

## UvA-DARE (Digital Academic Repository)

### Designed Synthesis of Multiluminescent Materials Using Lanthanide Metal-Organic Frameworks and Carbon Dots as Building-Blocks

Gao, Y.; Hilbers, M.; Zhang, H.; Tanase, S.

**DOI**

[10.1002/ejic.201900876](https://doi.org/10.1002/ejic.201900876)

**Publication date**

2019

**Document Version**

Final published version

**Published in**

European Journal of Inorganic Chemistry

**License**

Article 25fa Dutch Copyright Act (<https://www.openaccess.nl/en/policies/open-access-in-dutch-copyright-law-taverne-amendment>)

[Link to publication](#)

**Citation for published version (APA):**

Gao, Y., Hilbers, M., Zhang, H., & Tanase, S. (2019). Designed Synthesis of Multiluminescent Materials Using Lanthanide Metal-Organic Frameworks and Carbon Dots as Building-Blocks. *European Journal of Inorganic Chemistry*, 2019(35), 3925-3932. <https://doi.org/10.1002/ejic.201900876>

**General rights**

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

**Disclaimer/Complaints regulations**

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

*UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)*

## Molecular Sensing

## Designed Synthesis of Multiluminescent Materials Using Lanthanide Metal-Organic Frameworks and Carbon Dots as Building-Blocks

Yuan Gao,<sup>[a][‡]</sup> Michiel Hilbers,<sup>[a]</sup> Hong Zhang,<sup>[a,b]</sup> and Stefania Tanase\*<sup>[a]</sup>

**Abstract:** A multiluminescent composite material, CDs@EuW-MOF, is synthesized by self-assembling molecular building-blocks in the presence of carbon dots (CDs). Using water soluble CDs within the growth media of a hydrophilic metal-organic framework (MOF) enables the incorporation of the CDs within MOF pores through a one-pot synthesis. The emission spectra obtained using a broad range of excitation wavelengths (295–400 nm) show multiple emissions including the Eu<sup>3+</sup> red emission and the dual-color (blue and green) emissions of the CDs.

The red emission intensity of Eu<sup>3+</sup> ions decreases in the presence of water molecules, leading to the ratiometric detection of water in methanol within a wide response range of 0–30 % (V/V). Due to the quenching effect on the CDs emission, this composite can also sense acetonitrile. The results demonstrate that using a molecular building-block approach is an efficient route towards the design of multiluminescent functional materials.

## Introduction

Metal-organic frameworks (MOFs) containing lanthanide ions as nodes have emerged as important luminescent materials due to their unique optical features (e.g. narrow bandwidth, long lifetime, large Stokes shift and ligand-dependent luminescence sensitization).<sup>[1–4]</sup> Combining the intrinsic luminescence features of the lanthanide ions (Ln<sup>3+</sup>) with the inherent porosity of MOFs provides a valuable platform of materials with applications in light devices,<sup>[5,6]</sup> drug delivery<sup>[7]</sup> and chemical sensing.<sup>[8]</sup> Although important achievements are made in tuning the optical and molecular recognition properties of the lanthanide MOFs (Ln-MOFs) for sensing applications,<sup>[9–15]</sup> a challenging task is still their integration in sensing devices. One approach is to combine MOFs with other functional materials (e.g. polymers<sup>[16–18]</sup> dyes,<sup>[17]</sup> carbon nanostructures or biomolecules<sup>[18]</sup>) to form composite materials which not only retain the properties of the individual components but also display new functionalities. This approach gives a more effective path to achieve multifunctionality as compared with the common synthetic routes used for making MOFs.<sup>[19–21]</sup> Moreover, such composite

materials are much easier processed for their integration in existing devices.<sup>[20–24]</sup>

Synthesis of luminescent Ln-MOFs composites is usually performed by post impregnation with organic dyes<sup>[25]</sup> or through a two-step procedure involving the functionalization of nano/micro-particles and then the introduction of multiple luminescent centers.<sup>[26–29]</sup> Carbon dots (CDs), however, as a new class of quantum-sized and wavelength dependent materials, with unique optical and electrical properties, are much less studied in combination with Ln-MOFs (e.g. Eu-MOFs/N,S-CDs, CQDs/ZIF-8 composites).<sup>[30–32]</sup> They are superior to the traditional quantum dots and dye materials in terms of their chemical inertness. Moreover, they are environmentally friendly and have excellent biocompatibility, therefore they are widely employed to make smart multifunctional materials.<sup>[30,33–36]</sup> Notably, the CDs containing heteroatoms such as N, O, S are also known to have multiple emissions.<sup>[37–40]</sup> A few examples of CDs@MOFs composites were reported so far.<sup>[30,39–41]</sup> Their synthesis involves multiple-step procedures, including the post-infiltration of the guest precursors into the preformed MOF host,<sup>[30]</sup> pre-modification of the CDs,<sup>[42]</sup> or post-functionalization of the composite.<sup>[43]</sup>

We reported recently on achieving high proton conductivity and the electro-optical sensing in a series of cyanide-bridged lanthanide-based MOFs (abbreviated as LnM-MOFs) which have porous flexible structures.<sup>[44–46]</sup> These materials are obtained using a molecular building-block approach which employs the self-assembly of mononuclear lanthanide complexes, [Ln(mpca)<sub>2</sub>]<sup>+</sup> (Ln<sup>3+</sup> = Eu, Tb, Gd, mpca = 5-methyl-2-pyrazine-carboxylate) and octacyanometallate ions, [M(CN)<sub>8</sub>]<sup>4-</sup> (M<sup>4+</sup> = Mo, W)<sup>[44–46]</sup> in aqueous solution. The resulting porous structures contain highly hydrophilic 1D channels due to the pres-

[a] Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands  
E-mail: s.grecea@uva  
<https://www.uva.nl/profile/s.grecea>

[b] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China

[‡] Current address: School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu, P. R. China

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.201900876>.

ence of multiple carboxylate functional groups and coordinated water molecules.<sup>[44]</sup> The 1D channels are filled with water molecules engaged in a rich hydrogen bonding network which is responsible for the high proton conductivities observed in these materials.<sup>[44]</sup> We have also demonstrated that these materials retain their structural integrity during multiple dehydration/hydration cycles.<sup>[45]</sup> Taking advantage of this structural flexibility, we aimed to further extend the general applicability of our building-block approach and to design novel functional MOF-based composites using a one-pot synthetic method. We have chosen CDs having hydrophilic groups at their surface because it facilitates their homogeneous dispersion in water which is the growth media of the above discussed LnM-MOFs. This enables to obtain crystalline luminescent MOFs in the presence of dual-color CDs to form CDs@LnM-MOF composites. Such advanced materials have multiple luminescent centers for chemical sensing which enable using the response of different centers to various sensing species, thereby broadening the application range of the sensing material. In this study, we report on the synthesis and characterization of a novel CDs@EuW-MOF composite material and its multiluminescence properties. Currently, there is an increasing interest in sensing of inorganic ions<sup>[30]</sup> and toxic organic molecules<sup>[31,32]</sup> using luminescent composite materials. Equally important, the monitoring of water in methanol and acetonitrile is important in various industrial processes as well as food processing, biomedical and environmental monitoring. Therefore, we discuss the applicability of the new composite material for the detection of water in water/methanol mixtures as well as the recognition of the acetonitrile in solvent mixtures.

## Results and Discussion

This study focused on water soluble CDs with carboxyl, hydroxyl, and amide functional groups at their surface. The carboxylic groups are known to coordinate strongly to the lanthanide ions.<sup>[33]</sup> Therefore, by combining water soluble CDs with the EuM-MOF reported earlier,<sup>[45]</sup> it is possible to obtain a material with different luminescence properties as a result of replacing the coordinated water of the EuM-MOF with the carboxylate groups from the surface of the CDs (see Figure 1). Thus, it is expected that the CDs will bind covalently to the MOF framework via the lanthanide ions which have accessible coordination sites. As the EuW-MOF has longer emission lifetime than the isostructural EuMo-MOF,<sup>[45]</sup> we focused on synthesising the novel CDs@EuW-MOF composite. The hydroxyl and amine groups of the CDs render a hydrophilic surface and it facilitates the synthesis of the composite in water using a building-block approach. The presence of hydrophilic functional groups at the CDs surface is the key parameter for the spontaneous self-assembly of the CDs@MOF composite.<sup>[15,16,33]</sup> Moreover, the combination of distinct emissive centers, the Eu<sup>3+</sup> ion and the CDs, enable the design of a multiluminescent material.

Figure 1 shows the growth route of the CDs in aqueous solution and the self-assembly of the composite material. In the first step, citric acid and urea assemble into a nanoplate structure through intermolecular hydrogen bonding. Under microwave

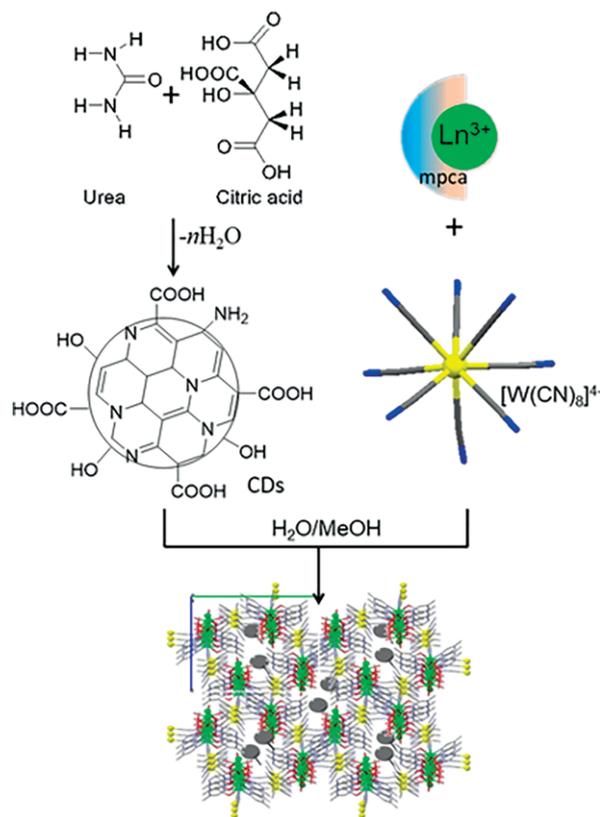


Figure 1. The molecular building-block approach used to synthesise the CDs@EuW-MOF composite.

irradiation, the dehydration process occurs.<sup>[33]</sup> The nitrogen-rich CDs are formed with abundant carboxyl, hydroxyl and little amide groups at the surface. Using the microwave treatment, the reaction time can be used to tune the degree of the dehydration and the carbonization processes between citric acid and urea.<sup>[35,38,47]</sup> Using a 5 min reaction time gives CDs which display dual-emission under certain excitation wavelengths (e.g. 270–290 nm and 360–400 nm).<sup>[48–50]</sup> The coordinated water molecules of the MOF can be removed without the collapse of the framework.<sup>[45]</sup> Therefore, the stability and flexibility of the MOF framework upon removing the coordinated water molecule give the opportunity to bind other donor atoms at the lanthanide sites which are coordinatively unsaturated. Consequently, the CDs were added directly into the growth medium of the MOF's crystals. The CDs@EuW-MOF composite formed during one week and it was isolated by decantation and centrifugation.

To confirm the successful synthesis of the CDs and the self-assembly of the CDs@MOF composite, a detailed characterization of the material was performed by Fourier-transform infrared (FTIR), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and ultraviolet-visible spectroscopy (UV/Vis) studies. It is important to prove the location of CDs particles in the MOF host. The most suitable method is the transmission electron microscopy (TEM). However, the critical drawback of this technique is the damaging of the framework under the measurement conditions.<sup>[21]</sup> Fortunately, the reversibility of the dehydration-rehydration process provides the possibility to iden-

tify the relative location of CDs within the MOF framework using photoluminescence measurements. This is because the photoluminescence properties of the EuW-MOF are sensitive to the coordination environment of the  $\text{Eu}^{3+}$  ion.<sup>[45]</sup>

The surface functional groups of the CDs were identified by FTIR spectroscopy and the measured IR spectra are in agreement with earlier reports (Figure S1).<sup>[33]</sup> The broad absorption bands in the range  $3100\text{--}3500\text{ cm}^{-1}$  are assigned to  $\nu(\text{O-H})$  and  $\nu(\text{N-H})$  stretching vibrations whilst those in the range  $1350\text{--}1460\text{ cm}^{-1}$  are due to  $\nu(\text{C-H})$  bending vibrations of the nitrogen heterocyclic ring. The peaks around  $1500$  and  $1100\text{ cm}^{-1}$  are from the  $\nu(\text{C=N})$  and  $\nu(\text{CH}_2)$  vibrations, confirming the form of conjugated system after the dehydration process. Moreover, the bands at  $1730$  and  $1400\text{ cm}^{-1}$  correspond to  $\nu(\text{COO})$  stretching vibrations and the band at  $1680\text{ cm}^{-1}$  is due to the  $\nu(\text{NH})$  bending vibrations, thus confirming the presence of the carboxylic and amine groups. The formation of CDs@MOF composite is clearly supported by the  $\nu(\text{C}\equiv\text{N})$  stretching vibrations of the cyanide groups which are observed in the range  $2090\text{--}2120\text{ cm}^{-1}$ . As compared with the as-synthesized MOF, the CDs@MOF displays the  $\nu(\text{C}\equiv\text{N})$  at the same position. The bands in the range of  $1550\text{--}1700\text{ cm}^{-1}$ , at  $1500\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  are the characteristic peaks of the EuW-MOF structure<sup>[44,45]</sup> and they indicate that the MOF framework is retained upon CDs uptake. These peaks are slightly shifted towards lower energy as compared with the as-synthesised MOF due to the replacement of the water molecules by the CDs nanoparticles. As shown in Figure 2 (right), the IR bands of the CD@EuW-MOF composite in the range  $1350\text{--}1750\text{ cm}^{-1}$  are also slightly shifted to lower energy as compared with the as-synthesized CDs. It indicates that some interactions are established between CDs and EuW-MOF.

The PXRD pattern of the CDs@MOF composite contains the main peaks corresponding to the as-synthesized EuW-MOF (see Figure 3) as well as a broad feature in the range of  $15^\circ$  to  $40^\circ$  which belongs to the CDs. Based on the data reported previously,<sup>[44]</sup> water molecules have an important role in retaining the crystallinity of the MOF materials. Therefore, it is very likely that the small shift in the PXRD peaks of the MOF together with

their broad character is due to the partial removal of water molecules upon the coordination of CDs to the lanthanide centers.

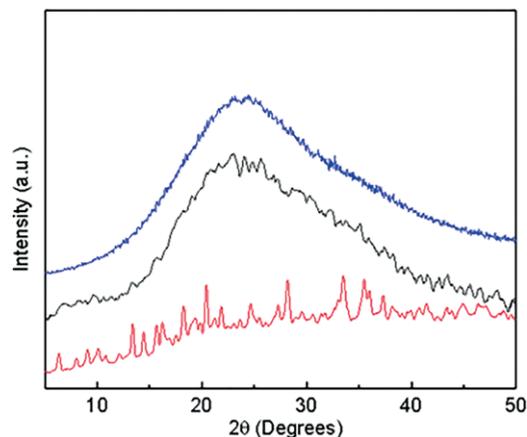


Figure 3. The PXRD patterns of the CDs (blue), EuW-MOF (red) and the CDs@EuW-MOF (black).

The TGA curve of CDs@EuW-MOF above  $100^\circ\text{C}$  shows less weight loss as compared with the EuW-MOF, indicating the replacement of coordinated water by CDs. This is consistent with DSC curves (Figure 4). Above  $150^\circ\text{C}$ , the endothermic peak from the coordinated water can be seen in the EuW-MOF. While the exothermic peak is observed in the both composite and the CDs (Figure 4). The TGA analysis of the CDs, as-synthesized EuW-MOF and CDs@EuW-MOF was carried out to determine the amount of CDs loaded in the EuW-MOF. By the end of the measurement, the residue  $r_{\text{MOF}}$  after full combustion corresponds to 57.5% and the residue  $r_{\text{CDs}}$  is 26.7%. The CDs loading ( $X_{\text{CDs}}$ , in wt% of the composite) can be calculated with the formula  $r_{\text{Composite}} = r_{\text{CDs}} \cdot X_{\text{CDs}} + (1 - X_{\text{CDs}}) \cdot r_{\text{MOF}}$  (where  $r_{\text{Composite}}$  is 56.2%), hence  $X_{\text{CDs}} = 4.3\text{ wt.-%}$ . The DSC curves provide another evidence for the presence of the CDs and the absence of the coordinated water within the MOF framework. At about  $100^\circ\text{C}$  where most lattice water is removed, the endothermic peak observed for the composite is much smaller than the cor-

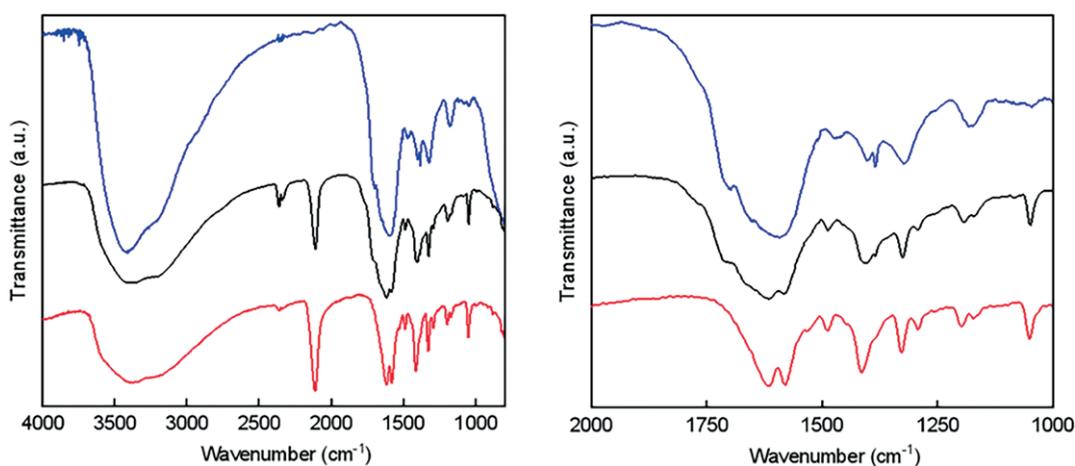


Figure 2. The FTIR spectra of the CDs (blue), EuW-MOF (red) and the CDs@EuW-MOF (black). The right graph highlights the  $2000\text{ cm}^{-1}$  to  $1000\text{ cm}^{-1}$  range.

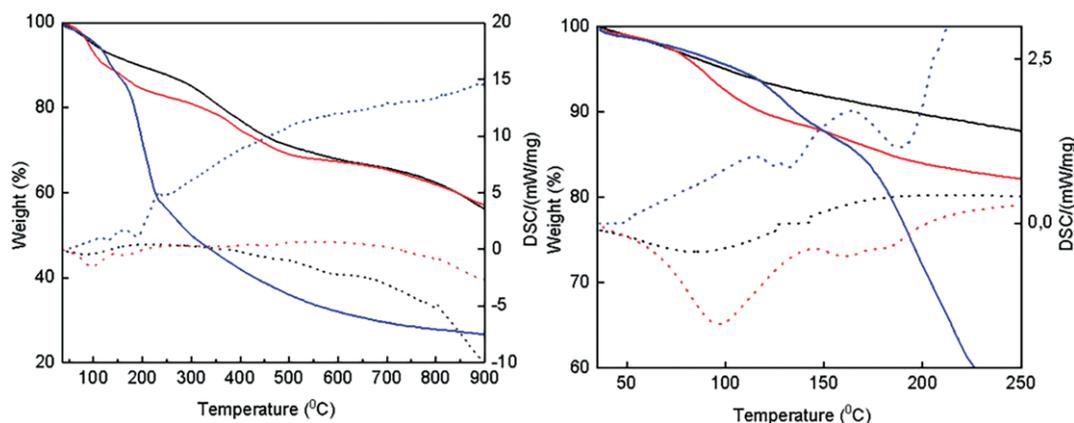


Figure 4. TGA (continuous line) and DSC (dotted line) curves of the CDs (blue), EuW-MOF (red) and the CDs@EuW-MOF (black). The right graph highlights the temperature range from 35°C to 200°C.

responding one for the EuW-MOF. This indicates less lattice water in the channels of the MOF, supporting the presence of the CDs in the MOFs pores. There is no endothermic peak observed above 150°C associated with coordinated water. Instead, the exothermic peak observed at 140°C corresponds to the CDs. This is strong evidence that the CDs are covalently bound to the lanthanide ions and that most coordinated water is replaced by CDs.

The diluted solutions (0.33 mg mL<sup>-1</sup>) of CDs in both water and methanol have absorption spectra displaying the typical features of a  $\pi$  system (Figure S2). In aqueous solution, the bands with maxima around 336 nm and 406 nm are due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The diluted methanol solution also displays two broad bands centered at 340 nm and 410 nm. Compared with the aqueous solution, the red shift absorption bands of this CDs are from its polarization-dependent feature.<sup>[33]</sup> The band with the maximum at 250 nm is due to the  $\pi \rightarrow \pi^*$  transitions. These absorption peaks are in agreement with earlier reports<sup>[35,38,47]</sup> and confirm the structure proposed in Figure 1.

The properties of the EuW-MOF and CDs@EuW-MOF composite in both aqueous and methanol solutions were also stud-

ied by UV/Vis spectroscopy (Figure 5). In aqueous solution, the UV/Vis spectrum of the composite shows three absorption bands. The band centered at 285 nm corresponds to the  $\pi \rightarrow \pi^*$  absorption of the MOF whilst the broad band centered at 406 nm is due to the surface functional group (C=O,  $n \rightarrow \pi^*$ ) of the CDs. Although only a 4 wt.-% loading of the CDs in the EuW-MOF is achieved, the CDs trailing edge of the spectra at long wavelength is still observed (Figure 5 inset). In methanol, the composite shows two absorption bands in the range from 250 to 300 nm. As compared with the CDs, covalent binding of the CDs to the EuW-MOF leads to the red shift.<sup>[31]</sup> As the result, the  $\pi \rightarrow \pi^*$  absorption band centered at 250 nm in the CDs is observed at 260 nm in the composite.

To understand the interactions between the CDs and the MOF in the composite, the photoluminescence properties of the composite material in methanol were studied in detail, as the composite in methanol suspension shows higher excitation and emission intensities (Figure S6). The diluted solution of the CDs (0.33 mg mL<sup>-1</sup>) exhibits photoluminescence properties which are dependent on the excitation wavelength (Figure 6). This behavior is commonly observed for fluorescent carbon materials.<sup>[51-53]</sup> The emission bands are observed in the 400 nm

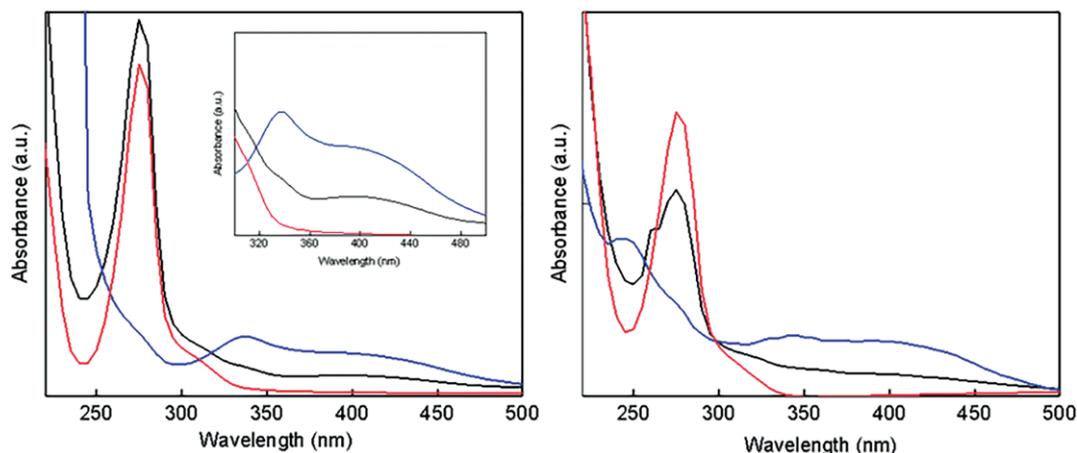


Figure 5. The UV/Vis spectra of the CDs (blue), EuW-MOF (red) and the CDs@EuW-MOF (black) measured in water (left) and methanol (right). The inset on the left shows the amplified UV/Vis absorption in the range of 250–450 nm.

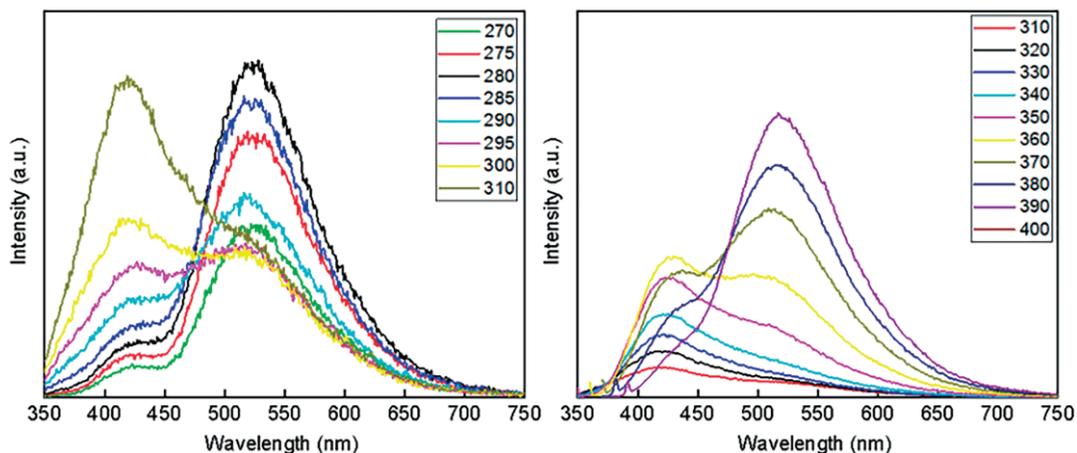


Figure 6. Fluorescence emission spectra of the as-synthesized CDs in methanol measured at various excitation wavelengths. Left: dual to blue emission characteristics excited from 270 to 310 nm. Right: blue to dual emission characteristics excited from 310 to 400 nm.

(blue) to 520 nm (green) range when the excitation wavelength varies from 270 to 410 nm. Notably, a dual-color emission can be seen under specific excitation wavelengths in agreement with the earlier reports.<sup>[54]</sup> Specifically, in the 270 nm to 300 nm and 360 to 400 nm excitation ranges, the CDs have a dual-color behavior with major contribution of the green color whilst the blue color dominates at 310 nm and 350 nm excitation wavelengths. A single emission is observed at excitation wavelengths ranging from 310 to 350 nm.

The wavelength-dependent emission of the CDs can also be seen in the composite (Figure S3). The single green emission is observed upon excitation in the range from 270 nm to 300 nm while the dual-emission is occurring at the excitation wavelengths in the range 310 to 400 nm. As compared with the CDs, these changes indicate that interactions are established between the CDs and the EuW-MOF in the composite. As the mechanism of the wavelength-dependent emission feature of the CDs is still difficult to understand, the diluted physical mix-

tures of CDs + Hmpca ( $0.33 \text{ mg mL}^{-1}$ ) and CDs + EuW-MOF ( $0.33 \text{ mg mL}^{-1}$ ) were also measured under different excitation wavelengths (Figure S4 – S5). The CDs + Hmpca mixture shows the same emission characteristics as the as-synthesized CDs. The intensity differences between the CDs and CDs + Hmpca in the range of 270 – 290 nm is the influence of the effective emission from the Hmpca ligand under these excitation wavelengths. This indicates that the changes of the photoluminescence properties of the CDs in the composite material is not due to the energy transfer between the CDs and the organic linkers. Table 1 summarizes the photoluminescence characteristics of the different mixtures studied. The results show a direct energy transfer from the CDs to the  $\text{Eu}^{3+}$  ions in the composite, which indicates the covalent binding of the CDs to the  $\text{Eu}^{3+}$  centers of the host MOF. The ligand to metal energy transfer is proven by the excitation spectrum obtained by monitoring the 617 nm emission (see Figure S6 (left)). In our earlier study,<sup>[45]</sup> when monitoring at the characteristic 617 nm emission for

Table 1. The photoluminescence properties of the CDs in different environments: as-synthesized CDs, CDs + Hmpca, CDs + EuW-MOFs and CDs@EuW-MOF in methanol under different excitation wavelengths.

Compound \ Wavelength	Wavelength			
	270-290 nm	295-350 nm	360 nm	370-400 nm
CDs	Dual emission	Blue	Dual emission	Dual emission
CDs+Ligand	Dual emission	Blue	Dual emission	Dual emission
CDs+EuW-MOF	Green	Blue	Green	Dual emission
CDs@ MOF	Green	Dual emission	Dual emission	Dual emission

EuW-MOF, the solid-state excitation spectrum showed a sharp band centered at 290 nm, which is assigned to the  $\pi-\pi^*$  electron transition of the ligand. The excitation spectra of the composite have a new broad band centered at 400 nm, which is from the  $n-\pi^*$  transition of the CDs. All these results confirm the energy transfer between the organic ligands, CDs and the  $\text{Eu}^{3+}$  center.

A key feature of the composite dispersed in water and methanol separately is that the emission properties of the CDs remain unchanged (Figure S6 (right)) although the solvents affect the emission intensity of the  $\text{Eu}^{3+}$  center. The emission spectrum of the CDs@EuW-MOF composite in methanol shows the five characteristic peaks of the  $\text{Eu}^{3+}$  (582 nm, 596 nm, 617 nm, 655 nm and 705 nm) as well as the dual-color emission (green at 520 nm, and blue at 450 nm) of the CDs. Consequently, the composite material displays multi-color emissions under single excitation. This behavior is observed under different excitation wavelengths. Figure 7 shows the efficient excitation of the CDs ( $\lambda_{\text{ex}} = 360$  nm) and EuW-MOF ( $\lambda_{\text{ex}} = 285$  nm) in methanol. A comparison between the composite and the physical mixture of CD + EuW-MOF is given in Figure S7. In both aqueous and methanol solution, the CDs can decrease the  $\text{Eu}^{3+}$  photoluminescence intensity as compared with the EuW-MOF (see Figure S6 and Figure S8). However, this is due to the presence of strong oscillators at the surface of CDs ( $-\text{OH}$ ,  $-\text{NH}$  functional groups). Nevertheless,  $\text{Eu}^{3+}$  ions still show the characteristic red emission. This is due to the effective energy transfer from the CDs to the  $\text{Eu}^{3+}$  ions, strongly supported by the fact that red emission of  $\text{Eu}^{3+}$  is quenched completely in the CDs + EuW-MOF physical mixture.

Inspired by the efficient emission of the composite in methanol and its quenching in water (Figure S6), detailed studies were carried out with a methanol/water binary system. Figure 8 shows that by increasing gradually the water content in methanol, the intensity of the red emission peaks decreases continuously. At the same time, the emission intensity of the CDs component remains unchanged. The decrease of the luminescence originates from the energy transfer between  $\text{Eu}^{3+}$  energy levels and the vibrational states of the OH groups of water molecules adsorbed inside the inner sphere of the framework. As shown

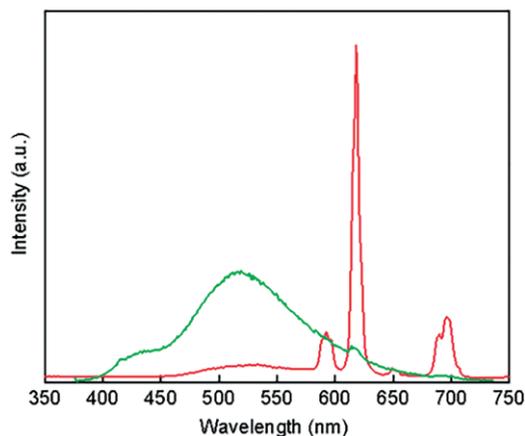


Figure 7. The emission spectra of the CDs@EuW-MOF composite measured in methanol using  $\lambda_{\text{ex}} = 285$  nm (red) and  $\lambda_{\text{ex}} = 360$  nm (green).

in Figure 8 (right), the intensity ratio of the two emission wavelengths ( $I_{617}/I_{520}$ ) also decreases continuously as the water content in methanol increases from 0 to 30 % (V/V). Therefore, this multiluminescent composite can be regarded as a highly sensitive and reliable sensing material for monitoring relative low water contents (0 – 5 %) in methanol solutions.

Furthermore, comparing with the as-synthesised EuW-MOF, the key feature of the CDs@EuW-MOF composite is the availability of multiple emission centers. This means that not only the emission of the  $\text{Eu}^{3+}$  centers but also the characteristic emissions of the CDs can be used as response signals under different experimental conditions. Figure 9 shows the emission profile of the composite material in both aqueous and acetonitrile solutions. The characteristic red emission of the  $\text{Eu}^{3+}$  is quenched in both solvents. Due to the abundant functional groups at the surface of the CDs, the photoluminescence originating from the surface state of the CDs can be suppressed by the strong interactions established between solvent molecules and CDs. The typical green emission of the CDs is quenched in acetonitrile whilst in water a strong emission is observed at 520 nm. Such behavior indicates that the CDs@MOF material can also be used as a sensor for acetonitrile.

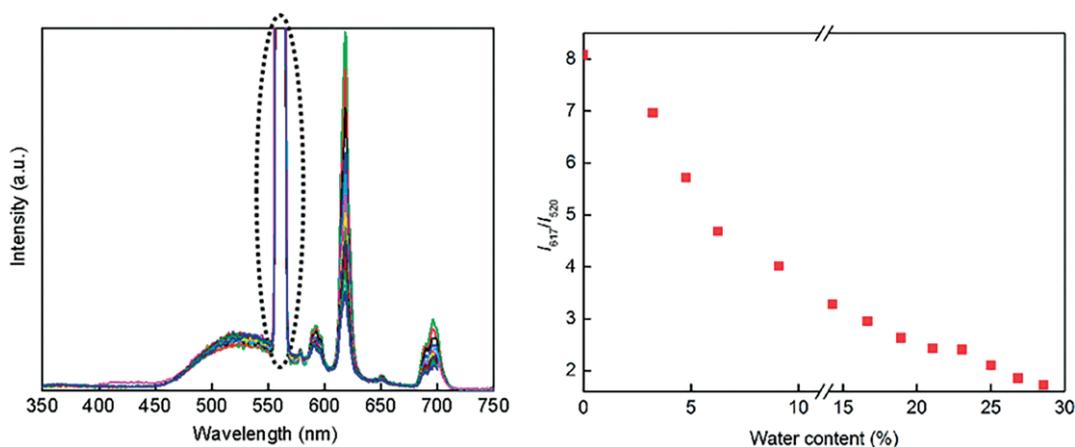


Figure 8. The emission spectra ( $\lambda_{\text{ex}} = 285$  nm) of  $0.33 \text{ mg mL}^{-1}$  CDs@EuW-MOF in methanol upon the gradual addition of water (left) and the plot of  $I_{617}/I_{520}$  vs. the water content in methanol (right).

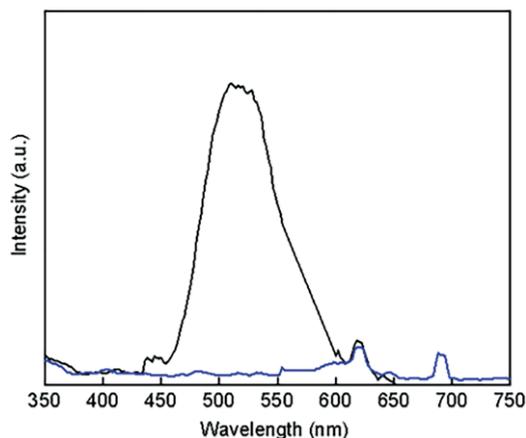


Figure 9. The emission ( $\lambda_{\text{ex}} = 280 \text{ nm}$ ) spectra of  $0.33 \text{ mg mL}^{-1}$  of the CDs@EuW-MOF in water (black) and acetonitrile (blue).

## Conclusions

A novel multiluminescent lanthanide material (CDs@EuW-MOF) was synthesized using the self-assembly of molecular building-blocks in one step. This strategy enables designing multiluminescent materials whose properties derive from the combined functionalities encoded in the individual building-blocks. By using wavelength-dependent photoluminescent CDs, the CDs@EuW-MOF composite shows changes in the emission properties based on the excitation wavelength. By comparing the optical properties of the as-synthesized CDs, the physical mixture of the CDs and EuW-MOF, it was found that the composite shows different emission behavior than these components. The differences observed provide the evidence that the composite material is formed by the covalent binding between the CDs and the flexible EuW-MOF framework. The composite can be used as effective sensor for detecting water in methanol/water mixtures, due to the quenching effect of water on the characteristic red emission of  $\text{Eu}^{3+}$  ion. Using the photoluminescence characteristics of the CDs counterpart, the composite material can also be used as a luminescent sensor for acetonitrile. The facile one-pot synthesis of the CDs@EuW-MOF composite described in this work provides a new strategy for designing multifunctional materials.

## Experimental Section

### Materials and instrumentation

Unless stated otherwise, all chemicals were commercially available (Aldrich, >99 % pure) and used as received. The  $\text{K}_4[\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$  precursor and the  $[\text{Eu}(\text{mpca})_2\text{Eu}(\text{H}_2\text{O})_6\text{W}(\text{CN})_8] \cdot n\text{H}_2\text{O}$  (abbreviated as EuW-MOF, mpca = 5-methyl-2-pyrazinecarboxylate) were synthesized as reported previously.<sup>[38]</sup> Infrared spectra ( $4000\text{--}400 \text{ cm}^{-1}$ , resol.  $0.5 \text{ cm}^{-1}$ ) were recorded on a Varian 660 Fourier-transform infrared (FTIR) spectrometer using KBr pellets and the transmission technique. Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku Miniflex X-ray diffractometer. The data were collected from  $3^\circ$  to  $50^\circ$  with a turning speed of  $2.0^\circ/\text{min}$ . Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a NETZSCH Jupiter® STA 449F3 instru-

ment. The measurements were done under argon ( $20 \text{ mL min}^{-1}$ ) at  $35\text{--}800^\circ \text{C}$  with a speed of  $10 \text{ K/min}$ .

### Synthesis

**Carbon Dots (CDs):** The CDs used in this study were synthesized by the microwave irradiation of citric acid and urea.<sup>[39]</sup> Typically, citric acid ( $15.6 \text{ mmol}$ ) and urea ( $50 \text{ mmol}$ ) were dissolved in distilled water ( $10 \text{ mL}$ ) to form a transparent solution. This was then heated in a domestic  $700 \text{ W}$  microwave oven for  $5 \text{ min}$ , during which it changed the color from a colorless liquid to a brown solution. At the end of the reaction, a dark-brown solid was formed which indicates the formation of the CDs. The resulting solid was transferred to a vacuum oven and heated at  $60^\circ \text{C}$  for  $1 \text{ h}$  to remove the residual small molecules. The obtained dark-brown solid was further dispersed in distilled water ( $10 \text{ mL}$ ), then purified in a centrifuge ( $3000 \text{ r} \cdot \text{min}^{-1}$ ) to remove the large or agglomerated particles. Finally, the solid was dried in an oven at  $60^\circ \text{C}$  for  $1 \text{ h}$ .

**CDs@EuW-MOF composite:** A water solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 5-methyl-2-pyrazine carboxylic acid (Hmpca) and  $\text{K}_4[\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$  were mixed and stirred for  $10 \text{ min}$  under ambient conditions. Then the CDs were added to this solution (molar ratio CDs/EuW-MOF =  $1:8$ ) and the resulting mixture was stirred for another  $1 \text{ h}$ . The slow diffusion of methanol (water/MeOH =  $1:3$ ) into this solution gives brown solids after one week. The final product was separated by centrifugation and the solid washed with water and methanol.

### Photophysical Measurements

Samples were prepared for photophysical measurements by grinding the powder products to uniform particle size. In a typical measurement,  $1 \text{ mg}$  solid was suspended in  $3 \text{ mL}$  aqueous solution, and then was ultrasonicated for  $1 \text{ h}$  to obtain uniform suspensions. For the samples in methanol, the solids were dried in the oven at  $80^\circ \text{C}$  for  $2 \text{ h}$  before preparing the suspensions. Ultraviolet-visible spectroscopy (UV/Vis) analysis was performed on a Varian UV/Vis spectrometer using quartz tubes with  $1 \text{ cm}$  light path length in the  $200\text{--}500 \text{ nm}$  regions. Excitation and emission spectra were recorded on a Fluorescence Fluorolog3 Jobin-Yvon equipped with a  $1 \times 1 \text{ cm}^2$  quartz cell. The emission and excitation slit widths are  $2 \text{ nm}$  with Xe lamp. The emission spectra intensity was corrected for the sensitivity of the detector.

## Acknowledgments

Y. G. thanks the China Scholarship Council for a PhD fellowship. This work is part of the Research Priority Area Sustainable Chemistry of the University of Amsterdam, <http://suschem.uva.nl>.

**Keywords:** Lanthanides · Carbon dots · Multiluminescence · Composites · Self-assembly

- [1] H. Dong, L. D. Sun, C. H. Yan, *Chem. Soc. Rev.* **2015**, *44*, 1608.
- [2] A.-L. Gassner, J.-C. G. Bunzli, A.-S. Chauvin, *Inorg. Chem.* **2008**, *47*, 7802.
- [3] J.-C. G. Bunzli, A.-S. Chauvin, C. D. B. Vandevyver, *J. Rare Earths* **2007**, *25*, 257–274.
- [4] J. A. Kitchen, *Coord. Chem. Rev.* **2017**, *340*, 232.
- [5] P. Falcaro, S. Furukawa, *Angew. Chem. Int. Ed.* **2012**, *51*, 8431; *Angew. Chem.* **2012**, *124*, 8557.
- [6] C. R. Wade, M. Li, M. Dincă, *Angew. Chem. Int. Ed.* **2013**, *52*, 13377; *Angew. Chem.* **2013**, *125*, 13619.
- [7] T. Kundu, P. Patra, A. Goswami, D. D. Díaz, R. Banerjee, *Chem. Eur. J.* **2014**, *20*, 10514.

- [8] L. E. Kreno, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105.
- [9] S. Chorazy, M. Wyczęsany, B. Sieklucka, *Molecules* **2017**, *22*, 1902.
- [10] J.-C. G. Bünzli, *Coord. Chem. Rev.* **2015**, *293*, 19.
- [11] Y. Zhang, P. Cui, X. Feng, L. Chen, Y. Yang, X. Liu, *RSC Adv.* **2015**, *5*, 40393.
- [12] L. D. Carlos, V. de Zea Bermudez, B. Julián-López, P. Escribano, *Chem. Soc. Rev.* **2011**, *40*, 536.
- [13] J.-C. G. Bünzli, *Acc. Chem. Res.* **2006**, *39*, 53.
- [14] J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048.
- [15] M. L. Cable, H. B. Gray, A. Ponce, *Acc. Chem. Res.* **2013**, *46*, 2576.
- [16] D. Chen, C. Liu, M. Du, *ACS Appl. Mater. Interfaces* **2017**, *9*, 24671.
- [17] Y. Cui, J. Yu, M. Liu, Z. Wang, C. Wu, Y. Yang, Z. Wang, B. Chen, G. Qian, *Adv. Mater.* **2015**, *27*, 1420.
- [18] Y. Wang, F. Zhang, T. Chu, Y. Yang, *Sens. Actuators B* **2017**, *251*, 667.
- [19] Y. Cui, H. He, W. Zhou, B. Chen, G. Qian, *Acc. Chem. Res.* **2016**, *49*, 483.
- [20] Q.-L. Zhu, Q. Xu, *Chem. Soc. Rev.* **2014**, *43*, 5468.
- [21] N. Stock, S. Biswas, *Chem. Rev.* **2011**, *112*, 933.
- [22] T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabrés, I. Xamena, J. Gascon, *Nat. Mater.* **2014**, *14*, 48.
- [23] C. M. Doherty, D. Buso, A. J. Hill, S. Furukawa, *Acc. Chem. Res.* **2014**, *47*, 396.
- [24] D. Bradshaw, A. Garai, J. Huo, *Chem. Soc. Rev.* **2012**, *41*, 2344.
- [25] P. Falcaro, M. Takahashi, P. Scopece, H. Amenitsch, S. Costacurta, C. M. Doherty, J. S. Laird, M. D. Lay, F. Lisi, *Adv. Mater.* **2011**, *23*, 3901.
- [26] G. Zhan, H. C. Zeng, *Chem. Commun.* **2017**, *53*, 72.
- [27] See ref.<sup>[17]</sup>.
- [28] S. H. Hewitt, S. J. Butler, *Chem. Commun.* **2018**, *54*, 6635.
- [29] Z. Dou, Y. Cui, Y. Yang, Z. Wang, D. Yang, G. Qian, *J. Am. Chem. Soc.* **2014**, *136*, 5527.
- [30] X. Lin, L. Zheng, Y. Chi, G. Chen, *Anal. Chem.* **2013**, *86*, 1223.
- [31] Y. Dong, Q. Fang, X. You, Y. Chi, *Anal. Chem.* **2016**, *88*, 1748.
- [32] B. Yan, H. Weng, *Dalton Trans.* **2016**, *45*, 8795.
- [33] X. Li, B. Song, H. L. Zhang, H. Chen, H. Cai, W. Liu, Y. Tang, *Angew. Chem. Int. Ed.* **2017**, *56*, 2689; *Angew. Chem.* **2017**, *129*, 2733.
- [34] L. Wang, H. Wang, S. Qu, Y. Zhang, J. Zhang, Q. Chen, H. Xu, W. Han, B. Yang, H. Sun, *ACS Nano* **2014**, *8*, 2541.
- [35] D. Zhou, P. Jing, Y. Zhai, D. Shen, S. Qu, A. L. Rogach, *Chem. Mater.* **2017**, *29*, 1779.
- [36] P. Jing, D. Li, D. Zhou, L. Zhang, H. Zhang, D. Shen, S. Qu, *Adv. Opt. Mater.* **2017**, *5*, 160.
- [37] X. Zhang, Y. Wang, S. Kalytchuk, S. V. Kershaw, Y. Wang, P. Wang, T. Zhang, Y. Zhao, H. Zhang, *ACS Nano* **2013**, 11234.
- [38] S. Zhu, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang, B. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3953; *Angew. Chem.* **2013**, *125*, 4045.
- [39] S. N. Baker, G. A. Baker, *Angew. Chem. Int. Ed.* **2010**, *49*, 6726; *Angew. Chem.* **2010**, *122*, 6876.
- [40] X. Wang, B. Xu, J. Ren, X. Qu, *J. Mater. Chem.* **2011**, *21*, 2445.
- [41] S. Yang, T. Kim, J. H. Im, H. Jung, J. H. Kang, S. Wi, B. Park, C. R. Park, *J. Am. Chem. Soc.* **2013**, *135*, 7394.
- [42] A. R. Chowdhuri, S. K. Ghosh, S. K. Sahu, *ACS Appl. Mater. Interfaces* **2016**, *8*, 16573.
- [43] J. X. Wu, B. Yan, *Dalton Trans.* **2017**, *46*, 7098.
- [44] Y. Gao, W. Hageman, N. Yan, M. C. Mittelmeijer-Hazeleger, G. Rothenberg, S. Tanase, *J. Mater. Chem. A* **2015**, *3*, 22347.
- [45] Y. Gao, P. Jing, N. Yan, M. Hilbers, H. Zhang, G. Rothenberg, S. Tanase, *Chem. Commun.* **2017**, *53*, 4465.
- [46] S. Tanase, M. C. Mittelmeijer-Hazeleger, G. Rothenberg, C. Mathoniere, V. Jubera, J. M. M. Smits, R. de Gelder, *J. Mater. Chem.* **2011**, *21*, 15544.
- [47] M. Sun, Z. Hao, W. Ji, P. Jing, H. Zhang, L. Zhang, J. Zhao, D. Shen, *Nano-scale* **2014**, *6*, 13076.
- [48] R. Mohan, J. Drbohlavova, J. Hubalek, *Chem. Phys. Lett.* **2018**, *692*, 196.
- [49] M. J. Krysmann, P. Dallas, E. P. Giannelis, *J. Am. Chem. Soc.* **2012**, *134*, 747.
- [50] X. Zhai, C. Liu, T. Bai, W. Li, L. Dai, W. Liu, *Chem. Commun.* **2012**, *48*, 7955.
- [51] C. H. Ding, Y.-Y. Ma, J.-L. Kong, H.-M. Xiong, *New J. Chem.* **2013**, *37*, 2515.
- [52] S. Sahu, T. K. Maiti, S. Mohapatra, *Chem. Commun.* **2012**, *48*, 8835.
- [53] Q. Liu, Z. Rao, B. Zhang, J. R. Gong, *Nano Lett.* **2013**, *13*, 2436.
- [54] S. Qu, D. Li, W. Ji, P. Jing, D. Han, L. Liu, H. Zeng, D. Shen, *Adv. Mater.* **2016**, *28*, 3516.

---

Received: August 13, 2019