A saturated red color converter for visible light communication using a blend of star-shaped organic semiconductors

M. T. Sajjad,[1] P. P. Manousiadis,[1] C. Orofino,[2] A. L. Kanibolotsky,[2,3] N. J. Findlay,[2] S. Rajbhandari,[4] D. A. Vithanage,[1] H. Chun,[4] G. E. Faulkner,[4] D. C. O'Brien,[4] P. J. Skabara,[2,a)] G. A. Turnbull,[1,b)] and I. D. W. Samuel[1,c)]

[1]*Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews KY16 9SS, United Kingdom*
[2]*WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, United Kingdom*
[3]*Institute of Physical-Organic Chemistry and Coal Chemistry, 02160 Kyiv, Ukraine*
[4]*Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, United Kingdom*

We report a study of blends of semiconducting polymers as saturated red color converters to replace commercial phosphors in hybrid Light emitting diodes (LEDs) for visible light communication (VLC). By blending two star-shaped organic semiconductor molecules, we found a near complete energy transfer (>90% efficiency) from the green-emitting truxene-cored compound T4BT-B to the red-emitting boron dipyrromethene (BODIPY) cored materials. Furthermore, we have demonstrated the capability of these materials as fast color converters for VLC by measuring their intrinsic optical modulation bandwidth and data rate. The measured 3 dB modulation bandwidth of blends ($\sim$55 MHz) is more than 10 times higher than commercially available LED phosphors and also higher than the red-emitting BODIPY color converter alone in solution. The data rate achieved with this blend is 20 times higher than measured with a commercially available phosphor based color converter. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4971823]

Visible Light Communication (VLC) is an emerging field which aims to implement fast and safe wireless communication to replace/complement existing broadband radio frequency (RF)/microwave wireless technologies.[1] VLC has many potential advantages over existing RF communication such as the potential for room-scale cellular networks with no electromagnetic interference (EMI), the availability of unlicensed bandwidth (BW), and the potential for very high data rates. Furthermore, in VLC, solid-state LED lighting can be used for both illumination and wireless data communication.[1–5] Commercially available white LEDs usually comprise blue LEDs with a yellow phosphor coating that converts a fraction of the blue light to longer wavelengths to give a two-color white light. However, the use of phosphors for additive coloration in white LEDs imposes limitations for VLC due to the long luminescence lifetime of the phosphors.[3] The excited state lifetimes of the phosphor used in white LEDs is typically 0.6 μs, which restricts the modulation bandwidth (BW) to a few MHz.[6] There is therefore a strong need for alternative color converter materials, which combine high illumination efficiency with shorter natural radiative lifetime to permit ultra-high modulation bandwidth.

Organic semiconductors are strong candidates as color converters for VLC due to their visible band gaps, their tuneable optical properties, short radiative lifetime, high photoluminescence quantum yield (PLQY), and their scope for integration with nitride semiconductors.[7–13] In our recent publications, we demonstrated the use of conjugated polymers as high bandwidth materials for additive coloration for white VLC.[7–9] However, to achieve higher quality white light with wider color rendering, a saturated red color converter with short radiative lifetime is needed. Most red-emitting organic materials have low absorption at 450 nm (the emission wavelength of commercially available Gallium Nitride (GaN) LEDs). Therefore, an absorption sensitizer (molecular antenna) is required to efficiently convert the blue emission of a high performance GaN LED to longer wavelength to match the absorption wavelength of red-emitting materials without affecting their fast modulation characteristics. We demonstrate that this is possible through an efficient photoinduced energy transfer process between solution processed star-shaped organic molecules. Unlike conjugated polymers whose blends often give only partial energy transfer due to phase separation,[9] the star-shaped molecules can achieve near complete energy transfer to generate a saturated red emission.

To achieve this efficient color conversion, we blended the highly fluorescent green-emitting truxene star-shaped compound T4BT-B[14] (Fig. 1(a)) with a red-emitting boron dipyrromethene (BODIPY) chromophore[8,15,16] and investigated their capabilities for VLC. A different substitution pattern of oligofluorene arms on the BODIPY core makes the corresponding star-shaped structure either T-shaped or Y-shaped (Fig. 1(a)). We performed steady-state and time-resolved measurements, which allow us to quantitatively determine efficiencies of the photoinduced energy transfer from T4BT-B to T-B3 and Y-B3. A near complete energy transfer (>90% efficiency) from T4BT-B to Y-B3 was found. Finally, we demonstrated the capabilities of these materials for VLC by measuring modulation bandwidth and

a)peter.skabara@strath.ac.uk
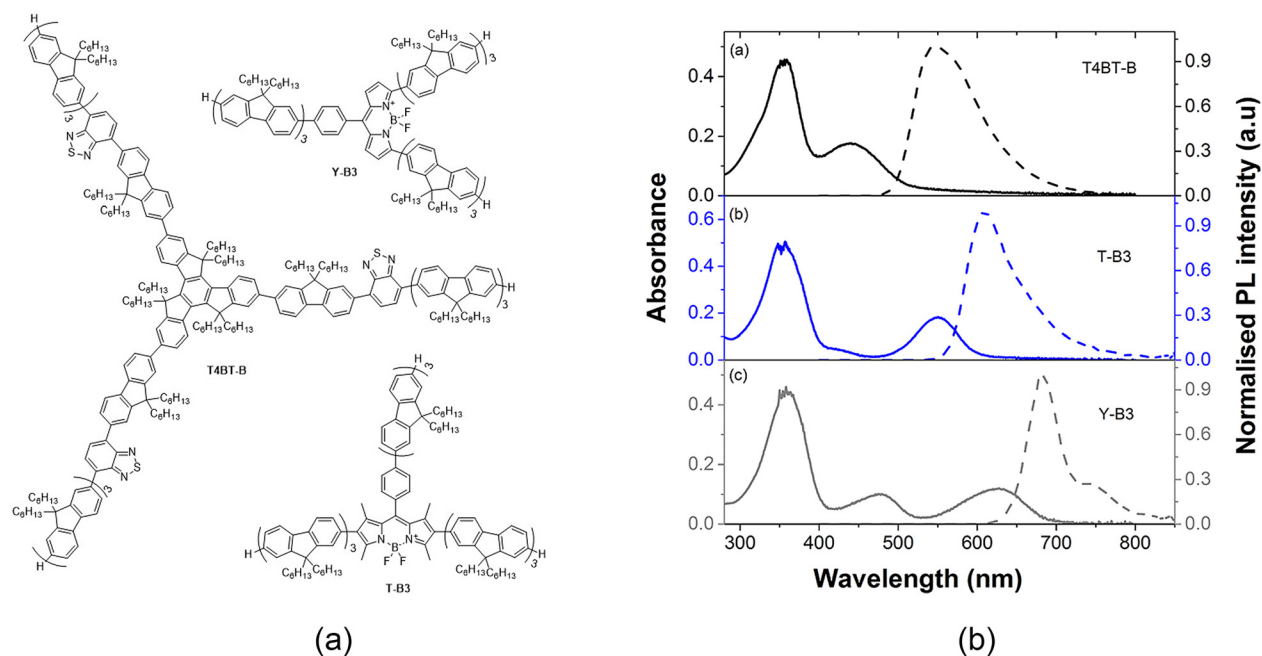b)gat@st-andrews.ac.uk
c)idws@st-andrews.ac.uk

FIG. 1. (a) Molecular structure of T4BT-B, Y-B3, and T-B3. (b) Absorption and photoluminescence (PL) spectra of neat thin films of the above materials. PL spectra that are shown as dashed lines were measured following excitation at 355 nm.

data transmission rates. The measured 3 dB modulation bandwidth of blends (~55 MHz) and data rate (>200 Mbits/s) are significantly higher than the commercially available phosphor LED and previously reported red-emitting color converters in solution.[8]

Solutions of neat T-B3 and Y-B3 were prepared by mixing 10 mg of each chromophore in 1 ml of toluene; solutions of neat T4BT-B and blends of T4BT-B and BODIPY were prepared by mixing 15 mg total mass of chromophore in 1 ml of chlorobenzene. Thin film preparation, photophysical characterization, and bandwidth and data rate measurements were performed following a similar experimental procedure to that reported previously.[9] For photoluminescence (PL) lifetime, a 379 nm PicoQuant picosecond pulsed laser was used and PL decays were measured using time correlated single photon counting (TCSPC) at the emission peak wavelengths of 550, 610, and 682 nm for T4BT-B, T-B3, and Y-B3, respectively.

Thin films were characterized by measuring absorption, photoluminescence (PL), photoluminescence quantum yield (PLQY), and PL lifetimes. The absorption and PL spectra of neat T4BT-B, T-B3, and Y-B3 are shown in Fig. 1. The absorption and PL spectra of the BODIPY compounds show

similar features to those previously reported in solution[8] except they are red-shifted. The PLQY (given in Table I) of neat films is lower than solution and for T-B3 and Y-B3 lower than desired for VLC. The absorption spectra show that T-B3 has weak absorption around 450 nm. This low absorption means that it is not suitable by itself as an LED color converter for VLC. To address this limitation, we blended the BODIPY stars with T4BT-B to act as an absorption sensitizer. The absorption, PL, and PL lifetimes of T4BT-B in films are shown in Figs. 1 and 3. The absorption spectra have two peaks at 355 and 430 nm, while the PL spectra obtained at an excitation wavelength of 355 nm have a single dominant peak around 550 nm (see Fig. 1(b)). The excited state lifetime of ~3 ns was obtained by fitting the experimental data of film with mono-exponential decay, and a film PLQY of more than 80% was measured. These attributes make T4BT-B a suitable material to be used in blends with the BODIPY derivatives.

We next blended T4BT-B with T-B3 and Y-B3 to investigate the energy transfer from T4BT-B to the BODIPY stars. For this study, the blends were assessed in T4BT-B/BODIPY ratios of 50/50 and 94/6. The resultant absorption and PL spectra of the blends are shown in Fig. 2. The relative enhancement

TABLE I. Summary of PLQY, energy transfer efficiency (η_{et}), and CIE coordinates of thin films of all materials investigated.

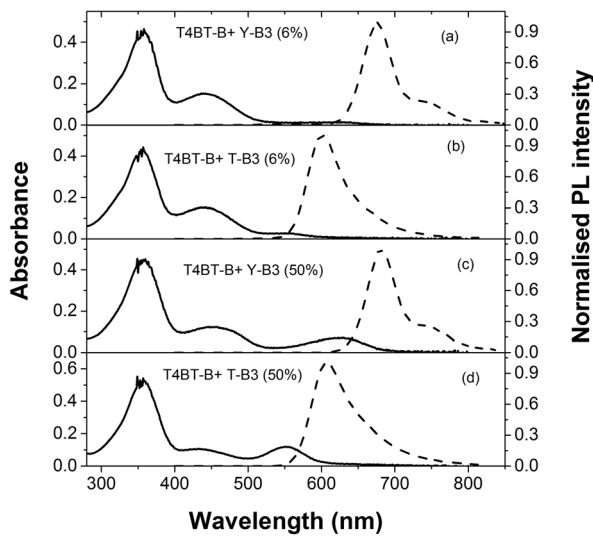| Polymer	PLQY (%) at $\lambda_{ex} = 358$ nm		PLQY (%) at $\lambda_{ex} = 450$ nm		η_{et} (%)	CIE coordinates
	Overall	>600 nm	Overall	>600 nm		
T4BT-B	95.3	28.6	84.9	25.2	…	0.42, 0.57
T-B3	45.2	41.2	47.4	44.9		0.63, 0.37
Y-B3	47.8	47.7	40.6	40.6		0.71, 0.27
T4BT-B + T-B3 (50:50)	69.6	60.7	60.5	53.6	56	0.63, 0.37
T4BT-B + Y-B3 (50:50)	60.9	60.8	54.9	54.9	87	0.72, 0.27
T4BT-B + T-B3 (94:6)	92.3	69.1	82.6	61.6	70	0.61, 0.39
T4BT-B + Y-B3 (94:6)	86.8	86.1	76.9	76.3	91	0.68, 0.31

FIG. 2. Absorption and PL spectra of films of T4BT-B blended with different ratios of T-B3 and Y-B3. For each case, the PL spectra were obtained at an excitation wavelength of 355 nm.

of PL intensity of BODIPY stars and quenching of PL of T4BT-B (see Fig. 2) clearly indicates an energy transfer from host T4BT-B to the BODIPY guests. PL spectra of the blends show that almost all energy has been transferred from T4BT-B to BODIPY stars and that the T4BT-B acts as an effective sensitizer. The measured values of PLQY (Table I) show that there is a more efficient energy transfer from T4BT-B to Y-B3 than to T-B3. Furthermore, the PLQYs of blends are increased compared to the neat BODIPY stars, which makes these blends highly suitable to be used for light emitting devices and visible light communication. We also calculated the Comission Internationale de l'Eclairage (CIE) coordinates of blends and the values are given in Table I.

Further insight into the energy transfer process is obtained by measuring the time-resolved PL. The PL decays of neat films and blends measured at the emission peaks of T4BT-B, T-B3, and Y-B3 are given in Fig. 3. In the case of T4BT-B, the observed fast decay in the blends compared to the neat films indicates potential energy transfer from T4BT-B to the BODIPY stars (Fig. 3(a)). The PL decay of T4BT-B in the blend with Y-B3 is much faster compared to its blend with T-B3. This confirms that Y-B3 is a better material as guest for energy transfer. On the other hand, the PL decay of T-B3 and Y-B3 does not change significantly (Figs. 3(b) and 3(c)). This shows that blending of T-B3 and Y-B3 with T4BT-B has little effect on their PL decays. In order to obtain quantitative information about energy transfer from T4BT-B to BODIPYs, we next calculated the ET efficiency. This can be calculated from either PL quenching of the donor (T4BT-B) or PL enhancement of the acceptor (BODIPY).[17,18] However, this approach cannot be used here due to the emission overlap of T4BT-B and the BODIPYs. Therefore, we used an alternative approach by integrating the entire decay of neat T4BT-B and T4BT-B with the BODIPY guests present. We then used the difference to calculate energy transfer efficiency η_{ET} as follows[19]

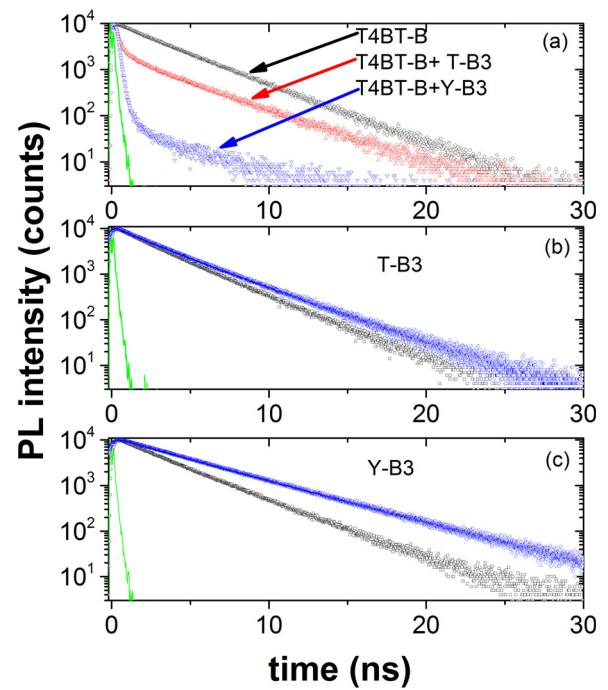$$\eta_{ET} = 1 - \frac{\int I_{T4BT-B\,with\,BODIPYs}\,dt}{\int I_{T4BT-B}\,dt}, \qquad (1)$$

FIG. 3. Photoluminescence decay of neat T4BT-B and blends at an excitation wavelength of 379 nm. (a) PL decay of neat T4BT-B (black dots) and T4BT-B (94%) in blend with T-B3 (red dots) and Y-B3 (blue dots). The PL was measured at a detection wavelength of 550 nm. (b) PL decay of neat T-B3 (black dots) and T-B3 (6%) in blend with T4BT-B (blue dots). The PL was measured at a detection wavelength of 610 nm. (c) PL decay of neat Y-B3 (black dots) and Y-B3 (6%) in blend with T4BT-B (blue dots). The PL was measured at a detection wavelength of 682 nm.

where $I_{T4BT-B\ with\ BODIPYs}$ and I_{T4BT-B} are PL decays of T4BT-B with BODIPYs (i.e., T-B3 or Y-B3) and neat T4BT-B. An ET efficiency of more than 90% is obtained for the Y-B3 guest and more than 70% is obtained for T-B3 using this approach. The calculated energy transfer efficiencies for all blends are given in Table I.

To test the capabilities of these color converter blends for VLC, we measured their intrinsic modulation bandwidth and data rate following a similar procedure to that reported previously.[8,9] Fig. 4(a) presents the bandwidth measurements for the two films made from 94% T4BT-B and 6% of each BODIPY compound. For comparison, the results for a commercial phosphor plate (CL-840) used in white LEDs (pcLEDs) are also plotted. The higher bandwidth achieved (~55 MHz) with the blend of T-B3 compared to Y-B3 (~40 MHz) is due to the shorter radiative lifetime (~6.7 ns) of T-B3 compared to Y-B3 (~11 ns). The modulation bandwidth achieved with a blend of T4BT-B and T-B3 is comparable to the bandwidth of the blue GaN microLED used for the 3 Gbps VLC system.[20]

A free space data link was next implemented using a simple On-Off Keying (OOK) modulation scheme. At different data rates, the resulting bit error rates were recorded and are presented in Fig. 4(b). Using a stream of 10^5 data bits, the data rate recorded for these blends was more than 200 Mbits/s (~207 Mbits/s for Y-B3 and ~218 Mbits/s for T-B3) which are twice that achieved with the previously reported oligofluorene-BODIPY in solution[8] and more than 20 times higher than the commercially available phosphor plate used in comparative measurements.
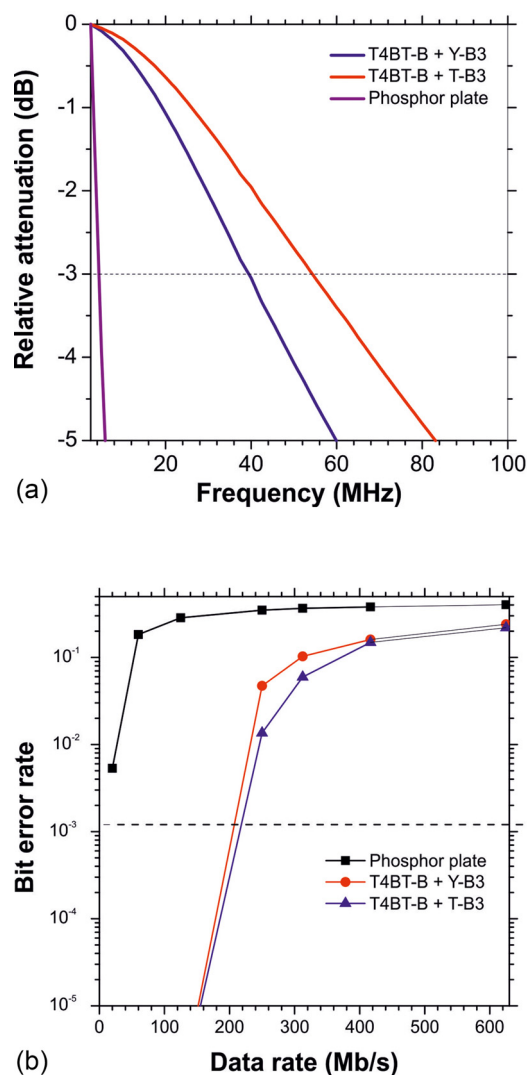
FIG. 4. (a) Modulation Bandwidth and (b) Data rate of blend of 94% T4BT-B with either 6% of Y-B3 or 6% of T-B3. For a comparison, results of a commercial phosphor plate (CL-840) are also plotted.

In conclusion, the use of the BODIPY stars as saturated red materials for additive coloration for VLC is explored. We found efficient photoinduced energy transfer (>90% efficiency) from T4BT-B to Y-B3, which makes it an attractive candidate to be used for red color conversion. Furthermore, we demonstrated the capabilities of these materials for VLC by measuring modulation bandwidth and data rate using an OOK modulation scheme. The measured 3 dB modulation bandwidth of T4BT/T-B3 blends (∼55 MHz) was more than 10 times higher, and the achieved data rate with this blend was 20 times higher than that measured with the commercially available phosphor based color converter.

[1]H. Elgala, R. Mesleh, and H. Haas, IEEE Commun. Mag. **49**, 56 (2011).
[2]T. Komine and M. Nakagawa, IEEE Trans. Consum. Electron. Mag. **50**, 100 (2004).
[3]D. O'Brien, L. Zeng, H. Le-Minh, G. Faulkner, J. W. Walewski, and S. Randel, paper presented at the IEEE 19th International Symposium on Personal, Indoor and Mobile Radio Communications (PIMRC 2008), Cannes, French Riviera, France, September (2008).
[4]Z. Ghassemlooy, W. Popoola, and S. Rajbhandari, *Optical Wireless Communications: System and Channel Modeling with MATLAB* (CRC Press, 2012).
[5]R. Kraemer and M. Katz, *Short-Range Wireless Communications: Emerging Technologies and Applications* (John Wiley & Sons, 2009).
[6]C.-H. Yeh, Y.-L. Liu, and C.-W. Chow, Opt. Express **21**, 26192 (2013).
[7]H. Chun, P. P. Manousiadis, S. Rajbhandari, D. A. Vithanage, G. Faulkner, D. Tsonev, J. J. D. McKendry, S. Videv, E. Xie, E. Gu, M. D. Dawson, H. Haas, G. A. Turnbull, I. D. W. Samuel, and D. C. O'Brien, IEEE Photonics Technol. Lett. **26**, 2035 (2014).
[8]M. T. Sajjad, P. P. Manousiadis, C. Orofino, D. Cortizo-Lacalle, A. L. Kanibolotsky, S. Rajbhandari, D. Amarasinghe, H. Chun, G. Faulkner, D. C. O'Brien, P. J. Skabara, G. A. Turnbull, and I. D. W. Samuel, Adv. Opt. Mater. **3**, 536 (2015).
[9]M. T. Sajjad, P. P. Manousiadis, H. Chun, D. A. Vithanage, S. Rajbhandari, A. L. Kanibolotsky, G. Faulkner, D. C. O'Brien, P. J. Skabara, I. D. W. Samuel, and G. A. Turnbull, ACS Photonics **2**, 194 (2015).
[10]F. Hide, P. Kozodoy, S. P. DenBaars, and A. J. Heeger, Appl. Phys. Lett. **70**, 2664 (1997).
[11]N. J. Findlay, J. Bruckbauer, A. R. Inigo, B. Breig, S. Arumugam, D. J. Wallis, R. W. Martin, and P. J. Skabara, Adv. Mater. **26**, 7415 (2014).
[12]G. M. Farinola and R. Ragni, Chem. Soc. Rev. **40**, 3467 (2011).
[13]D. Di Martino, L. Beverina, M. Sassi, S. Brovelli, R. Tubino, and F. Meinardi, Sci. Rep. **4**, 4400 (2014).
[14]C. R. Belton, A. L. Kanibolotsky, J. Kirkpatrick, C. Orofino, S. E. T. Elmasly, P. N. Stavrinou, P. J. Skabara, and D. D. C. Bradley, Adv. Funct. Mater. **23**, 2792 (2013).
[15]C. Orofino-Pena, D. Cortizo-Lacalle, J. Cameron, M. T. Sajjad, P. P. Manousiadis, N. J. Findlay, A. L. Kanibolotsky, D. Amarasinghe, P. J. Skabara, T. Tuttle, G. A. Turnbull, and I. D. W. Samuel, Beilstein J. Org. Chem. **10**, 2704 (2014).
[16]D. A. Vithanage, P. P. Manousiadis, M. T. Sajjad, S. Rajbhandari, H. Chun, C. Orofino, D. Cortizo-Lacalle, A. L. Kanibolotsky, G. Faulkner, N. Findlay, D. C. O'Brien, P. J. Skabara, I. D. W. Samuel, and G. A. Turnbull, Appl. Phys. Lett. **109**, 013302 (2016).
[17]A. A. Lutich, G. Jiang, A. S. Susha, A. L. Rogach, F. D. Stefani, and J. Feldmann, Nano Lett. **9**, 2636 (2009).
[18]B. Valeur and M. Nuno Berberan-Santos, *Molecular Fluorescence: Principles and Applications* (John Wiley & Sons, 2012).
[19]J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Springer Science & Business Media, 2007).
[20]R. X. G. Ferreira, E. Xie, J. J. D. McKendry, S. Rajbhandari, H. Chun, G. Faulkner, S. Watson, A. E. Kelly, E. Gu, R. V. Penty, I. H. White, D. C. O'Brien, and M. D. Dawson, IEEE Photonics Technol. Lett. **28**, 2023 (2016).