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[Marcus N. A. Fetzer](#) , [Maximilian Vieten](#) , Aysenur Limon , [Christoph Janiak](#) \*

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Article

# Encapsulation of a Highly Acid-Stable Dicyano-Bodipy in Zr-Based Metal-Organic Frameworks with Increased Fluorescence Lifetime and Quantum Yield Within the Solid-Solution Concept

Marcus N. A. Fetzer, Maximilian Vieten, Aysenur Limon and Christoph Janiak \*

Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany

\* Correspondence: janiak@uni-duesseldorf.de

## Abstract

In this work, we have synthesized a more acid-stable variant of the classic chromophore difluoro-Bodipy by substituting the difluoro ligands at boron with cyano groups. This dicyano-Bodipy variant allowed the in situ incorporation during the MOF formation under acidic conditions and was investigated for the first time as dye@MOF composites using both post-synthetic and in situ incorporation into the zirconium-based metal-organic frameworks (MOFs) UiO-66, MOF-808, DUT-67 and MIP-206. The successful incorporation of dicyano-Bodipy was confirmed by PXRD, N<sub>2</sub> sorption, digestion UV-Vis and fluorescence spectroscopy. Depending on the incorporation method used, significant lower BET surface areas could be determined. The luminescence properties of the resulting dicyano-Bodipy@MOF composites from the in situ incorporation had up to almost eight-fold extended photoluminescent lifetimes of 9.0 ns, compared to the neat dye in its solid state with 1.2 ns, which suggests the formation of a solid solution in which the incorporated Bodipy is protected from external influences within a well-defined MOF pore. The quantum yield could be enhanced to as high as 77% through post-synthetic incorporation into the MOF DUT-67 compared to the neat dye in its solid state with 9%.

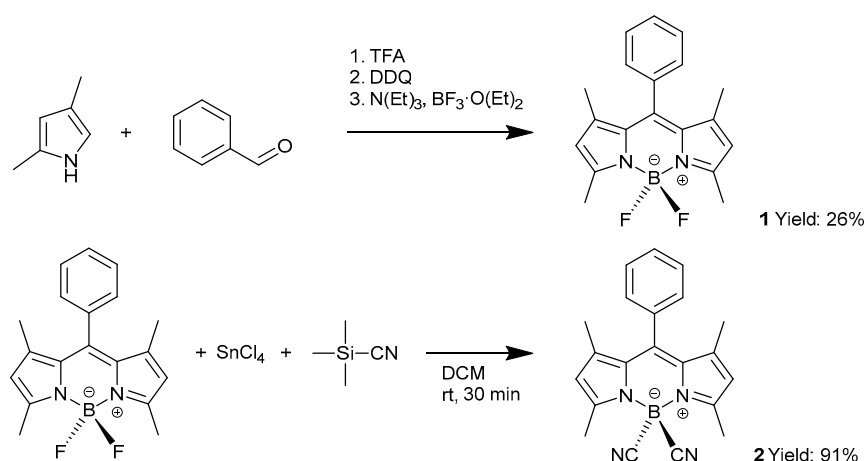
**Keywords:** dicyano-Bodipy; metal-organic framework (MOF); UiO-66; MOF-808; DUT-67; MIP-206; dicyano-Bodipy@MOF; fluorescence; solid solution; fluorescence lifetime; quantum yield; post-synthetic; in situ incorporation

## 1. Introduction

Metal-organic frameworks (MOFs) represent a unique class of hybrid compounds in which metal atoms or metal clusters as secondary building units (SBUs) are connected by organic linkers [1]. The resulting frameworks often exhibit high crystallinity and porosity, with specific surface areas of several thousand square meters per gram [2]. Compared to traditional porous materials such as activated carbon, zeolites or silica gel, the properties of MOFs such as defined pores and pore size [3,4], surface area, morphology [5–8], defects [9,10] or stability can be designed by the use of different SBUs or organic linkers [11–16]. For these reasons, MOFs are investigated for a wide range of applications, such as heterogeneous catalysis [17,18], drug transport [19,20], gas and liquid adsorption and separation [21–23], heat transformation [24–26], or for the post-synthetic or in situ encapsulation of dyes to modulate their photophysical properties [27–30]. For example, Chen et al. were able to optimize the emission maximum of composites obtained by post-synthetic encapsulation of different rhodamine dyes in bio-MOF-1 [31]. Tang et al. produced white light emitting composites by simultaneous encapsulation of different dyes in the MOF ZJU-28 [32]. An important aspect of dye

encapsulation is the stability of the resulting composites. Zirconium-based MOFs have proven to be particularly robust compounds in this regard [33,34], making them suitable for the encapsulation of various dyes and their application in different fields. The class of Bodipy dyes is of particular interest in this context [35,36].

Bodipy is the abbreviation for boron dipyrromethene and was first synthesized and characterized by Treibs and Kreuzer in 1968 [37]. Bodipy represents a class of boron complexes formed by a dipyrromethene ligand and two other anionic ligands, usually fluorine (Scheme 1). Due to their chemical and photophysical properties, such as fluorescence with high quantum yield and narrow emission line width, high thermal and photochemical stability as well as good solubility in a wide range of solvents, interest in this class of dyes is constantly increasing [38,39]. It is widely used as a fluorescent sensor [40,41], in photothermal and photodynamic therapy for the treatment of cancer [42,43], in the development of lasers [44], or for the labelling of proteins and nucleic acids [45]. It is also of great interest for catalysis research in various fields, such as selective oxidation or the coupling of a wide range of compounds [46,47]. In addition to the most widely used difluoro variant **1**, a large number of other Bodipy compounds have been prepared and analyzed in recent years by substitution of the fluorine atoms at the boron nucleus with other groups (Scheme 1) [48]. With several new dipyrromethene-based ligands, which form the backbone of the Bodipy compounds, the variety of different Bodipy compounds is constantly increasing, demonstrating the continuing interest in this class of dyes [49].



**Scheme 1.** Synthesis of 5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-Bodipy **1** and 5,5-dicarbonitril-1,3,7,9-tetramethyl-10-phenyl-Bodipy **2**.

A problem of Bodipy dyes is that their exceptional photophysical properties are usually only observed in solution. In the solid state, strong intermolecular interactions such as  $\pi$ – $\pi$  stacking and aggregation often lead to fluorescence quenching and spectral shifts. This limitation restricts their applicability in various fields that require stable and efficient solid-state emitters, such as LED technology or sensors. To preserve their luminescent properties in the solid state, formulation strategies such as the incorporation of Bodipy into solid matrices are necessary. We expect that the encapsulation or incorporation of Bodipy into MOFs will give the photophysical properties of the dye as in solution. This should enable us to produce composites for a wide range of applications, such as heterogeneous catalysis, cancer therapy or sensing. Another interesting approach for such dye composites comes from LED technology, where interactions between the molecules, such as  $\pi$ – $\pi$  stacking or aggregation-induced quenching, can be suppressed by targeted separation of the dye molecules in the individual MOF pores. The increased stability is highly beneficial for all types of applications. For these reasons, we present here the synthesis of a variety of zirconium-based Bodipy@MOF composites, both by post-synthetic and in situ encapsulation of Bodipy in the MOF.

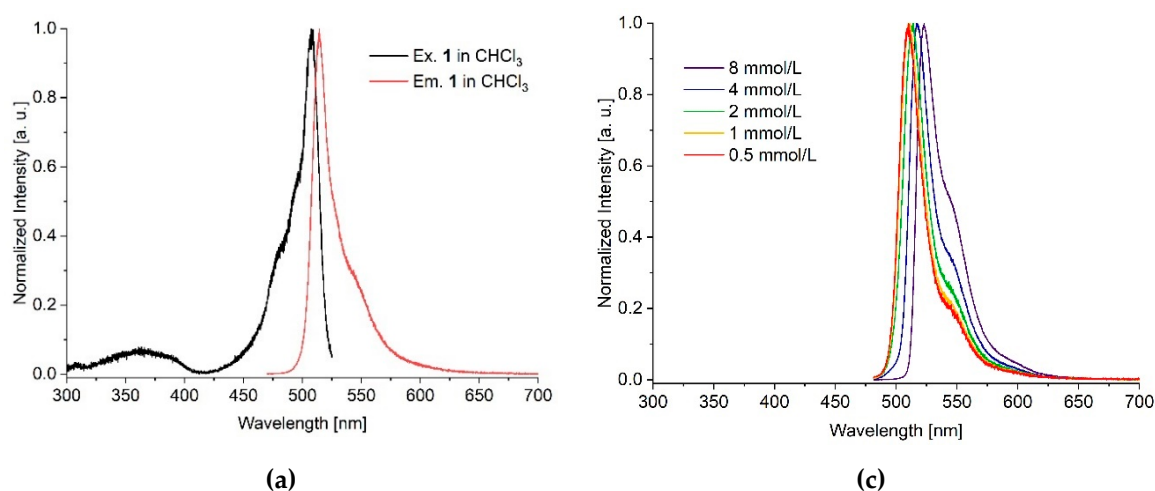
## 2. Results and Discussion

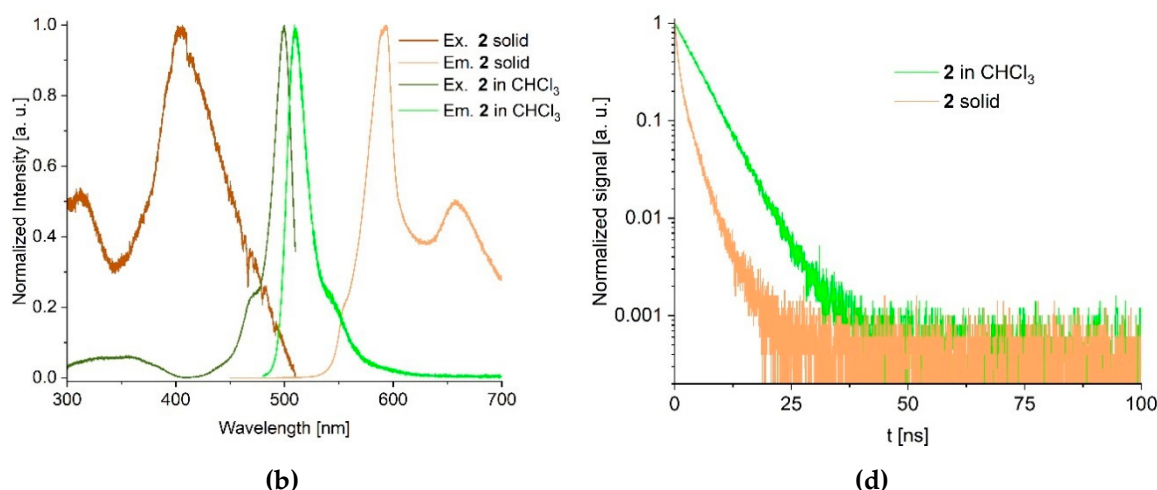
The synthesis and analysis of the Bodipy dyes and the MOFs used in this work is described in detail in the Supplementary Materials. In short, the synthesis in Scheme 1 was carried out according to Caruso et al. [50] and Nguyen et al. [51]. The MOFs were prepared according to the synthesis described in the literature. For the synthesis of UiO-66, the procedure described by Katz et al. was used with minor modifications [52]. The MOFs MOF-808 and DUT-67 were both synthesized according to Reinsch et al. [53]. MIP-206 was prepared according to a procedure by Wang et al. [54].

The successful synthesis and identity of the Bodipy derivatives **1** and **2** was verified by NMR and high-resolution mass spectrometry. The neat MOFs were prepared by synthesis routes reported in the literature and characterized by powder X-ray diffraction (PXRD) together with N<sub>2</sub> gas sorption for BET surface area and porosity determination.

Initial encapsulation experiments with the zirconium-based MOFs UiO-66 and UiO-67, using the difluoro variant **1** gave no detectable luminescence, probably due to the acidity of the inherently defective UiO structures [55]. This confirms the statement by Wang et al. that the dye cannot be effectively stabilized under strongly acidic conditions. In their study on the stability of Bodipy compounds, it was found that the addition of trifluoroacetic acid led to the degradation of the Bodipy structure [56]. Since the dicyanide variants exhibited increased stability under acidic conditions, we decided to use the less studied but more stable dicyano-Bodipy **2**. Another advantage of this dicyano-Bodipy **2** is, in addition to the increased stability against acids, the increased quantum yield compared to difluoro-Bodipy **1**. By going from the difluoro species **1** to the dicyano species **2**, the quantum yield of the Bodipy dye in THF solution could be increased from approximately 37% for **1** [57] to 89% for **2** [51].

Luminescence studies in solution show that both the difluoro and dicyano species **1** and **2** have narrow excitation and emission bands (Figure 1a and b) and are similar in their photophysical properties. The emission maxima at 514.4 nm for **1** and 510.0 nm for **2** in highly diluted chloroform solution correspond to values given in the literature [51,57]. The Stokes shifts are 7.7 nm (295 cm<sup>-1</sup>) for **1** and 9.7 nm (381 cm<sup>-1</sup>) for **2** and their full width at half-maximum (FWHM) values are 19 nm (720 cm<sup>-1</sup>) for **1** and 22 nm (850 cm<sup>-1</sup>) for **2**, making both species very narrow band emitters. Lifetime measurements of both compounds in chloroform yielded an average lifetime value of 5.7 ns for **1** and 4.8 ns for **2** (Figure S6, SM). Investigations of compound **2** in different solvents at the same concentration showed that the emission maxima are almost unaffected by the polarity of the solvent. All maxima were consistently in the range of 525 nm ± 2 nm (Figure S7, SM). This indicates that the photophysical behavior of compound **2** is largely independent of the solvent environment, suggesting minimal interaction between the solvent and the emission states of the compound. However, a concentration-dependent bathochromic shift of the emission maxima was observed in CHCl<sub>3</sub> solution (Figure 1c).





**Figure 1.** (a) Excitation and emission spectra of **1** in  $\text{CHCl}_3$ . Emission spectra were measured with an excitation at 360 nm. Excitation spectra were measured at an emission at 540 nm. (b) Excitation and emission spectra of **2** in  $\text{CHCl}_3$  and in the solid state. Emission spectra in solution were measured with an excitation at 360 nm and as a solid with an excitation at 400 nm. Excitation spectra in solution were measured at an emission at 540 nm and as a solid at an emission at 600 nm. (c) Concentration-dependent bathochromic shift of **2** in  $\text{CHCl}_3$ . Emission maxima: 510 nm (0.5 mmol/L), 511 nm (1 mmol/L), 514 nm (2 mmol/L), 517 nm (4 mmol/L), 523 nm (8 mmol/L). Emission spectra were measured with an excitation at 360 nm. (d) Lifetime measurements of **2** in solution (0.5 mmol/L) and in solid state at the respective emission maxima of 510 nm and 594 nm ( $\lambda_{\text{exc}} = 375 \text{ nm}$ ).

The wavelength increases for the emission maxima with increasing concentration of compound **2** which implies the presence of concentration-dependent aggregation phenomena such as  $\pi$ - $\pi$  interactions and an associated reduction in free rotation. This assumption is also supported by the increasing intensity of the shoulder at 540 nm. These interactions can change the electronic environment of the emission states, which in our case leads to a bathochromic shift of the fluorescence.

As a solid, Bodipy **2** is a red crystalline powder while the  $\text{CHCl}_3$  solution has a green color (Figure S8). Under UV light excitation with  $\lambda_{\text{exc}} = 400 \text{ nm}$ , solid **2** emits an orange to red luminescence with emission maxima at 594 nm and 659 nm (Figure 1b, Figure S8). The formation of two emission maxima and the clear bathochromic shift are discussed in the literature and can be attributed mainly to the formation of J-aggregates [58,59]. The excitation maximum for the solid occurs at 404 nm (Figure 1b), corresponding to Stokes shifts of 190 nm ( $7917 \text{ cm}^{-1}$ ) and 255 nm ( $9577 \text{ cm}^{-1}$ ) for the two emission peaks, respectively. A comparison of these values with those of the  $\text{CHCl}_3$  solution shows the influence of aggregation effects in **2**. In addition to the clear differences in the steady-state luminescence measurements, there is also a significant change in luminescence lifetime and quantum yield for **2** in solid state versus **2** in solution. Solid **2** had a lifetime of only 1.2 ns and an average quantum yield of only 9% compared to a lifetime of 4.8 ns in  $\text{CHCl}_3$  and an average quantum yield of 89% in THF solution (Figure 1d, Figure S6 and S9) [51]. The increased quantum yield of **2** when going from the solid to the solution state and the drastically improved stability against organic and inorganic acids make compound **2** in solution very interesting for various applications. With the concept of solid solutions for dye@MOF composites the embedding or encapsulation of non-aggregated Bodipy in the defined pores of MOFs could open up interesting future applications in areas such as optoelectronic devices or chemical sensors.

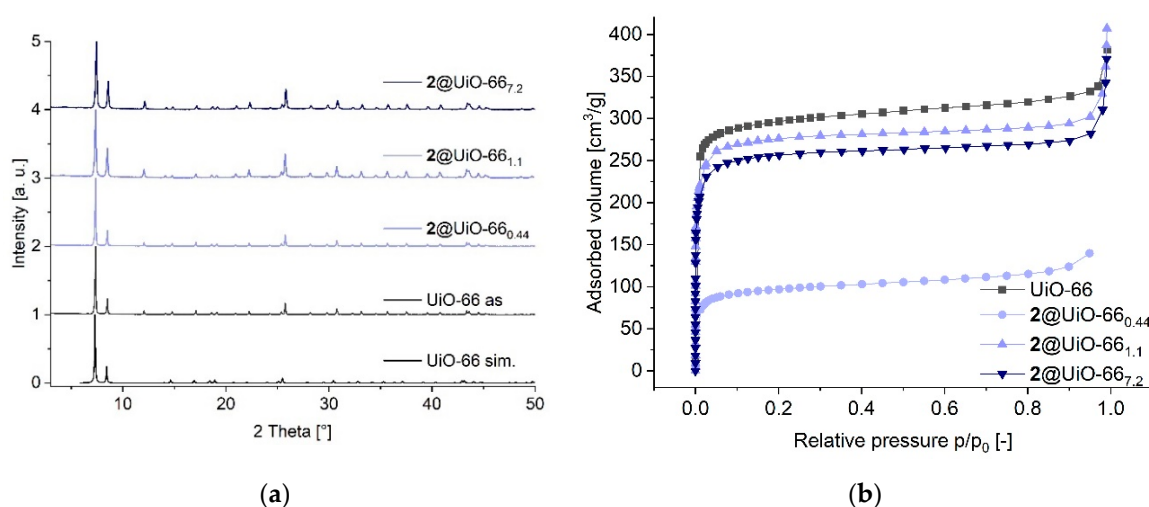
The inclusion of dyes in MOFs can be carried out post-synthetically by wet infiltration in the already prepared MOF or in situ, that is during the MOF synthesis [60]. Furthermore, the presence of defects, such as missing linkers or missing cluster defects, can facilitate the incorporation of the dye molecules and enable the production of composites with both higher dye loadings and high  $\text{N}_2$  uptake. We chose the MOFs UiO-66, MOF-808, DUT-67 and MIP-206. All MOFs are colorless, microcrystalline powders with BET surface areas as reported in the literature. All of them show only

a weak linker-based luminescence in the range between 350 and 440 nm, depending on the linkers used. We were able to perform both post-synthetic and in situ encapsulations for **2** in all MOFs except MIP-206. For comparison purposes, the same initial concentration of Bodipy was used for both the post-synthetic and in situ approaches for MOF-808 and DUT-67.

### 2.1. Composite 2@UiO-66

We started our studies on the encapsulation of **2** in MOFs with the zirconium MOF UiO-66. The encapsulation was carried out in a post-synthetic approach over a period of 5 days at a concentration of 1.0 mmol/L Bodipy in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) with activated UiO-66 (see Section S5, SM for details). With pore sizes of about 8 Å for the tetrahedral pore and 11 Å for the octahedral pore in UiO-66, it is clear that the post-synthetic encapsulation of the Bodipy dye **2**, with molecular dimensions of about 10 Å, is restricted to the larger octahedral pores of UiO-66 (see Section S7, SM for details) [61,62]. Up to 0.44 wt% (4.4 mg of **2** per g of UiO-66 or 21.7 mmol of **2** per mol of UiO-66) could be embedded, based on the UiO-66 formula of  $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6]$  (1664.01 g/mol), denoting the composite as 2@UiO-66<sub>0.44</sub>. No structural change could be detected by powder X-ray diffraction (PXRD, Figure 2a). The loading was determined by UV-Vis digestion analysis (section S6, SM) [63]. This apparent low loading results from only a short diffusion path of the dye molecules into the crystal lattice, slightly beneath the surface layer [29]. This is in line with the significant decrease in the BET surface area from 1192 m<sup>2</sup>/g for neat UiO-66 down to 381 m<sup>2</sup>/g for 2@UiO-66<sub>0.44</sub> due to pore blocking (Figure 2b). Even these small amounts of **2** resulted in a composite with strong emission in the green wavelength range.

Further, the dye was also incorporated in situ into the MOF structure of UiO-66. Four different concentrations of **2** in DMF were used in the MOF reaction mixture of  $\text{H}_2\text{BDC}$  and  $\text{ZrCl}_4$  (see Table S1, SM). Noteworthy, the synthesis of UiO-66 was carried out at 80 °C with hydrochloric acid as a modulator (see Section S5, SM for details) [52]. The improved stability of dicyano-Bodipy **2** versus difluoro-Bodipy **1** allowed us to use acids as modulators giving acidic reaction conditions. The resulting 2@UiO-66 composites were washed with dimethylformamide until the solution no longer showed any residual luminescence. The recorded PXRDs in Figure 2a show no differences compared to the reference sample or the simulation of neat UiO-66. This indicates that the presence of **2** does not affect the MOF structure and face-centered cubic UiO-66 is the only crystalline product which is formed (see Figure S10, SM for all PXRDs).



**Figure 2.** (a) PXRD of UiO-66, 2@UiO-66<sub>0.44</sub> (post-synthetic encapsulated) and the in situ encapsulated 2@UiO-66<sub>1.1</sub> and 2@UiO-66<sub>7.2</sub> composites. Simulated diffractogram of UiO-66 from CCDC No. 752051 [64]. (b) Nitrogen adsorptions isotherms at 77 K of neat UiO-66 (1192 m<sup>2</sup>/g), 2@UiO-66<sub>1.1</sub> (1115 m<sup>2</sup>/g), 2@UiO-66<sub>7.2</sub> (916 m<sup>2</sup>/g), and 2@UiO-66<sub>0.44</sub> (381 m<sup>2</sup>/g). For the desorption isotherms see Figures S11 and S12 in SM.

The amount of Bodipy incorporated in situ in each composite was determined by UV-Vis digestion analysis between 1.1 and 7.2 wt% (11.1 to 77.5 mg of **2** per g of UiO-66 or 54.7 to 381 mmol of **2** per mol of UiO-66, see Section S6 for details), denoting the composites as **2**@UiO-66<sub>1.1</sub> to **2**@UiO-66<sub>7.2</sub>, respectively. This corresponds to an average octahedral pore filling ( $n_{av}(\text{Bodipy}/\text{pore})$ ) of 5.5 to 29.3%, taking into account the number of octahedral pores and asymmetric units in the unit cell of UiO-66 (For a detailed description of the pore calculation, see S7 in SM). A higher concentration of **2** in the reaction mixture resulted in a higher loading in the in situ method, also in comparison to the post-synthetic incorporation. While the low loading from post-synthetic encapsulation of **2** in UiO-66 still gave a colorless composite akin to the color of neat UiO-66, the higher amounts of **2** through in situ encapsulations were also evident from an increasingly pinkish color of **2**@UiO-66 (Figure 3a and Figure S13). Nitrogen sorption measurements and BET surface area determinations of the activated in situ **2**@UiO-66 composites listed in Table 1 showed a decrease in surface area with increasing Bodipy loading compared to neat UiO-66 (for all isotherms, see Figures S11 and S12). This trend supports the successful incorporation of the dye into the MOF structure, as higher loadings of Bodipy reduce the number of accessible pores available for N<sub>2</sub> adsorption. The determined BET surface areas of the composites range from 1115 m<sup>2</sup>/g for the least in situ loaded composite **2**@UiO-66<sub>1.1</sub> to 916 m<sup>2</sup>/g for the composite with the highest Bodipy loading **2**@UiO-66<sub>7.2</sub>. The even lower N<sub>2</sub> uptake and concomitant lower surface area of only 381 m<sup>2</sup>/g for the post-synthetically prepared sample with only 0.44 wt% dye loading is interpreted through pore blocking by the dye molecules which diffuse only slightly beneath the outer surface [29].

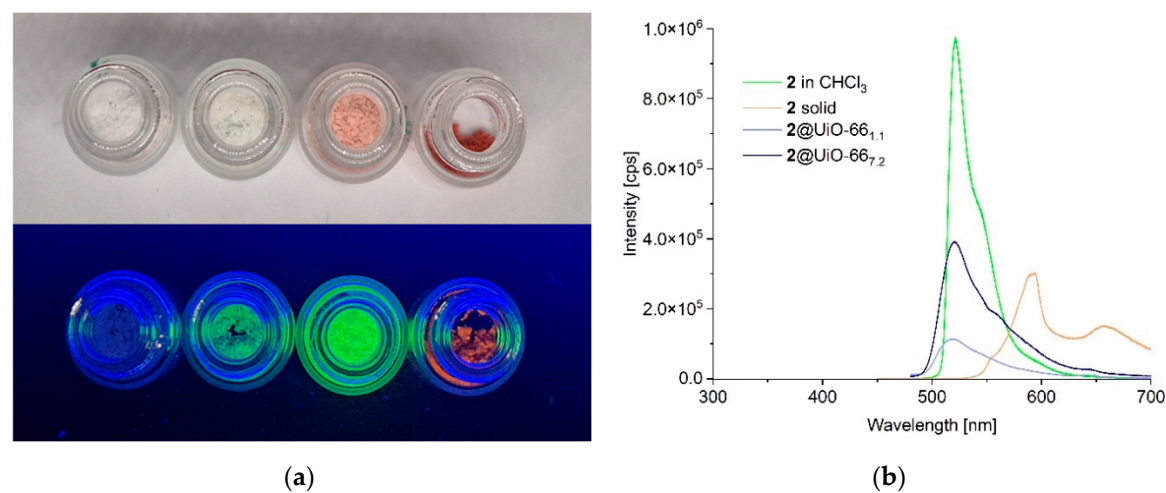
Photophysical measurements show that all **2**@UiO-66 composites exhibit strong green emission, as seen for CHCl<sub>3</sub> solutions of **2** (Figure 3a and Figure S8), hence indicating solid-solution behavior and in contrast to the red emission characteristics of solid **2** (emission maxima at 594 nm and 659 nm, cf. Figure 1b).

**Table 1.** Results of nitrogen sorption measurements for neat UiO-66 and **2**@UiO-66 composites.

| Compound                                       | Bodipy Loading<br>[wt%] <sup>a</sup> | S <sub>BET</sub><br>[m <sup>2</sup> /g] | V <sub>pore(total)</sub><br>[cm <sup>3</sup> /g] <sup>b</sup> | V <sub>pore(micro)</sub><br>[cm <sup>3</sup> /g] <sup>c</sup> |
|------------------------------------------------|--------------------------------------|-----------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| UiO-66 literature                              | -                                    | 1580 [52]                               | -                                                             | -                                                             |
|                                                | -                                    | 1175 [65]                               | 0.63                                                          | -                                                             |
| UiO-66 synthesized                             | -                                    | 1192                                    | 0.55                                                          | 0.55                                                          |
| <b>2</b> @UiO-66 <sub>0.44</sub> (post-synth.) | 0.44                                 | 381                                     | 0.19                                                          | 0.19                                                          |
| <b>2</b> @UiO-66 <sub>1.1</sub> (in situ)      | 1.1                                  | 1115                                    | 0.63                                                          | 0.63                                                          |
| <b>2</b> @UiO-66 <sub>2.3</sub> (in situ)      | 2.3                                  | 1096                                    | 0.6                                                           | 0.61                                                          |
| <b>2</b> @UiO-66 <sub>4.7</sub> (in situ)      | 4.7                                  | 1022                                    | 0.57                                                          | 0.59                                                          |
| <b>2</b> @UiO-66 <sub>7.2</sub> (in situ)      | 7.2                                  | 916                                     | 0.56                                                          | 0.53                                                          |

<sup>a</sup> Calculated by UV-Vis digestion analysis. <sup>b</sup> Total pore volume at p/p<sub>0</sub> = 0.9. <sup>c</sup> Micropore volume calculated from NLDT method using the N<sub>2</sub> adsorption isotherm at 77 K for cylindrical pores ≤2 nm.

The **2**@UiO-66 composites exhibit emission maxima at 521 nm ± 2 nm and are thus all comparable to **2** in solution (8 mmol/L), which shows its emission maximum at 523 nm. Figure 3b illustrates the emission intensities of the lowest and highest in situ loaded **2**@UiO-66 composites together with **2** in CHCl<sub>3</sub> (8 mmol/L) and **2** as a solid (for the emission spectra of all UiO-66 composites see Figure S21). The intensity of this band increases with higher Bodipy loading, yet without any bathochromic shift being observed as for higher concentration in CHCl<sub>3</sub> solutions of **2** (cf. Figure 1c). However, the emission maximum of 521 nm is already as seen for the higher-concentrated Bodipy CHCl<sub>3</sub> solution of 8 mmol/L, which can be attributed to the suppression of the rotation of **2** within the MOF pore [66,67].



**Figure 3.** (a) From left to right: neat UiO-66, post-synthetically encapsulated 2@UiO-66<sub>0.44</sub> (0.44 wt%), in situ prepared 2@UiO-66<sub>2.3</sub> (2.3 wt%) and 2 as a solid both under daylight (top) and under UV-light ( $\lambda_{exc}$  = 365 nm, bottom). (b) Emission spectra ( $\lambda_{exc}$  = 330 nm) of the 2@UiO-66 in situ composites with the lowest (1.1 wt%) and highest (7.2 wt%) achieved loading together with the emission spectra of 2 in CHCl<sub>3</sub> solution (8 mmol/L,  $\lambda_{exc}$  = 360 nm) and the emission spectra of 2 as solid ( $\lambda_{exc}$  = 400 nm).

The constant emission maxima of the 2@UiO-66 composites with different loading strongly suggest that the encapsulation of 2 into the MOF structure effectively limits interactions and aggregation of Bodipy molecules. All composites show by their emission behavior a desired separation of the Bodipy molecules, similar to that in the 8 mmol/L solution. However, it can be assumed that as the load increases, the probability of finding more than one Bodipy molecule in a pore also increases. This assumption is based on the shoulder at 550 nm which is most prominent for the 2@UiO-66<sub>7.2</sub> composite with the highest loading. It indicates some formation of J-aggregates. The emission maximum remains unchanged at this low degree of aggregation. Based on the above loading, we calculated the probability  $p$  of multiple occupation in a random distribution of Bodipy in UiO-66 and listed this probability in Table 2 (for a more detailed description of the calculation see Section 7, SM). The same behavior was observed and discussed in the work of Püschel et al. [68].

**Table 2.** Probability  $p$  of multiple occupation of Bodipy molecules in a pore of the 2@UiO-66 composites.<sup>a</sup>

|                              | 2@UiO-66 <sub>1.1</sub> | 2@UiO-66 <sub>2.3</sub> | 2@UiO-66 <sub>4.7</sub> | 2@UiO-66 <sub>7.2</sub> |
|------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| $n_{av}(\text{Bodipy/pore})$ | 0.055                   | 0.12                    | 0.243                   | 0.293                   |
| $p(\text{one})$ [%]          | 96.4                    | 94                      | 86.7                    | 78.1                    |
| $p(\text{two})$ [%]          | 3.6                     | 5.7                     | 12.1                    | 18.4                    |
| $p(\geq \text{three})$ [%]   | 0                       | 0.2                     | 1.1                     | 3.5                     |

<sup>a</sup> Calculations are based on the UiO-66 formula of [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>6</sub>], the amount of Bodipy in mol per mol MOF and the ratio of pores per formula unit (1:1). Pore refers to the octahedral pore in UiO-66.

The probability calculations confirmed our assumptions of some J-aggregate formation already at low loadings. At the same time, we were able to determine that the majority of the Bodipy molecules are embedded separately, which explains the solution-like luminescence behavior of the composites. Furthermore, based on the measured emission wavelengths and increasing intensities with loading, we assume that there is no strong interaction of the dye molecules with the MOF pore surface that would affect the wavelength of the emission maxima. Time-resolved fluorescence spectroscopy of the 2@UiO-66 composites show that a tri-exponential decay of the post-synthetically prepared 2@UiO-66<sub>0.44</sub> composite and bi-exponential decay of all in situ prepared composites were needed to describe the luminescence lifetimes decays of all composites (for the decay plots of all UiO-66 composites, see Figure S22). The difference in decay can be explained by the presence of different luminescent species. These species can be traced back to the formation of different aggregates, whose

respective properties significantly influence the lifetimes of the composite materials. Furthermore, the environment formed by the MOF can also affect the luminescence lifetime decay. This can result in either a prolongation or a shortening of the lifetime [69–71]. The lifetimes of 2@UiO-66 were significantly extended compared to the lifetime of solid 2 (Table 3).

The average lifetimes  $\tau_x$  of the composites are comparable to the lifetime of 2 in solution, with the lowest loadings of 0.44 and 1.1 wt% showing slightly increased lifetimes of 5.3 and 5.1 ns, respectively. Interestingly, the lifetimes show an inverse relationship to the Bodipy loading in the composites (Table 3). The sample with the highest loading of 7.2 wt% gave the shortest lifetime, measured at 4.0 ns. This trend is consistent with the observed quantum yields, which also decrease with increasing loading. In particular, the composites with the lowest loadings exhibited average quantum yields around 30%, while the composite with the highest loading exhibited a reduced quantum yield of 19%. The presence of  $\pi$ - $\pi$  interactions between neighboring Bodipy molecules can influence the lifetime. However, it is mainly explained by the presence and increase of aggregates in higher loaded composites (cf. Table 2) [72]. In addition to the increased aggregation, Bodipy-to-MOF wall interactions play a decisive role, as the excited state loses its energy more quickly through a Bodipy contact with the MOF pore wall. This can contribute to both a reduced quantum yield and a reduced lifetime. Although the quantum yields of 2@UiO-66 are lower than the quantum yield of 2 in THF solution, they are significantly improved over the quantum yield of solid 2, which is only 9%.

**Table 3.** Photophysical data for 2 as a solid, in solution and for the 2@UiO-66 composites.

| Compound                               | $\lambda_{F, \max}$ [nm] <sup>a</sup> | $\tau_1$ (x <sub>1</sub> ), $\tau_2$ (x <sub>2</sub> ), $\tau_3$ (x <sub>3</sub> ) [ns] <sup>b</sup> | $\tau_x$ [ns] <sup>b</sup> | $\Phi_F$ [%] <sup>c</sup> |
|----------------------------------------|---------------------------------------|------------------------------------------------------------------------------------------------------|----------------------------|---------------------------|
| 2 solid                                | 594/659                               | 0.6 (0.74), 2.8 (0.29)                                                                               | 1.2                        | 9                         |
| 2 in CHCl <sub>3</sub> (0.5 mmol/L)    | 510                                   | 4.8 (1)                                                                                              | 4.8                        | 89 <sup>d</sup>           |
| 2@UiO-66 <sub>0.44</sub> (post-synth.) | 519                                   | 0.7 (0.10), 5.3 (0.8), 11.1 (0.09)                                                                   | 5.3                        | 29                        |
| 2@UiO-66 <sub>1.1</sub> (in situ)      | 521                                   | 1.0 (0.08), 5.4 (0.91)                                                                               | 5.1                        | 32                        |
| 2@UiO-66 <sub>2.3</sub> (in situ)      | 523                                   | 0.6 (0.09), 5.1 (0.89)                                                                               | 4.6                        | 28                        |
| 2@UiO-66 <sub>4.7</sub> (in situ)      | 519                                   | 1.4 (0.21); 4.8 (0.8)                                                                                | 4.2                        | 21                        |
| 2@UiO-66 <sub>7.2</sub> (in situ)      | 520                                   | 0.9 (0.14), 4.6 (0.85)                                                                               | 4.0                        | 19                        |

<sup>a</sup> Wavelength of the fluorescence maximum;  $\lambda_{exc}$  = 400 nm for solid 2;  $\lambda_{exc}$  = 360 nm for 2 in CHCl<sub>3</sub>;  $\lambda_{exc}$  = 330 nm for 2@UiO-66. <sup>b</sup> Fluorescence lifetime ( $\lambda_{exc}$  = 375 nm):  $\tau_i$  (x<sub>i</sub>) species i lifetime (fraction),  $\tau_x$  species-weighted average lifetime. <sup>c</sup> Fluorescence quantum yield. <sup>d</sup> Measured in THF taken from the literature [51].

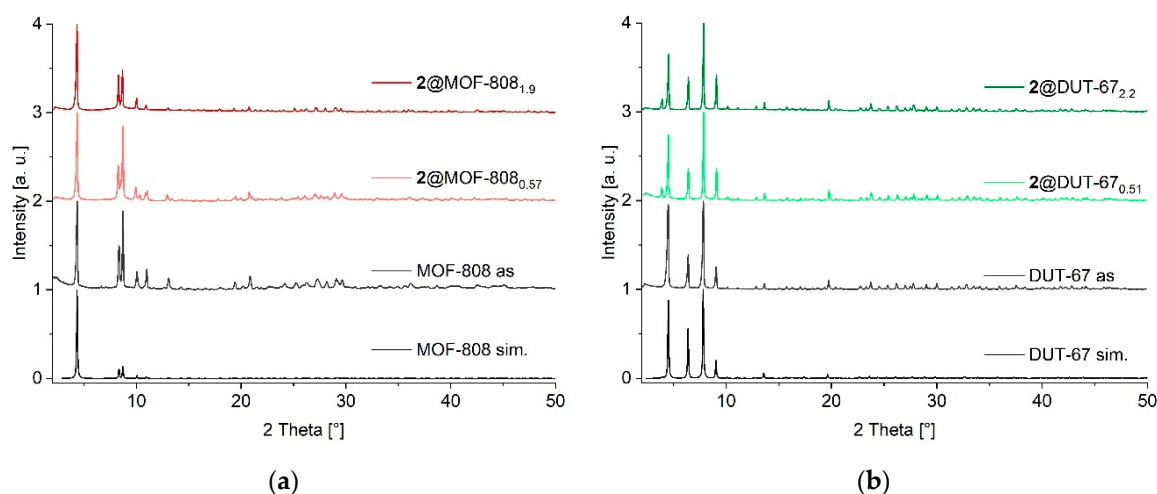
2.2. Composites 2@MOF-808, 2@DUT-67 and 2@MIP-206

To investigate the influence of the MOF host on the photophysical properties of 2@MOF composites, a post-synthetic and an in situ composite were synthesized for MOF-808 and DUT-67, and a post-synthetic composite for MIP-206. The same MOF to Bodipy ratio was used in the preparation for both the post-synthetic and in situ composites. Due to the increased stability of 2, we were able to use glacial acetic acid in a large excess in the in situ syntheses of the 2@MOF-808 and 2@DUT-67 composites. However, due to the extremely harsh synthesis conditions required for MIP-206, with formic acid as the sole solvent at temperatures of 180 °C, the in situ encapsulations of 2 could not be successfully carried out for MIP-206.

MOF-808 contains a hierarchical pore structure of large, interconnected hexagonal channels with diameters of approximately 18 Å (1.8 nm) and isolated tetrahedral cages with internal pore diameters around 4.8 Å (or 0.48 nm); the latter being not accessible for Bodipy [73]. DUT-67 has a hierarchical porous structure containing cuboctahedral pores with a diameter of 14.2 Å (1.42 nm) and an octahedral pore with a diameter of 11.7 Å (1.17 nm) [74]. Both of which can encapsulate Bodipy and

we took both pores into account when calculating pore filling. The structure of MIP-206 has uniform meso-voids with a diameter of ca. 26 Å (2.6 nm) [54]

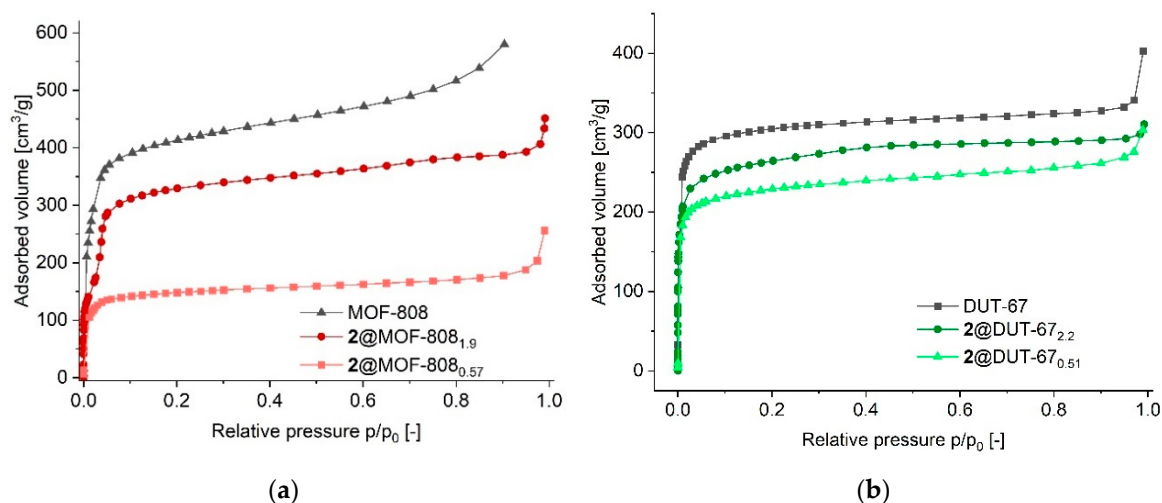
The post-synthetic 2@MOF-808 and 2@DUT-67 composites show no detectable changes in their PXRD patterns in Figure 4, indicating that the crystalline structures of the MOFs were unchanged.



**Figure 4.** (a) PXRD of MOF-808, post-synthetic 2@MOF-808<sub>0.57</sub> and in situ encapsulated 2@MOF-808<sub>1.9</sub> composites. Simulated diffractogram of MOF-808 from CCDC No. 1002672 [73]. (b) PXRD of DUT-67, post-synthetic 2@DUT-67<sub>0.51</sub> and in situ encapsulated 2@DUT-67<sub>2.2</sub> composites. Simulated diffractogram of DUT-67 from CCDC No. 921644 [74]. For the PXRDs of MIP-206 and 2@MIP-206<sub>0.3</sub> see Figure S20a.

From UV-Vis digestion analysis the post-synthetic loadings were determined to be 0.57 wt% for MOF-808 and 0.51 wt% for DUT-67 (see Table S2) [75,76]. The resulting composites are designated as 2@MOF-808<sub>0.57</sub> and 2@DUT-67<sub>0.51</sub>. This corresponds to a molar ratio of 22.1 mmol Bodipy per mol of MOF-808 and 23.3 mmol Bodipy per mol of DUT-67. The formulas for MOF-808 [ $\text{Zr}_6\text{O}_4(\text{OH})_{10}(\text{BTC})_2(\text{H}_2\text{O})_6$ ] (1303.7 g/mol) and DUT-67 [ $\text{Zr}_6\text{O}_4(\text{OH})_8(\text{TDC})_4(\text{H}_2\text{O})_6$ ] (1536.1 g/mol) were used for the calculation [53].

In agreement with such a low loading we observed only very slight changes in the color of both post-synthetic composites which were almost colorless, microcrystalline powders (see section S9, Figures S23c and S25c). However, a significant decrease in the determined BET surface area was observed for the 2@MOF-808<sub>0.57</sub> composite, with a reduction of up to 65% versus neat MOF-808. By comparison, an only 31% reduction of the BET surface area was observed for the 2@DUT-67<sub>0.51</sub> composite compared to neat DUT-67 (Figure 5, Table 4).



**Figure 5.** (a) Nitrogen adsorptions isotherms at 77 K of neat MOF-808 (1683  $\text{m}^2/\text{g}$ ), 2@MOF-808<sub>1.9</sub> (1200  $\text{m}^2/\text{g}$ , in situ), and 2@MOF-808<sub>0.57</sub> (596  $\text{m}^2/\text{g}$ , post-synthetic) composites. (b) Nitrogen adsorptions isotherms at 77 K of

neat DUT-67 (1207 m<sup>2</sup>/g), 2@DUT-67<sub>2.2</sub> (1020 m<sup>2</sup>/g, in situ), and 2@DUT-67<sub>0.51</sub> (840 m<sup>2</sup>/g, post-synthetic) composites. For the desorption isotherms see Figures S18 and S19, for the isotherms of 2@MIP-206<sub>0.3</sub> see Figure S20b.

The BET surface area reductions for the two post-synthetic composites compared to in situ prepared composites (see below) can be attributed to the accumulation predominantly in the outer layers of the MOF crystallites, rather than uniformly penetrating the entire porous network [29]. Thereby access to the inner dye-free pore structure is restricted by pore blocking, which leads to reduced N<sub>2</sub> adsorption and, consequently, lower BET surface areas.

The in situ encapsulations of 2 into MOF-808 and DUT-67 resulted in the composites 2@MOF-808<sub>1.9</sub> and 2@DUT-67<sub>2.2</sub> with loadings of 1.9 wt% and 2.2 wt%, corresponding to 74.7 and 102 mmol Bodipy per mol of MOF-808 and DUT-67, respectively. The in situ prepared composites 2@MOF-808<sub>1.9</sub> and 2@DUT-67<sub>2.2</sub> showed a slight color change to pale yellow compared to the neat MOFs (see Figures S23c and S25c, SM). PXRD analysis of the in situ prepared composites, which are shown in Figure 4, revealed no differences from the simulated patterns of MOF-808 and DUT-67. These observations indicate the formation of the neat MOF structure and a crystalline phase-pure synthesis of the composites produced in situ. Their N<sub>2</sub> adsorption measurements, shown in Figure 5, yielded BET surface areas of 1200 m<sup>2</sup>/g for 2@MOF-808<sub>1.9</sub> and 1020 m<sup>2</sup>/g for 2@DUT-67<sub>2.2</sub>. These values are comparable to those reported in the literature. We assume that the in situ encapsulation enables homogeneous distribution of the Bodipy dye within the MOF frameworks. This results in better pore availability compared to post-synthetic loading.

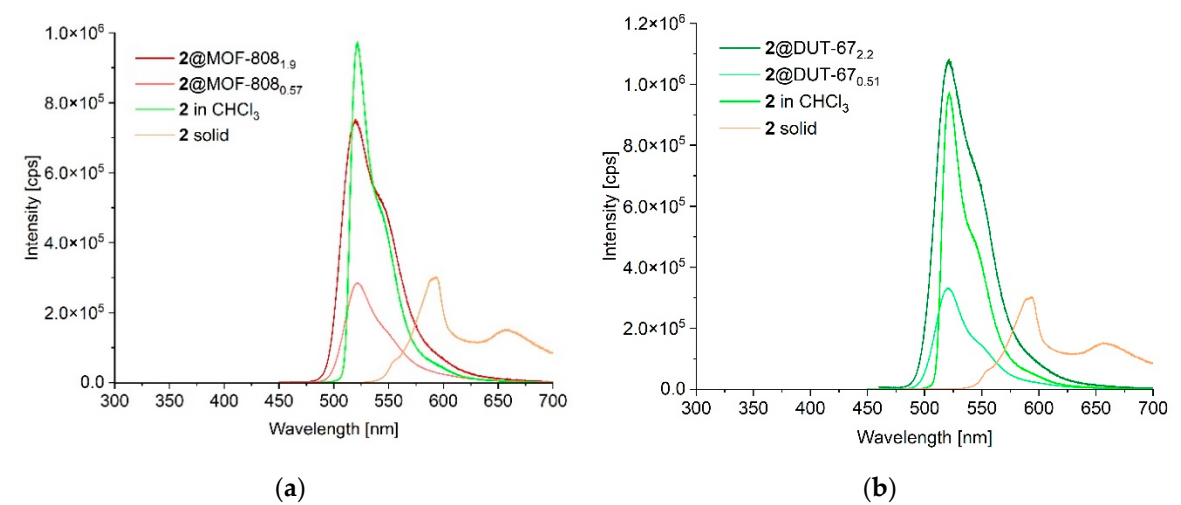
**Table 4.** Results of nitrogen sorption measurements for neat MOF-808, 2@MOF-808 composites, neat DUT-67, 2@DUT-67 composites, neat MIP-206, and 2@MIP-206<sub>0.3</sub>.

| Compound                                | Bodipy Loading<br>[wt%] <sup>a</sup> | S <sub>BET</sub><br>[m <sup>2</sup> /g] | V <sub>pore(total)</sub><br>[cm <sup>3</sup> /g] <sup>b</sup> | V <sub>pore(micro)</sub><br>[cm <sup>3</sup> /g] <sup>c</sup> |
|-----------------------------------------|--------------------------------------|-----------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| MOF-808 literature                      | -                                    | 2060 [73]                               | 0.84                                                          | -                                                             |
|                                         | -                                    | 1210 [53]                               | 0.53                                                          | -                                                             |
| MOF-808 synthesized                     | -                                    | 1683                                    | 0.8                                                           | 0.76                                                          |
| 2@MOF-808 <sub>0.57</sub> (post-synth.) | 0.57                                 | 596                                     | 0.27                                                          | 0.27                                                          |
| 2@MOF-808 <sub>1.9</sub> (in situ)      | 1.9                                  | 1200                                    | 0.68                                                          | 0.24                                                          |
| DUT-67 literature                       | -                                    | 1171 [77]                               | -                                                             | -                                                             |
|                                         | -                                    | 1150 [53]                               | -                                                             | -                                                             |
| DUT-67 synthesized                      | -                                    | 1207                                    | 0.56                                                          | 0.52                                                          |
| 2@DUT-67 <sub>0.51</sub> (post-synth.)  | 0.51                                 | 840                                     | 0.4                                                           | 0.37                                                          |
| 2@DUT-67 <sub>2.2</sub> (in situ)       | 2.2                                  | 1020                                    | 0.47                                                          | 0.51                                                          |
| MIP-206 literature                      | -                                    | 1059 [54]                               | 0.45                                                          | -                                                             |
| MIP-206 synthesized                     | -                                    | 1062                                    | 0.42                                                          | 0.41                                                          |
| 2@MIP-206 <sub>0.3</sub> (post-synth.)  | 0.3                                  | 701                                     | 0.39                                                          | 0.37                                                          |

<sup>a</sup> Calculated by UV-Vis digestion analysis. <sup>b</sup> Total pore volume at p/p<sub>0</sub> = 0.9. <sup>c</sup> Micropore volume calculated from NLDFT method using the N<sub>2</sub> adsorption isotherm at 77 K for cylindrical pores ≤ 2 nm.

Steady-state luminescence measurements showed that both the post-synthetically loaded and in situ fabricated composites of MOF-808 and DUT-67 exhibit the characteristic luminescence of 2 in solution with emission maxima in the region of 521 nm ± 2 nm with a shoulder at 550 nm (Figure 6). Due to the higher loading in the composites produced in situ, a significant increase in luminescence intensity can be measured (for MIP-206 see SM, S9). Again, as for 2@UiO-66, the shoulder around 550 nm indicates multiple occupancy of some pores and thus the formation of aggregates. The probability p of a multiple pore occupation of 2 in both MOFs is listed in Table 5, taking into account that the pores are formed with the molecular formula units of [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>10</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] for MOF-808 and

[Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(TDC)<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>] for DUT-67 (for a more detailed description of the structures and the ratios of pore-to-molecular formula units, see SM Section S7).



**Figure 6.** (a) Luminescence spectra of in situ and post-synthetic 2@MOF-808 composites together with 2 in CHCl<sub>3</sub> solution (8 mmol/L) and as a solid. (b) Luminescence spectra of in situ and post-synthetic 2@DUT-67 composites together with 2 in CHCl<sub>3</sub> solution (8 mmol/L) and as a solid. Emission spectra were measured with excitation at 360 nm for all composites and the CHCl<sub>3</sub> solution and at 400 nm for solid 2. For the luminescence spectra of post-synthetic 2@MIP-206 see Figure S27a.

**Table 5.** Probability *p* of multiple occupation of 2 in the in situ prepared 2@MOF-808 and 2@DUT-67 composite materials.<sup>a</sup>

|                                      | 2@MOF-808 <sub>1.9</sub> | 2@DUT-67 <sub>2.2</sub> |
|--------------------------------------|--------------------------|-------------------------|
| <i>n</i> <sub>av</sub> (Bodipy/pore) | 0.298                    | 0.155                   |
| <i>p</i> (one) [%]                   | 83.4                     | 91.7                    |
| <i>p</i> (two) [%]                   | 14.7                     | 7.7                     |
| <i>p</i> (≥ three) [%]               | 1.9                      | 0.6                     |

<sup>a</sup> The calculations are based on encapsulated 74.7 and 102 mmol Bodipy per mol of MOF-808 and DUT-67, respectively, and the ratio of pores per formula unit of each MOF. The latter ratio for MOF-808 is 0.25:1 and for DUT-67 it is 0.66:1. For more details about the calculation see SM Section S7.

Looking at the lifetimes of the prepared composites in Table 6, the post-synthetic composites gave tri-exponential decays, the in situ composites bi-exponential ones as seen in the 2@UiO-66 composites. The observed tri-exponential and bi-exponential decays suggests the coexistence of different emitting species, a property often associated in the literature with the formation of J-aggregates [69]. Compared to the lifetime of 2 in solution (4.8 ns for 0.5 mmol/L) and as a solid (1.2 ns), all composites show significantly longer lifetimes. For the post-synthetic composites of MOF-808, DUT-67, and MIP-206 average lifetimes  $\tau_x$  of 6.5 ns to 7.9 ns were measured. The in situ synthesized composites 2@MOF-808<sub>1.9</sub> and 2@DUT-67<sub>2.2</sub> showed a further significant increase in average lifetimes, with values of 9.0 ns and 8.5 ns, respectively (see Section S9, SM for the decay plots of all 2@MOF composites). The average lifetime of these composites represents a doubling compared to 2 in solution (0.5 mmol/L) and an eight-fold increase compared to solid 2. For the 2@UiO-66 composites the average lifetimes  $\tau_x$  was close to the lifetime of 2 in solution (0.5 mmol/L) (cf. Table 3). Compared to the UiO-66 composites, the extended lifetimes in MOF-808 and DUT-67 reveal the influence of both pore size and pore environment. The latter two MOFs have pores that are significantly larger than the embedded dye molecules. This results in better separation of the Bodipy molecules within the pores and fewer interactions, such as  $\pi$ - $\pi$  interactions or aggregation, both between individual Bodipy molecules and the pore walls and between neighboring Bodipy molecules. Lower interactions between the Bodipy molecules and the MOF walls are evident when comparing the aggregation (cf.

Tables 2 and 5) and respective lifetimes (cf. Tables 3 and 6) of UiO-66 vs. MOF-808 and UiO-66 vs. DUT-67. At comparable degrees of aggregation of 2@MOF-808<sub>1.9</sub> ( $\tau_x = 9.0$  ns) vs. 2@UiO-66<sub>4.7</sub> ( $\tau_x = 4.2$  ns), and of 2@DUT-67<sub>2.2</sub> ( $\tau_x = 8.5$  ns) vs. 2@UiO-66<sub>2.3</sub> ( $\tau_x = 4.6$  ns) the lifetime increases with pore size and, thus, the weaker interaction with the MOF walls.

The presence of such monomers has already been described in the work of Xiong et al. using rhodamine B in ZIF-8. [70]. However, the significant increase in lifetime in the 2@MOF-808 and 2@DUT-67 composite compared to the lifetime in solution is not only due to the formation of such isolated monomers through enlarged pores, but also to the pore-forming MOF environment. Studies such as those by Liu et al. demonstrate the significant impact that changes in the MOF environment due to the introduction of functional groups can have on the photophysical properties of dyes [78]. In their work, they modified ZIF-8 by introducing 1,2,4-benzenetricarboxylic acid with carboxyl functional groups, which significantly increased the quantum yield of the dye@MOF composite.

**Table 6.** Photophysical data for 2 as a solid and in solution and the 2@MOF-808 and 2@DUT-67 composites.

| Compound                                | $\lambda_{F, max}$ [nm] <sup>a</sup> | $\tau_1$ (x <sub>1</sub> ), $\tau_2$ (x <sub>2</sub> ), $\tau_3$ (x <sub>3</sub> ) [ns] <sup>b</sup> | $\tau_x$ [ns] <sup>b</sup> | $\Phi_F$ [%] <sup>c</sup> |
|-----------------------------------------|--------------------------------------|------------------------------------------------------------------------------------------------------|----------------------------|---------------------------|
| 2 solid                                 | 594/659                              | 0.6 (0.74), 2.8 (0.29)                                                                               | 1.2                        | 9                         |
| 2 in CHCl <sub>3</sub>                  | 510                                  | 4.8 (1)                                                                                              | 4.8                        | 89 <sup>d</sup>           |
| 2@MOF-808 <sub>0.57</sub> (post-synth.) | 523                                  | 6.5 (0.85), 0.8 (0.09), 13.2 (0.07)                                                                  | 6.5                        | 48                        |
| 2@MOF-808 <sub>1.9</sub> (in situ)      | 519                                  | 6.6 (0.44), 11.3 (0.54)                                                                              | 9.0                        | 35                        |
| 2@DUT-67 <sub>0.51</sub> (post-synth.)  | 519                                  | 6.2 (0.78), 1.6 (0.07), 10.8 (0.16)                                                                  | 6.8                        | 77                        |
| 2@DUT-67 <sub>2.2</sub> (in situ)       | 521                                  | 8.4 (0.97), 19.8 (0.02)                                                                              | 8.5                        | 41                        |

<sup>a</sup> Wavelength of the fluorescence maximum ( $\lambda_{exc} = 360$  nm). <sup>b</sup> Fluorescence lifetime ( $\lambda_{exc} = 375$  nm):  $\tau_i$  (x<sub>i</sub>) species i lifetime (fraction),  $\tau_x$  species-weighted average lifetime. <sup>c</sup> Fluorescence quantum yield. <sup>d</sup> Measured in THF taken from the literature [51]. For the fluorescence lifetime of post-synthetic 2@MIP-206 see Table S6.

In addition to the extended lifetimes of 2 in 2@MOF-808 and 2@DUT-67, good quantum yields were observed. The composites prepared in situ had average quantum yields of 35% for MOF-808 and 41% for DUT-67. Significantly higher quantum yields were obtained for the post-synthetically encapsulated composites. For 2@MOF-808<sub>0.57</sub>, we measured an average quantum yield of 48% and for 2@DUT-67<sub>0.51</sub> an impressive 77%. These high quantum yields derive from the Bodipy concentration in the outer MOF layer which enables an efficient molecule excitation. The inner Bodipy molecules of the in situ composites may not be reached by the photons and their emission is also more readily absorbed within the MOF. Furthermore, the decreased dye-to-wall interactions between Bodipy in MOF-808 and DUT-67, with their larger pores, compared to UiO-66 result in less quenching. The quantum yield for 2@DUT-67<sub>0.51</sub> of 77% is comparable to the quantum yield of 89% for 2 in THF solution reported in the literature [51].

All composites far exceed the quantum yield of the solid dye. The 2@MOF-808 and 2@DUT-67 composites also gave higher quantum yields than the 2@UiO-66 composites. The UiO-66 composites ranged from 31% for 2@UiO-66<sub>1.1</sub>, which had the highest quantum yield, to 19% for 2@UiO-66<sub>7.2</sub>, which had the lowest quantum yield (cf. Table 3). Overall, the improved photophysical emission lifetimes and quantum yields make the Bodipy@MOF composites interesting for applications in solid-state devices.

3. Conclusions

In conclusion, we have shown that by substituting the well-known and well-studied difluoro groups of Bodipy with the less-investigated cyano groups, an acid-stable variant of Bodipy can be synthesized and used for both post-synthetic and in situ incorporation into zirconium-based MOFs

under highly acidic synthesis conditions. The 2@MOF composites show a distinct emission at  $521 \text{ nm} \pm 2 \text{ nm}$ , comparable to the emission of **2** in solution (8 mmol/L), in line with the solid-solution concept for dyes@MOFs. From  $\text{N}_2$  adsorption measurements with surface area determinations it could be inferred that the post-synthetic encapsulation method leads to a dye loading predominantly in the outer layers of the MOF crystallites. On the contrary, the in situ encapsulation method yields a more homogeneous distribution of the Bodipy molecules over the entire MOF crystallite. By means of distribution calculations and by fluorescence spectroscopic measurements it is suggested that isolated J-aggregates are formed as the loadings increase. Yet, the post-synthetic concentration of the dye in the outer layer was found advantageous to increase the quantum yield in case of large-pore MOFs. Through the choice of a MOF with a pore size larger than the dye molecule composites with a high quantum yield, close to the quantum yield of **2** in solution could be obtained, due to decreased dye-to-wall interactions and thereby reduced quenching. The advantage of the solid 2@MOF composites was their increased fluorescence lifetime and quantum yield, both up to eight-fold, compared to solid **2**. These results provide a starting point for the targeted development of solid dye@MOF composites with specific optical and structural properties.

**Supplementary Materials:** The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Section S1: General information; Section S2: Sources of chemicals; Section S3: Synthesis of Bodipy compounds **1** and **2**; Section S4: Photophysical properties of Bodipy **2**; Section S5: Synthesis of UiO-66 and 2@UiO-66 composites; Section S6: Digestion UV-Vis; Section S7: Calculation of pore filling and the probability  $p$ ; Section S8: Synthesis of MOF-808, DUT-67 and MIP-206 and their composites; Section S9: Photophysical properties of all composites; Section S10: Structural information; Section S11 References. References [79] and [80] are cited in the Supplementary Materials.

**Author Contributions:** Conceptualization: C.J. and M.N.A.F.; methodology: M.N.A.F.; validation: M.N.A.F.; formal analysis: M.N.A.F., M.V.; investigation: M.N.A.F., M.V. and A.L.; resources: C.J.; data curation: M.N.A.F.; writing—original draft preparation: M.N.A.F.; writing—review and editing: C.J.; visualization: M.N.A.F. and C.J.; supervision: C.J.; project administration: C.J.; funding acquisition: C.J. All authors have read and agreed to the published version of the manuscript.

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