 **Fig. 1**. Polyol-mediated synthesis of C-dots: a) Scheme illustrating the synthesis strategy; b) T/PEG (*λ$_{exc}$* = 366 nm); c) Mg^{2+}/PEG; d) Tb^{3+}/PEG; e) Eu^{3+}/PEG (c–e with blue-LED excitation *λ$_{max}$* = 465 nm (*cf. ESI: Fig. S2*); 230 °C, 1 h, 0.5 mmol MgCl$_2$x6H$_2$O/TbCl$_3$x6H$_2$O/EuCl$_3$x6H$_2$O).

Refluxing pure GLY, DEG, and PEG400 at 180 to 230 °C 65 (T/PEG), instantaneously resulted in colloidally very stable C-dot suspensions (Fig. 1). According to transmission electron microscopy (TEM), the as-prepared C-dots are 3–5 nm in diameter at narrow size distribution (Fig. 2a). High-resolution (HR)TEM images indicate the crystallinity of the C-dots with 70 lattice fringe distances of 2.05 Å that are well in accordance with graphite (*d*(101) with: 2.03 Å)[6a,10a,12] (Fig. 2b). Chemical composition and crystallinity are further confirmed by Fourier-transformed HRTEM images of single C-dots (Fig. 2c) and X-ray diffraction (XRD) of powder samples (*cf. ESI: Fig. S3a*) showing 75 the Bragg peaks of graphite as well. The high-viscous C-dot suspensions can be directly diluted in water and result in readily polyol-stabilized suspensions with mean diameters of 3–5 nm (Fig. 2d, *cf. ESI: Figs. S3b*). After acetone-driven destabilization, the C-dots are collected as a powder (20 mg C-dots/10 ml polyol) 80 (*cf. ESI: Fig. S4*). In sum, refluxing of polyols provides a most simple and reproducible one-pot access to high-quality C-dots as needed for widespread investigation and application.
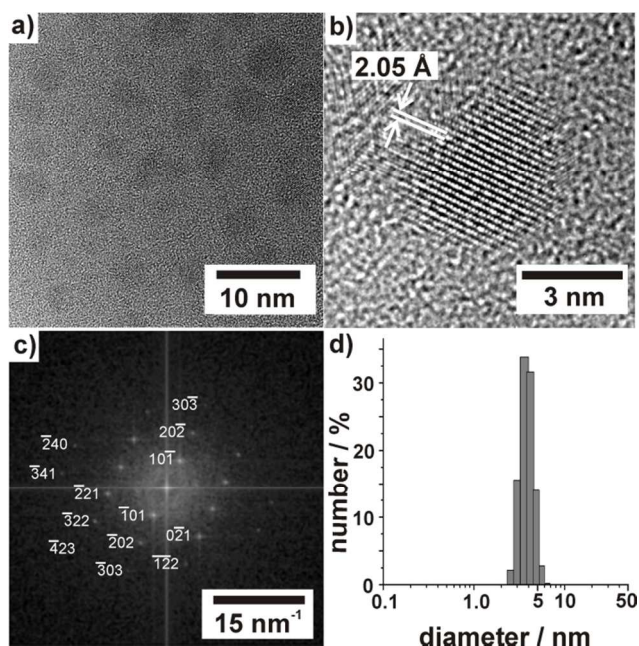
Fig. 2. Size, size distribution and composition of C-dots from polyol-mediated synthesis: a) Overview TEM image; b) HRTEM image with lattice fringes; c) Fourier-transformed HRTEM image of a C-dot in [212] zone-axis orientation with indexed Bragg reflections; d) Size distribution after dispersion in H_2O (according to DLS).

The as-prepared C-dots show well-known broad absorption (300–400 nm, *cf. ESI: Fig. S5a*) as well as broad emission in the blue spectral range (400–500 nm, Fig. 3a). Notably, the highest emission is observed for refluxed PEG400. The emission can be increased even further when refluxing in the presence of dissolved metal cations (Fig. 3b, *cf. ESI: Fig. S5b*). Here, $MgCl_2$ and $ZnCl_2$ have been selected as well-soluble metal salts of small-sized, slightly Lewis-acidic and oxophilic cations that do not show intrinsic fluorescence by themselves. Mg^{2+}/Zn^{2+} obviously support dehydration and carbonization of the polyols with the samples Mg^{2+}/PEG, Zn^{2+}/PEG, Mg^{2+}/DEG and Zn^{2+}/DEG showing the highest emission intensities (Fig. 3b). As the presence of $MgCl_2$ and $ZnCl_2$ clearly influences the photoluminescence, we have also evaluated the effect of different $MgCl_2$ concentrations (0.05, 0.5, 2.0 mmol, *cf. ESI: Fig. S6*). Accordingly, just the presence of the metal salt turned out as most relevant; increasing the metal salt concentration is only of minor influence. This finding indicates a catalytic effect of the metal salts on the C-dot formation as it was already postulated.[2b,9b]

For DEG and PEG400 heated to 230 °C without (T/DEG, T/PEG) or with $MgCl_2$ (Mg^{2+}/DEG, Mg^{2+}/PEG) showing the highest emission, we have studied the photoluminescence shift upon excitation at different wavelengths (Fig. 4). All these samples show the characteristic behavior of C-dots as reported in the literature: the higher the wavelength of excitation, the more the emission is red-shifted.[1-4,6a,7] This is attributed to surface-allocated trapping sites of different energy. For all samples, excitation and emission are broad and with the highest intensity for blue emission. In contrast, especially, red emission is weak.

For PEG400 showing the highest emission intensity, we have studied the influence of the heating temperature (150–230 °C, *cf. ESI: Fig. S7*) and the duration of heating (1–6 h, *cf. ESI: Fig. S8*). Up to temperatures of 150 °C, photoluminescence is weak and
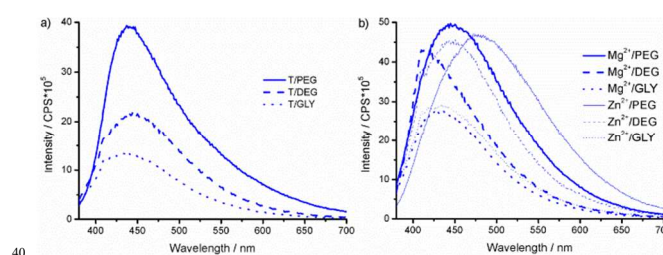

Fig. 3. C-dot emission after most simple refluxing of: a) Pure GLY, DEG and PEG400; b) GLY, DEG, PEG400 with dissolved $MgCl_2 \cdot 6H_2O$ and $ZnCl_2$ (230 °C, 1 h, 0.5 mmol $MgCl_2 \cdot 6H_2O/ZnCl_2$; normalized excitation at 366 nm, *cf. ESI: Fig. S4*).
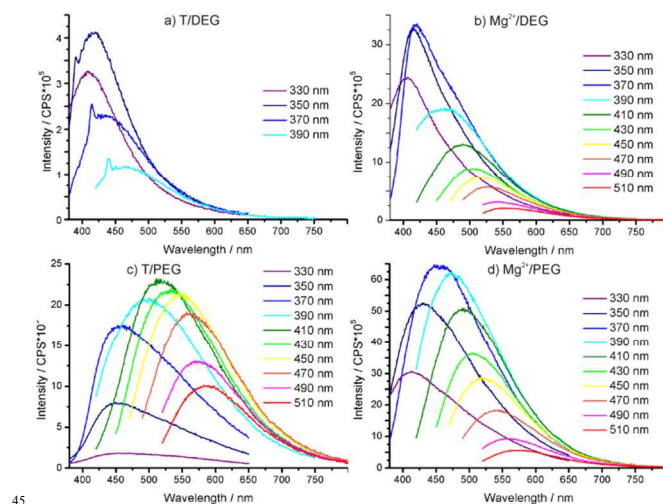

Fig. 4. Photoluminescence shift of the as-prepared C-dots upon excitation at different wavelength: a) T/DEG; b) Mg^{2+}/DEG; c) T/PEG; d) Mg^{2+}/PEG (230 °C, 1 h, 0.5 mmol $MgCl_2 \cdot 6H_2O$).

limited to broad emission in the blue spectral range (400–550 nm). At this temperature, dehydration and carbonization of the polyol have just started so that the number and quality of the C-dots are low. Suspensions exhibit a light yellow colour (*cf. ESI: Fig. S7a*). Heating at 190 °C leads to a four-times higher emission intensity and a colour shift, now ranging from blue to orange (400–650 nm) (*cf. ESI: Fig. S7b*). The proceeding dehydration and carbonization of the polyol is indicated by the light brown colour of the suspensions. After heating at 230 °C, the colour of suspensions became dark brown (*cf. ESI: Fig. S7c*). The fluorescence intensity is further increased, and–depending on the excitation–the emission now covers the complete optical spectrum (400–700 nm). At even higher temperatures (> 230 °C), the decomposition of the polyols became very fast and less controlled. Thus, the quality of the C-dots in terms of particle size, size distribution, agglomeration, and emission intensity is getting worse. Notably, the duration of heating has less influence on fluorescence intensity and colour shift than the temperature of heating (*cf. ESI: Figs. S7,S8*).

Although the polyol-mediated synthesis already resulted in C-dots with highly efficient blue and yellow emission with quantum yields of 50 % (blue, T/PEG, Fig. 1b) and 44 % (yellow, Mg^{2+}/PEG, Fig. 1c), red-light emission is still weak. This finding not only holds for polyol-mediated synthesis but also for other strategies of preparing C-dots. Red emission, on the other hand, is most essential for: (*i*) full-colour emission and additive colour mixing to white light; (*ii*) biomedical application since eventual

UV-excitation is harmful for tissue and autofluorescence of tissue overlays green emission.[1] Based on the enhanced photoluminescence intensity upon addition of $MgCl_2/ZnCl_2$, we intended achieving a similar effect with $TbCl_3/EuCl_3$, eventually including Förster resonance energy transfer (FRET) from the C-dot to Tb^{3+}/Eu^{3+} (Fig. 5a). As a close distance (<4 Å) between the corresponding luminescent centers is essentially required for efficient FRET,[13] only rare earth ions that are coordinated due to the polyol functionaliziation directly at the C-dot surface can serve as active emitters (Fig. 5a, *cf. ESI*).

Excitation of Tb^{3+}/Eu^{3+}-modified C-dots made of PEG400 (Tb^{3+}/PEG, Eu^{3+}/PEG) indeed results in intense characteristic, line-type $f{\rightarrow}f$ transitions of high intensity (Fig. 5b, *cf. ESI: Fig. S9*) and with excellent quantum yields of 85 % for Tb^{3+}/PEG and 75 % for Eu^{3+}/PEG (determined according to *Friend, cf. ESI: Fig. S1*). This is even more surprising as the parity-forbidden $f{\rightarrow}f$-transitions are typically quenched in OH-containing solvents due to relaxation via O–H vibrations.[14] Whereas certain emission of the C-dot is still visible at 350–550 nm, 275 nm excitation of Tb^{3+}/PEG results in Tb^{3+}-related emission only, indicating a very efficient FRET (Fig. 5b). For both samples Tb^{3+}/PEG and Eu^{3+}/PEG, notably, excitation is possible via a simple blue-light LED (λ_{max}: 465 nm) and results in intense green (Tb^{3+}/PEG, Fig. 1d) and red (Eu^{3+}/PEG, Fig. 1e) emission.
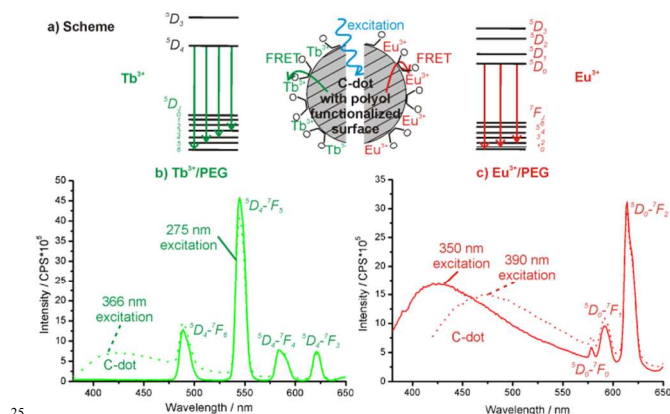

Fig. 5. Emission of polyol functionalized and Tb^{3+}/Eu^{3+}-modified C-dots upon excitation at different wavelengths (*cf. ESI*): a) Scheme of Förster resonance energy transfer (FRET); b) Emission of Tb^{3+}/PEG; c) Emission of Eu^{3+}/PEG (230 °C, 1 h, 0.5 mmol $TbCl_3\cdot 6H_2O$ /$EuCl_3\cdot 6H_2O$).

In conclusion, carbon dots (C-dots) are obtained via most simple refluxing of polyols to 180–230 °C. Dehydration and carbonization can be supported by addition of Lewis-acidic metal salts ($MgCl_2$, $ZnCl_2$). The as-prepared C-dots are collected in quantities of 20 mg per 10 ml of polyol and are suitable for direct dispersion in water due to the inherently available polyol-type surface coating. Aqueous suspensions show excellent colloidal stability and particle diameters of 3–5 nm at narrow size distribution and high quantum yields (up to 50 %). In the presence of $TbCl_3/EuCl_3$, the C-dots show efficient energy transfer upon excitation (UV or blue-LED) to Tb^{3+}/Eu^{3+} with characteristic line-type green/red emission and high quantum yields of 85 % (Tb^{3+}) and 75 % (Eu^{3+}). Altogether, the polyol-mediated synthesis as a most simple access to multicoloured C-dots can be highly relevant in view of intense research on C-dots for molecular imaging and optoelectronics.

Notes and references

[a]Karlsruhe Institute of Technology (KIT), Institute of Inorganic Chemistry, Engesserstraße 15, D-76131 Karlsruhe, Germany. Tel: +49(0)721-60842856; E-mail: claus.feldmann@kit.edu.
[b]Karlsruhe Institute of Technology (KIT), Laboratory of Electron Microscopy, Engesserstraße 7, D-76131 Karlsruhe, Germany.

† Electronic Supplementary Information (ESI) available: Details regarding analytical characterization (XRD, FT-IR, DLS); excitation spectra and quantum yield; effects of salt concentration, temperature and duration of heating on the C-dot formation are described in the Supplementary Information (see DOI: 10.1039/b000000x/.

‡ Experimental: As a standard recipe, 10 ml of glycerol (GLY), diethylene glycol (DEG), or polyethylene glycol 400 (PEG400) were heated (mantle heater) in a round-bottomed flask (Ar atmosphere) topped with a reflux condensor for 1 h to 230 °C. The as-prepared suspensions can be directly diluted with water. Alternatively, the C-dots can be sedimented upon addition of 50 ml of acetone. Metal salts ($MgCl_2\cdot 6H_2O$, $ZnCl_2$, $TbCl_3\cdot 6H_2O$, $EuCl_3\cdot 6H_2O$) were added with 0.5 mmol.

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