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Fluorescent Red-Emitting BODIPY Oligofluorene Star-Shaped Molecules as a Color Converter Material for Visible Light Communications

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The ever growing demand for wireless data communications is driving a need for new technologies to augment the existing radio frequency approaches (such as WiFi). Visible light communications (VLC) offers a means to do this, using the unlicensed visible region of the electromagnetic spectrum for wireless communications, where hundreds of terahertz of bandwidth are available. The adoption of light-emitting diode (LED) lighting makes this possible, as standard lighting fixtures can be used for both illumination and data communications.[1–3] Data are encoded by modulating the light source, and the rate of data transmission that can be achieved depends on the modulation bandwidth of the LED and its phosphor coating. In addition, it must emit sufficient optical power to create the required signal-to-noise ratio at the receiver for the particular modulation format used.

Conventional phosphor-converted LEDs (pcLEDs) use a blue InGaN LED coated with a yellow phosphor to convert a fraction of the blue light to longer wavelengths.[4] PcLEDs can operate at high efficiency and brightness, but the long excited state lifetime of the phosphors restricts modulation frequency and hence the transmission rate.[2] The photoluminescence (PL) lifetime typical of the phosphor materials used is on the microsecond timescale, which limits the system bandwidth to a few megahertz (MHz).[5,6] There is currently a strong need for alternative materials for fast color converters, which can combine high illumination performance with short PL lifetimes. This combination of properties implies that the key figure of merit for color converter materials is a short natural radiative lifetime.

Organic semiconductors offer many potential advantages as a novel color converter for VLC due to their visible band gaps, short radiative lifetime, and high photoluminescence quantum yield (PLQY). They have been applied as a color converter in vacuum-evaporated OLEDs[7] and we recently demonstrated the use of a yellow emitting conjugated polymer as a fast additive color converter for VLC.[8] To achieve high-quality sources for good color rendering, suitable materials with green or red PL are also needed to mix with the blue emission from the LED.

In this paper, we explore the potential of star-shaped organic semiconductors based on boron dipyrromethene (BODIPY) cores as red-conversion material for LEDs in VLC applications. We selected BODIPY as the core of the molecules because it is a red emitter of known stability.[10] We investigate the influence of different substitution patterns of the BODIPY core with oligofluorene arms, leading to different shapes of the molecules (T- and Y-shaped). In particular, we study the photophysical properties of these materials, measure their modulation bandwidth, and demonstrate their potential for VLC by achieving a data rate ten times higher than measured with a conventional phosphor color converter. BODIPY (4,4-difuoro-4-bora-3a,4a-diaza-s-indacene)-based organic semiconductors have attracted significant attention due to their electronic and optical properties with narrow absorption and emission bands, high PLQY, and good thermal stability.[9] Furthermore, they are solution-processable unlike previous red organic color converter materials.[7] They have been applied in many fields such as biology,[11] medicine,[12] solar energy,[13] and lasers[10]. BODIPYs can have red emission with lifetimes in the range of a few nanoseconds and can strongly absorb in the range of the GaN LEDs electroluminescence (≈450 nm) making them suitable candidates to be used in three-component additive coloration for VLC.

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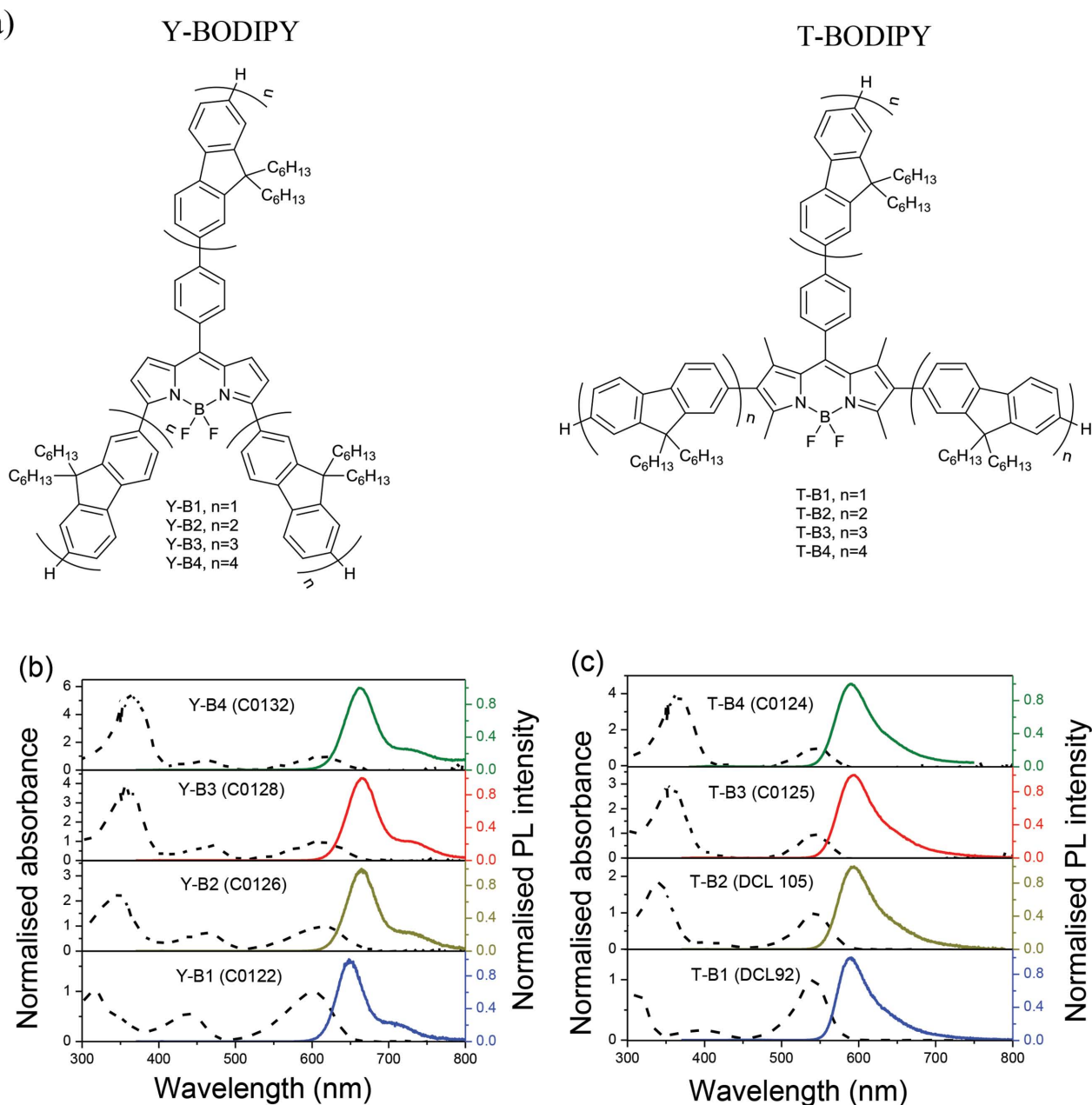University of Oxford
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Figure 1. a) Molecular structure of T- and Y-BODIPY materials. b) Absorption and emission spectra of Y-BODIPY materials. c) Absorption and emission spectra of T-BODIPY materials. For each compound, the PL spectra were obtained at an excitation wavelength of 360 nm.

The photophysical properties of organic semiconductors strongly depend on their molecular structure. We have previously shown that a star-shaped geometry based on a truxene core can effectively control the photophysics by changing arm lengths.[14,15] To optimize the photophysical properties of BODIPY as color converter in VLC, we synthesized two different oligofluorene-BODIPY families with different arrangements of oligofluorene arms attached to the BODIPY core. The reason for incorporating the BODIPY into a star structure is that a star enhances solution processability and controls intermolecular interactions.[14,15] The influence of core structure, arm position, and length on the photophysical properties of BODIPY core-based materials was

investigated by measuring absorption, PL, PLQY, and PL life-times in solution. As the star-shaped geometry controls intermolecular interactions,[14,15] the solid state photophysical properties are similar to those in solution. The absorption and PL spectra of all eight BODIPY (Y- and T-BODIPY) materials along with their molecular structures are given in **Figure 1**. We label the materials here by the shape of the molecules and number of fluorene units in each arm: the Y-BODIPY as Y-B1, Y-B2, Y-B3, Y-B4, and the T-BODIPY as T-B1, T-B2, T-B3, T-B4.

The absorption and PL spectra of all Y-BODIPYs have similar features, except for Y-B1 which is blue-shifted compared with the longer armed molecules. The absorption spectra of Y-BODIPYs

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have a peak around 600 nm ($S_0 \rightarrow S_1$ transition) and a peak around 450 nm ($S_0 \rightarrow S_2$ transition). In addition to these two peaks, there is a third peak below 400 nm due to the fluorene arms whose absorption increases with increasing arm lengths (Figure S1, Supporting Information).[15] This absorption study suggested that Y-BODIPYs are attractive materials for VLC due to their significant absorption at ≈450 nm, which matches well with the emission wavelength of commercially available high-power µLEDs. The fluorescence spectra of Y-BODIPYs show that the emission comes from the BODIPY core with a dominant emission peak around 650 nm due to the (0–0) transition and a shoulder around 715 nm due to the (0–1) transition.

Similar to Y-BODIPYs, the absorption spectra of T-B1 and T-B2 have three peaks. The peaks around 540 and 400 nm are due to strong $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the BODIPY core, and the peak around 320 nm is due to the oligofluorene arms, whose absorption increases with arm length in a similar way to Y-BODIPYs (Figure S2, Supporting Information). The methyl groups in the core of T-BODIPYs create a steric hindrance and decrease conjugation, which leads to hypsochromic shift of both $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions.[17] Unlike T-B1 and T-B2, where three absorption peaks are evident, the absorption spectra of T-B3 and T-B4 show only two peaks: one around 540 nm from the $S_0 \rightarrow S_1$ transition of BODIPY, and the other around 320 nm due to the oligofluorene. This is because the $S_0 \rightarrow S_2$ transition for the T-series molecules is blueshifted and overlaps with the $\pi \rightarrow \pi^*$ transition of the oligofluorene arms (especially in the case of T-B3 and T-B4) and has a transition dipole moment lower than that of Y-series (confirmed by TD-DFT calculations).[17] The PL spectra of all T-BODIPYs show a single dominant peak around 595 nm (0–0 transition of BODIPY). In contrast to Y-BODIPYs, no shift was observed in the PL spectra with increasing length of the fluorene arms. These steady-state measurements of BODIPY show that the photophysical properties including absorption and PL can be tuned by controlling the molecular shape and (in the case of Y-BODIPYs) lengths of the fluorene arms.
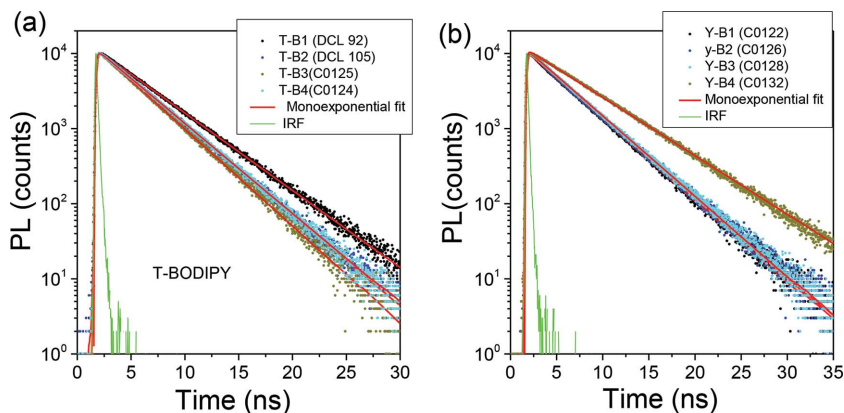

Figure 2. Photoluminescence decay of BODIPY materials at an excitation wavelength of 379 nm: a) T-BODIPY fitted with single exponential, b) Y-BODIPY fitted with single exponential. IRF is instrument response function of exciting source.

The solution-state PLQY of T- and Y-BODIPY materials recorded at an excitation wavelength of 360 nm is given in **Table 1**. All the materials are highly fluorescent with PLQYs ranging from 55% to 75%, making them suitable for light-emitting devices and for VLC. The PL lifetimes of these materials were measured at the PL emission peak for each material shown in Figures 1b,c. The PL transients (fitted with single exponential decay) for T- and Y-BODIPYs are shown in **Figure 2**a,b, respectively, and measured values of lifetimes are given in Table 1. Among all investigated BODIPYs, Y-B4 has the longest lifetime (5.2 ns), whereas T-BODIPYs with two to four fluorene arms have the shortest lifetimes (4.0 ns). We note that all the measured lifetimes for BODIPYs are much shorter than those of conventional phosphor color converters.[5] The radiative lifetime was calculated by taking the ratio of the measured lifetime and PLQY, i.e., ($\tau_r = \tau / $PLQY). The resulting values of radiative lifetimes are given in Table 1.

These photophysical studies show (see Figures 1 and 2) that the Y-BODIPYs are the more suitable candidates for trichromatic coloration for VLC because of their stronger absorption around ≈450 nm enabling them to be optically excited by nitride LEDs. In order to test the potential of the Y-B1, Y-B3 as a color converter material for VLC, we measured first their response to a small signal modulation of the excitation to determine their intrinsic modulation bandwidth. The experimental setup used for determination of the bandwidth is presented in the inset of **Figure 3**.

Initially, the system was calibrated to exclude the frequency response of the diode laser and avalanche photodiode (APD.) For this purpose, the frequency response $H_{LP\text{-}APD}(\omega)$ of the system was first measured by directly illuminating the APD with the diode laser. Next, the intrinsic frequency response of the materials $H_m(\omega)$ was determined by subtracting the $H_{LP\text{-}APD}(\omega)$ from frequency response of the whole system $H(\omega)$, i.e., $H_m(\omega) = H(\omega) - H_{LP\text{-}APD}(\omega)$. From Figure 3, it can be observed that both materials Y-B1 and Y-B3 show a similar response function with a –3 dB bandwidth of 38 and 39 MHz for Y-B1 and Y-B3, respectively.

After measuring the bandwidth of the materials, a data link was implemented. The laser diode was modulated using an On–Off Keying (OOK) data signal (where a zero bit is represented by the
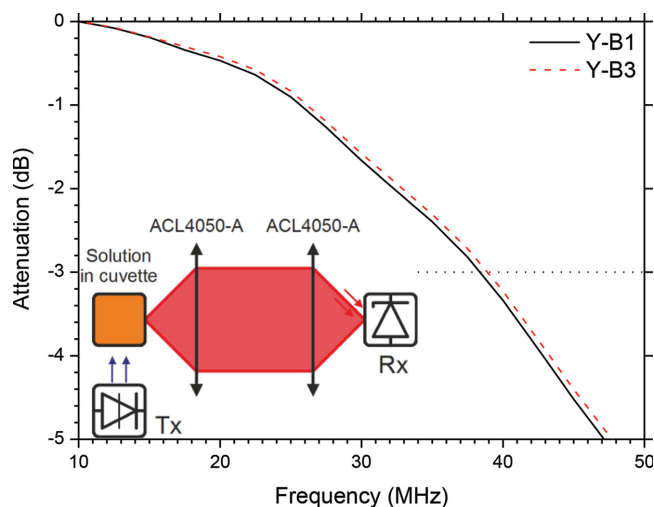
Table 1. The PLQY, measured lifetime, and radiative lifetime of Y- and T-BODIPY materials.

Material	PLQY [%]	Measured lifetime [ns]	Radiative lifetime [ns]
Y-B1 (C0122)	55.2	3.97	7.19
Y-B2 (C0126)	62.3	3.99	6.40
Y-B3 (C0128)	62.2	4.06	6.53
Y-B4 (C0132)	59.3	5.22	8.80
T-B1 (DCL92)	66.1	4.21	6.37
T-B2 (DCL 105)	69.8	3.57	5.11
T-B3 (C0125)	74.8	3.36	4.49
T-B4 (C0124)	65.7	3.62	5.51

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Figure 3. Plot of the attenuation of the small signal modulation for the materials Y-B1 and Y-B3. The dotted line corresponds to −3 dB attenuation which defines the bandwidth of the system. In the inset, there is a schematic of the experimental setup used in the measurement. The material under examination was excited with a diode laser at a wavelength of 450 nm and with power of 100 mW. The resulting PL of the material was collected with two lenses and focussed onto an APD. A network analyser was used to record the resultant bandwidth.

absence of a pulse, and a one bit is represented with an optical pulse).[3] These optical pulses are detected by the APD, and the resulting waveform displayed on an oscilloscope. **Figure 4b** shows eye diagrams for OOK at a data rate of 100 Mb s^{-1}. The eye diagram is an analysis tool in optical communications systems to visualize the quality of the optical channel and the open eye shows that in the color-converted links at 100 Mb s^{-1}, the difference between zero and one bits is clearly resolved.[16]

Figure 4a presents the bit error rate (BER) as a function of the data rate using OOK. For comparison, the corresponding BER measured for a commercial phosphor color converter CL-840 made by Intermatix ChromaLit is also plotted. We measured error-free communications at 100 Mb s^{-1} using a stream of 10^5 data bits for both Y-BODIPY materials (Y-B1 and Y-B3), and at 10 Mb s^{-1} for the phosphor plate. Although this length of data pattern is too short to prove error-free communication with a high degree of confidence, it is sufficient for comparison and to see the potential of the color converter. **Table 2** summarizes the results for bandwidth and data rate measurements. From Figure 4 and Table 2, one can easily observe the high capabilities of organic materials like Y-BODIPYs as alternative materials for additive coloration in VLC applications. Our materials increased bandwidths and data rates to ten times those of the commercial remote phosphor plate for pcLEDs.

In conclusion, we presented here oligofluorene-BODIPY chromophores as an alternative color conversion material for VLC. We measured the photophysical properties as well as frequency response including modulation bandwidth and data rate for two different families of oligofluorene-BODIPY materials with different substitution patterns of fluorene arms attached to the BODIPY core and found that all BODIPYs have much shorter lifetimes compared with commercially available phosphor-based materials. Furthermore, we show that
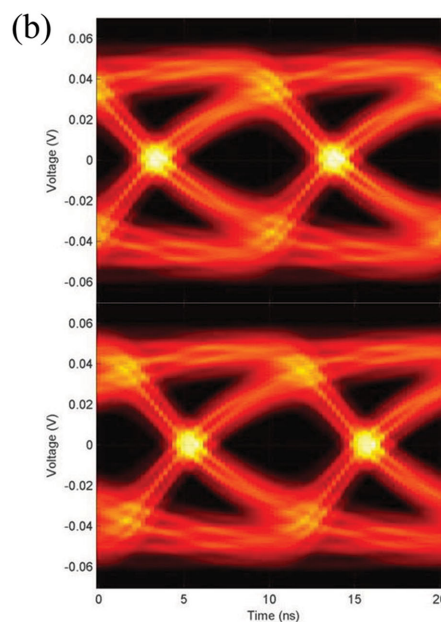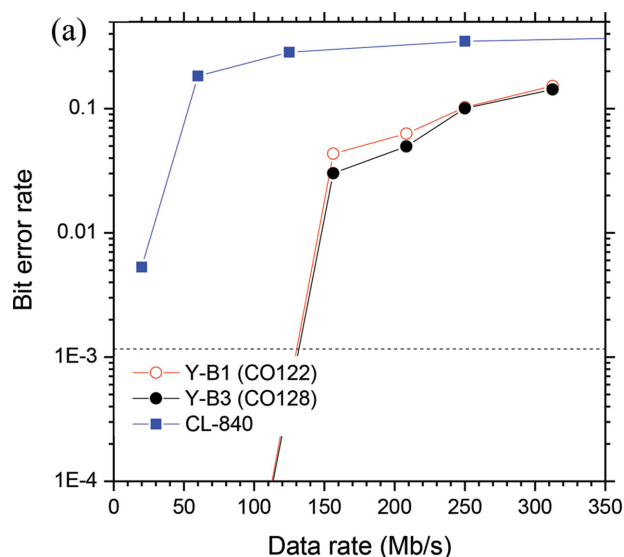

Figure 4. a) Bit error rate versus the data rate using on–off keying modulation. The dashed line corresponds to BER 1.2 × 10^{-3}, which corresponds to the error floor in VLC. b) The eye diagrams for the Y-B1 (top) and Y-B3 (bottom) materials at 100 Mb s^{-1} are shown.

Y-BODIPYs are the most attractive materials to replace slow commercially available phosphor-based LEDs for VLC due to an order of magnitude higher modulation bandwidth (≈39 MHz) and data rate (≈100 Mbits s^{-1}) achieved with this type of material than in current phosphors. Our results show that organic semiconductors are promising color converters for VLC.

Table 2. Bandwidths and measured data rates for different materials.

Material	CL-840	Y-B1	Y-B3
BW [MHz]	4.4	38	39
Data rate [Mb s^{-1}]	≈10	98	98

Experimental Section

Material Synthesis: The synthesis and characterization of Y-B1–4 and T-B1–4 will be reported elsewhere.[17]

Photophysical Characterization: The solution for this study was prepared by mixing the BODIPY derivative in toluene and keeping it overnight inside a glove box. A fused quartz cuvette (1 cm path length) was selected to hold the BODIPY solution for all spectroscopic measurements because of its purity and low absorption in the wavelength range of interest. A Varian Cary 300 UV–vis spectrophotometer was used to obtain linear absorption spectra of BODIPY samples in the wavelength range of 200–800 nm. Photoluminescence (PL) measurements were carried out using an Edinburgh Photonics Instrument FLS980. All PL spectra reported here were obtained at an excitation wavelength of 360 nm using a Xenon Lamp. Photoluminescence quantum yields (PLQY) were measured following a standard method[18] using quinine sulfate dihydrate (QSD) in 0.5 M sulfuric acid (refractive index of 1.35) as a reference solution, which has a PLQY of 0.546 at 360 nm excitation. The fluorescence lifetimes were measured using time-correlated single photon counting (TCSPC) with a time resolution of ≈200 ps. For these measurements, the sample was excited using a 379-nm ps laser and PL decays were measured using a microchannel plate photomultiplier tube (MCP PMT). All photophysical measurements were performed at room temperature.

Bandwidth and Data Rate Measurements: The experimental setup is sketched in the inset of Figure 3. To limit the influence of the excitation light source and the receiver, a diode laser and an avalanche photodiode (APD) with broad bandwidth were used. In addition, a refractive geometry was used to exclude the influence of the excitation light.

The excitation of the solutions in cuvettes was performed using a modulated diode LD450 from Roithner LaserTechnik GmbH. The modulation bias was a combination of a DC bias with AC bias through bias-T ZHL-6A from Mini-Circuits. A DC bias A LDC205C—Benchtop LD Current Controller from Thorlabs was used to provide a bias, and the AC modulation was controlled by the Agilent network analyzer 4395A using a ZHL-6A amplifier from mini-circuits. The optical systems were a combination of two ACL4050-A lenses from Thorlabs. Finally, the APD S8890 from Hamamatsu Photonics was used.

A standard technique was used to measure the small signal modulation bandwidth. In this approach, the laser was driven by a DC bias current with an addition of an AC voltage of small amplitude from the network analyser. The result was a modulated optical power output from the laser of the frequency of the AC source. The material was excited by this light and the resulting PL of the material was collected with a system of two lenses and concentrated onto an APD. The resulting electrical signal was recorded by the network analyser. The analyzer varies the AC excitation frequency, and the resulting PL intensity varies according to frequency, falling at higher frequencies due to the finite response (PL lifetime) of the material. This fall-off was recorded by the network analyzer and the frequency at which there was 3 dB reduction constituted the BW of the material.

Supporting Information

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

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