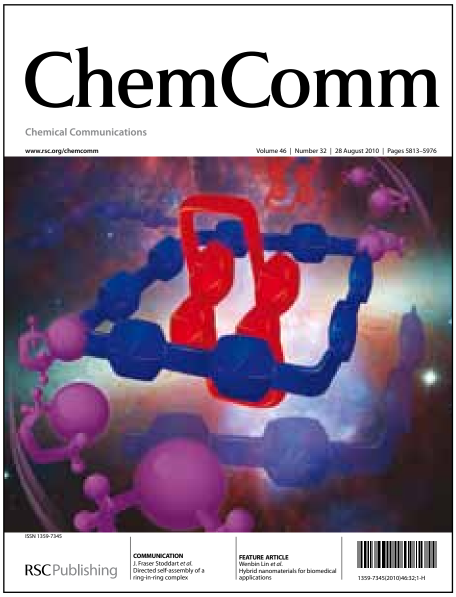
View Article Online / Journal Homepage

ChemComm

Downloaded by Universite de Sherbrooke on 03 December 2012
Published on 26 November 2012 on http://pubs.rsc.org | doi:10.1039/C2CC37381E

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/chemcomm
Registered Charity Number 207890

Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Optical Waveguide from 4-Aryl-4*H*-1,2,4-triazole-based Supramolecular Structures

David Cáceres [a], Cristina Cebrián [a], Antonio M. Rodríguez [a], José R. Carrillo [a], Ángel Díaz-Ortiz [a], Pilar Prieto [a]*, Fátima Aparicio,[b] Fátima García,[b] Luis Sánchez[b]*

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

The ribbon-like supramolecular structures prepared by the organized aggregation of 4-aryl-4*H*-1,2,4-triazoles act as optical waveguides that propagate photoluminiscence.

The self-assembly of π-conjugated systems provides valuable, organized supramolecular structures that can exhibit enhanced optical and/or electronic properties in comparison to the isolated molecules.[1] The chemical structure of the molecular building blocks and the processing conditions strongly affect the morphology of the aggregates. Thus, the aggregation of conjugated molecules in an ample variety of morphologies like spherical or cilindrical micelles,[2] helical tubes,[3] or flat lamellae[4] has been reported. Among these morphologies, 1D micro- and nanostructures have been applied as the active layer of thin devices like logic gates,[5] photodetectors,[6] and chemical sensors.[7] A challenging application of organized 1D supramolecular structures consists in optical waveguiding, that is, in efficiently propagating and handling the incident light on these structures, a process that plays a pivotal role in the implementation of photonic devices.[8]

Unlike many optical waveguides developed from inorganic materials,[9] those based on organic compounds are still scarce despite their high luminescence efficiency and facile processability. Some significant examples of organic-based optical waveguides have been reported for the supramolecular structures formed upon the self-assembly of 9,10-bis(phenylethynyl)anthracene,[10a] 2,4,5-triphenylimidazole,[10b] or 1,4-bis(1,2’:6’,1’’-bis(3-butyl-1*H*-3,4,5-triazolyl)pyridin-4’-yl)-benzene.[10c] A common feature of these two latter examples of organic waveguides is the presence of heteroaromatic rings with nitrogen atoms which exert a strong influence on the formation of supramolecular structures.

Herein, we report on the synthesis of two 4-aryl-4*H*-1,2,4-triazoles (compounds **1** and **2** in Figure 1) and their self-assembly into ribbon-like aggregates. These as-prepared aggregates exhibit waveguiding properties propagating the incident light along the length of the supramolecular structures. The unnatural 4-aryl-4*H*-1,2,4-triazole moiety has been selected as molecular building block to prepare the optical waveguides because of the easy and environmentally friendly synthetic protocol utilized[11] and, more importantly, because of its optical, electronic and geometrical chracteristics.[12]

The synthesis of the 4-aryl-4*H*-1,2,4-triazoles **1** and **2** has been straightforwardly performed from previously reported 1,2,3-tris(dodecyloxy)-5-(2-iodoethynyl)benzene[13a] and 4-aryl-4*H*-1,2,4-triazole[13b] by a direct arylation reaction catalyzed by copper[14] in 62% and 68% yield, respectively (Scheme S1 in Supporting Information).

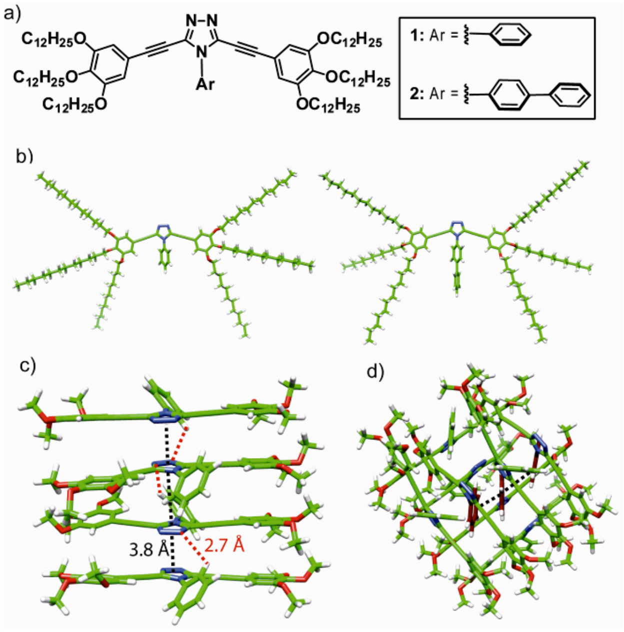


Fig. 1 (a) Chemical structure of the 4-aryl-4*H*-1,2,4-triazoles **1** and **2**. (b) Calculated geometries for the monomeric units **1** and **2**. (c) Columnar arrangement calculated for a tetramer of triazole **1** (side view; the H-bonds and the π-π aromatic interactions are depicted as red and black dotted lines, respectively). (d) Intercolumnar interaction in compound **1** (the π-π aromatic interactions between the aryl groups attached to the N at position 4 are depicted as dotted lines).

The self-assembly of triazoles **1** and **2** has been firstly studied by concentration dependent ^{1}H NMR experiments in deuterated chloroform as solvent. The ^{1}H NMR spectra for both triazoles **1** and **2** show negligible changes in all the aromatic and aliphatic resonances. These findings suggest the lack of remarkable supramolecular interactions in these experimental conditions (Figures S1 and S2). Unfortunately, both compounds **1** and **2** are insoluble in more polar solvents like acetonitrile —which would favor the aggregation of these heterocycles by a solvophobic effect[15]— that impedes performing these ^{1}H NMR studies. However, heating up a dispersion of triazoles **1** or **2** in acetonitrile gives rise to a white precipitate diagnostic of the formation of aggregates. The absorption and photoluminescence (PL) spectra of compounds **1** and **2** are collected in Figures 2 and S3, respectively. Both triazoles show an absorption band at 328 nm, ascribable to a $\pi \rightarrow \pi^*$ transition, and a narrow featureless peak in the PL spectra at 503 and 519 nm for **1** and **2**, respectively. The white precipitate formed by **1** or **2** in acetonitrile displays a higher-energy symmetric emission peak at 414 nm in compound **1** and 432 nm in compound **2**. The hypsochromic shift in the PL maximum for these compounds is indicative of an efficient self-assembly phenomenon.[16]

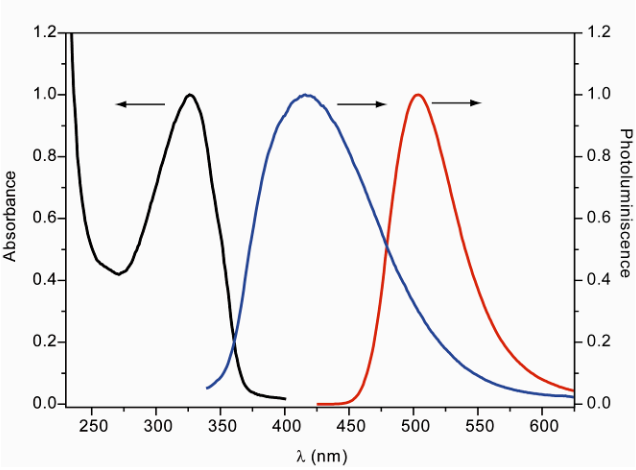


Fig. 2 Normalized UV-Vis and PL spectra of the triazoles **1** in solution (298 K, $CHCl_3$, 1 x 10^{-4} M) (black and red lines, respectively) and PL the aggregates formed by **1** in acetonitrile (blue line).

Organized supramolecular structures of triazoles **1** and **2** have been obtained by utilizing a slow diffusion technique. Thus, a diluted solution of (~1 x 10^{-4} M) of **1** or **2** in a good solvent like $CHCl_3$ was gently placed on a vessel containing acetonitrile that acts as bad solvent. After several days of slow diffusion, a white precipitate appears in the vial. SEM images of the precipitates obtained from compounds **1** and **2** show ribbon-like structures aggregated around a nucleation centre (Figure 3). The presence of the larger biphenyl unit in triazole **2** exerts a significant role in the thickness of the ribbons obtained from this compound. The aggregates formed by the self-assembly of **1** appear as thin and flexible ribbons with a uniform width of several micrometers and tens of micrometers length (Figure 3a and S4). In contrast, the self-assembly of **2** in these conditions gives rise to thicker ribbons with well-defined edges with typical thickness of ~ 1 µm and ~ 100 µm length (Figures 3b, S4 and S5). The thickness of the observed ribbons clearly suggests the aggregation of compounds **1** and **2** into stratified sheets stacked together by the operation of non-covalent forces, mainly π-π stacking between the aromatic units and the interdigitation of the peripheric alkyl chains.

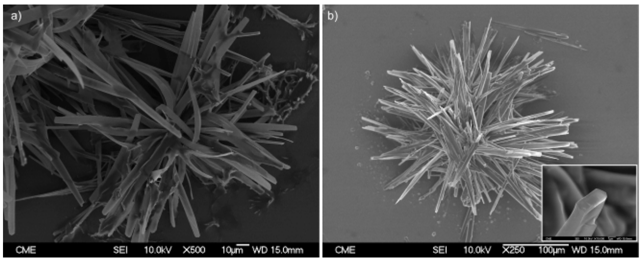


Fig. 3 SEM images (298 K, 1 x 10^{-4} M, glass substrate) of the ribbons formed by the self-assembly of **1** (a) and **2** (b).

The geometry of triazoles **1** and **2** together with a model of the aggregation of compound **1** have been elaborated by using computational calculations at the B3LYP/6-31G* and MPWB1K/6-31G** level. Both structures display a planar, π-conjugated core that comprises the triazole ring as well as the phenylethynyl fragments with the peripheral paraffinic chains as the flexible part of the molecule. The aryl substituent at the position 4 of the triazole remains out of the molecular plane, being the phenyl ring rotated 55.21° in compound **1** and the biphenyl unit 54.67° in **2** (Figure 1b and S6). The planar geometry of the 3,5-bis(2-(3,4,5-tris(alkyloxy)phenyl)ethynyl)-1,2,4-triazole units favors their intermolecular interaction by the operation of π-stacking. Thus, compounds **1** and **2** self-assemble into columnar stacks in which the adjacent molecules are separated by 3.8 Å (Figures 1c and 1d). The molecular electrostatic potentials calculated for **1** and **2** reveal a strong electronic density located at the nitrogen atoms of the triazole ring at positions 1 and 2 (Figure S7). To avoid the electrostatic repulsion between these electron-rich fragments of the molecule upon self-assembly, the adjacent molecules constitutive of the columnar aggregates are rotated 150 ° (Figure 1c). Importantly, the rotated aromatic ring on the nitrogen of position 4 of the triazole moieties plays a crucial role in the stabilization of the columnar aggregates. In very good agreement with previously reported X-ray diffraction data for referable 4-phenyl-4*H*-1,2,4-triazoles,[17] the aromatic C-H group at the *ortho* position of one molecule is able to form weak H-bonding arrays with the sp^2 nitrogen atoms of the heterocycle of the adjacent molecules within the same stack (Figure 1d). The computed H-bond value is 2.7 Å. Furthermore, the offset face-to-face π-stacking on this aromatic unit between adjacent columnar stack reinforces the three-dimensional growth of the aggregates (Figure 1d). The π-stacking between the aromatic units on the nitrogen of position 4 of the triazole ring is more efficient in the case of the biphenyl units exhibited by compound **2** which results in thicker and more robust aggregates.

The optical waveguiding behaviour of the ribbons formed upon self-assembly of triazole derivatives **1** and **2** has been investigated by utilizing confocal optical microscopy coupled to a camera. The irradiation of the ribbon-like aggregates with a laser beam with UV, blue or green light shows the intense luminescent character of the supramolecular structures formed by triazoles **1** and **2** (Figures 4a and 4b). A closer inspection of the PL images shown in Figures 4a and 4b demonstrates that the ends and the edges of the ribbons emit light which could be indicative of the ability of these aggregates to absorb the light and propagate PL toward the ends, thus behaving as optical waveguiding. Considering that compounds **1** and **2** do not exhibit any absorbance at wavelengths of 488 nm (blue) and 543 nm (green), the appearance of molecular excitation due to the laser energy is avoided. Pointing the ribbon-like aggregates of **1** with a laser beam at 488 nm or 543 nm generates a strong emission in the irradiated area. In addition, a brilliant emission point is clearly observed in the extreme and edges of the aggregates due to the propagation of laser light (Figure 4c). The ability of triazole **2** to propagate the laser light is more efficient than that observed for **1** (Figure 4d). Thus, the laser irradiation of the thick filament generated upon self-assembly of triazole **2** provokes the longitudinal propagation of the light and highly brilliant spots are visible at the opposite extremes of the ribbons.

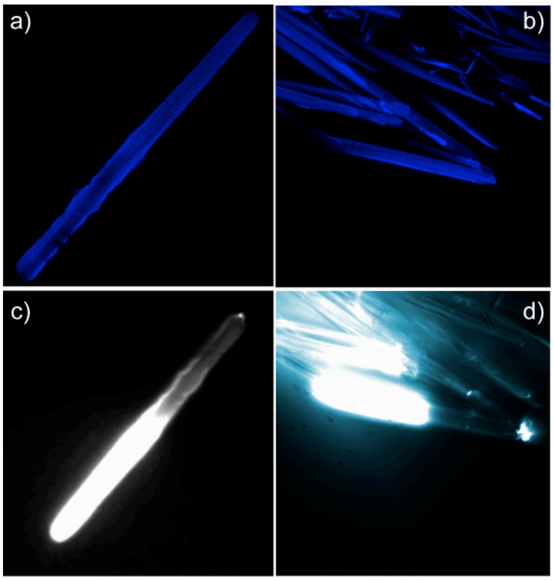


Fig. 4 PL microscopy images of the ribbon-like aggregates of triazoles **1** (a and c) and **2** (b and d).

The waveguiding behaviour of **1** and **2** can be reasonably justified by considering the separation between the emission and absorption bands mentioned above and diagnostic of the formation of H-aggregates.[16] This separation avoids the re-absorption of the emitted light by the aggregates. Furthermore, the thickness and the smooth surface of the aggregates strongly contribute to the efficient propagation of the light. It is well established that the presence of defects in the surface of the supramolecular structures produces light scattering due to internal reflections.[18]

In summary, the synthesis of two 4-aryl-4*H*-1,2,4-triazoles and their calculated geometries at B3LYP/6-31G* level are reported. These unnatural heterocycles are able to form supramolecular structures by the operation of π-π aromatic interactions and also weak H-bonding arrays, as predicted by the corresponding theoretical calculations at MPWB1K/6-31G** level. The as-prepared aggregates exhibit waveguiding properties that results in the propagation of the incident light along the length of the supramolecular structures, which can be ascribed to the large Stokes shift and smooth surfaces.

Financial support by UCM (GR42/10-962027), the MINECO of Spain (CTQ2011-22581 and CTQ2011-22410), and Consejería de Educación y Ciencia, JCCM through project PII2I09-0100 is acknowledged. F. A. and F. G. are indebted to MEC for a FPU studentship. The support from High Performance Computing Service of University of Castilla-La Mancha and the CAI of cytometry and microscopy of fluorescence at UCM are gratefully acknowledged.

Notes and references

[a] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real (Spain).Fax: (+) 34926295318.*
[b] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid (Spain).Fax: (+) 34913944103; E-mail: lusamar@quim.ucm.es*

† Electronic Supplementary Information (ESI) available: suplementary figures, S1-S12 and experimental section. See DOI: 10.1039/b000000x/

1 a) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev*., 2005, **105**, 1491; b) A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res*., 2007, **40**, 644; c) J. Wu, W. Pisula and K. Müllen, *Chem. Rev.,* 2007, **107**, 718; d) S. S. Babu, S. Prasanthkumar and A. Ajayaghosh, *Angew. Chem. Int. Ed*, 2012, **51**, 1766.

2 a) S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning and E. W. Meijer, *Angew. Chem. Int. Ed.,* 2004, **43**, 3422; b) A. Ajayaghosh, P. Chithra and R. Varghese, *Angew. Chem. Int. Ed.,* 2007, **46**, 230; c) S. Ghosh, X.-Q. Li, V. Stepanenko and F. Würthner, *Chem. Eur. J.,* 2008, **14**, 11343.

3 a) J. P. Hill, W. S. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science,* 2004, **304**, 1481; b) Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai and T. Aida, *Science,* 2006, **314**, 1761.

4 a) G. Fernández, F. García, F. Aparicio, E. Matesanz and L. Sánchez, *Chem. Comm.*, 2009, 7155; b) E. Lee, J.-K. Kim and M. Lee, *Angew. Chem. Int. Ed.*, 2009, **48**, 3657; c) J.-K. Kim, E. Lee, Y.-H. Jeong, J.-K. Lee, W.-C. Zin and M. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 6082.

5 J. Wang, M. S. Gudiksen, X. Duan, Y. Cui and C. M. Lieber, *Science,* 2001, **293**, 1455.

6 H. Kind, H. Yan, M. Law, B. Messer and P. Yang, *Adv. Mater.,* 2002, **14**, 158.

7 Z. L. Wang, *Adv. Mater*., 2003, **15**, 432.

8 a) P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He and H. J. Choi, *Adv. Funct. Mater.,* 2002, **12**, 323; b) M. Law, D. J. Sirbuly, J. C. Jonhson, J. Goldberger, R. G. Saykally and P. Yang, *Science,* 2004, **305**, 1269; c) A. B. Greytak, C. J. Barrelet, Y. Li, C. M. Lieber, *Appl. Phys. Lett.,* 2005, **87**, 151103; d) A. Pan, D. Liu, R. Liu, F.Wang, X. Zhu and B. Zou, *Small,* 2005, **1**, 980.

9 a) M. Law, D. J. Sirbuly, J. C. Johnson, J. Goldberger, R. J. Saykally, and P. Yang, *Science,* 2004, **305**, 1269; b) L. Tong, J. Lou, R. R. Gattass, S. He, X. Chen, L. Liu and E. Mazur, *Nano Lett.,* 2005, **5**, 259.

10 a) Y. S. Zhao, J. Xu, A. Peng, H. Fu, Y. Ma, L. Jiang and J. Yao, *Angew. Chem. Int. Ed.,* 2008, **47**, 7301; b) Y. S. Zhao, A. Peng, H. Fu, Y. Ma and J. Yao, *Adv. Mater.,* 2008, **9**, 1661; c) N. Chandrasekhar and R. Chandrasekar, *Angew. Chem. Int. Ed.,* 2012, **51**, 3556.

11 a) A. Díaz-Ortiz, P. Prieto, A. de Cózar, C. Cebrián, A. Moreno and A. de la Hoz, *Aus. J. Chem.,* 2009, **62**, 1600. b) C. Cebrian, A. de Cozar, P. Prieto, A. Diaz-Ortiz, A. de la Hoz, J. R. Carrillo, A. M. Rodriguez and F. Montilla, *Synlett,* 2010, 55.

12 M.-C. Hung, J.-L. Liao, S.-A. Chen, S.-H. Chen and A.-C. Su, *J. Am. Chem. Soc.*, 2005, **127**, 14577.

13 a) C.-Q. Ma, W. Pisula, C. Weber, X.-L, Feng, K. Müllen and P. Bäuerle. *Chem. Eur. J.,* 2011, **17,** 1507; b) R. K. Bartlett and I. R. Humphrey. *J. Chem. Soc. C,* 1967, 1664.

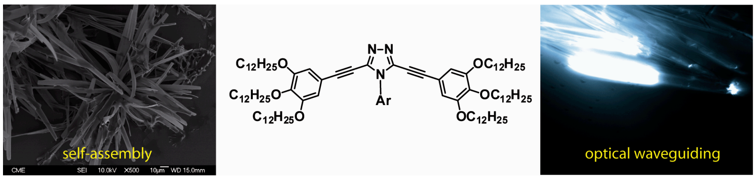
14 a) S. H. Kim and S. Chang. *Org. Lett.,* 2010, **12**, 1868; b) N. Matsuyama, K. Hirano, T. Satoh and M. Miura. *Org. Lett.,* 2009, **11**, 4156.

15 a) D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; b) J. C. Nelson, J. G. Saven, J. S. Moore and P. G. Wolynes, *Science,* 1997, **277**, 1793; c) F. García, F. Aparicio, G. Fernández and L. Sánchez, *Org. Lett.,* 2009, **11**, 2748; d) F. García and L. Sánchez, *Chem. Eur. J.,* 2010, **16**, 3138.

16 F. Würthner, T. E. Kaiser and C. R. Saha-Müller, *Angew. Chem. Int. Ed.,* 2011, **50**, 3376.

17 C. Liu, Z. Wang, H. Xiao, Y. Lan, X. Li, S. Wang, J. Tang and Z. Chen, *J. Chem. Chrystallogr.,* 2009, **39**, 881.

18 K. Takazawa, Y. Kitahama, Y. Kimura and G. Kido, *Nano Lett.,* 2005, **5**, 1293.



Optical Waveguide from 4-Phenyl-4*H*-1,2,4-triazole-based Supramolecular Structures

David Cáceres,[a] Cristina Cebrián,[a] Antonio M. Rodríguez,[a] José. R. Carrillo,[a] Ángel Díaz-Ortiz,[a] Pilar Prieto,[a]* Fátima Aparicio,[b] Fátima García,[b] Luis Sánchez[b]*

The ribbon-like supramolecular structures prepared by the organized aggregation of 4-aryl-4*H*-1,2,4-triazoles act as optical waveguides that propagate photoluminiscence.