Project no. 026365
Project acronym: POLYCOM
Project title: *Plastic optical fibers with embedded active polymers for data communications*

Instrument: STREP
Priority: [2] [Information society technologies]

Final
Activity Report

Date of preparation: July 3, 2009
Start date of project: May 1, 2006
Duration: 36 months

Project coordinator name: Prof. G. Lanzani
Project coordinator organization name: Politecnico di Milano

Revision: *draft*

Contents

1 Introduction

POLYCOM is an advanced research project with a large commitment to basic science and high risk targets. The main objective of the project is the development of **active organic photonic devices capable of all-optical ultrafast gain switching**. A further objective is the achievement of **pure knowledge**, related to the photophysical mechanism underlying the main application.

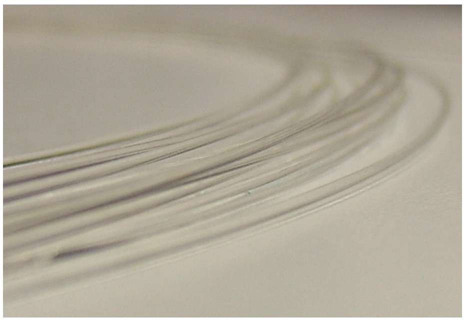

Figure 1: Plastic (or Polymer) Optical Fibers (POFs) are generally made of acrylic polymers such as poly(methylmethacrylate) and have transmission windows in the visible at 529, 570 and 650 nm. They are the main *passive* materials used in the POLYCOM project.

Many of today's photonic applications, from ICT to bio-medical, require low-cost, flexible, light-weight and robust solutions. Organic materials are ideal candidates to fulfill these needs, as they combine the mechanical and economical properties of plastics with a range of excellent photonic properties, such as large cross-sections, good optical transmission, broad spectral tuneability, and large and ultrafast non-linear responses. Plastic optical fibers (POFs, Figure 1), for example, have emerged as the best candidate for short-haul data communication applications in automotive or other local area networks. Active conjugated polymers, on the other hand (Figure 1), provide high gain over a broad visible spectral range, and can be used as active layers in a variety of plastic laser devices, in amplifiers and also for all-optical switching. All-optical switching is key for working towards optical computing or for time division multiplexing (TDM), a technology that is regaining attention for ICT applications. Within the POLYCOM project, due to improved material quality, better understanding of the photophysics and improved technology, several breakthroughs have occurred. These include ultrafast switching in polymer amplifiers, in conjugated-polymer doped POFs, and in DFB lasers and the realization of new devices such as ASE optofluidic chips. These advances pave the way for the up-take of polymer photonics in a wider context.

The POLYCOM project was based on the finding that *isolated* conjugated polymers can provide a new all-optical ultrafast switching mechanism, which derives from the one-dimensional dynamics of isolated chains [1]. (See also Box 1.) To exploit this finding and turn it into an easily integratable and usable photonic device, we used a multi-disciplinary strategy. We produced new materials, optimized and studied the blending process to achieve active polymer chain isolation (including the use of copolymerization), investigated, in detail, the photonic properties of these

Gain Switching Mechanism

The switching mechanism underpinning the POLYCOM project relies on two important characteristics of conjugated polymers and related materials.

1. **large stimulated emission cross-sections** (on the order of $10^{-16}\,\text{cm}^{-1}$) providing high gain co-efficients across a wide spectral range.

2. charge-transfer states absorb at the same wavelengths as the stimulated emission thus **quenching the gain**.

Control of generation and recombination of these charge-transfer states therefore allows total control of the gain.

The processes involved are shown in the figure below. Singlet excitons (S_1) (bound electron-hole pairs) are formed by absorption of light, process (1) in the figure below. These are capable of being stimulated to emit; producing gain, process (2). Charge-transfer states can be photo-generated through excitation to higher-lying singlet states (S_n), process (3) in the figure. Therefore, selectively exciting the polymer chains using a gating pulse can generate charge-transfer states on demand, **selectively quenching the stimulated emission**, process (4) in the figure. The recovery of the stimulated emission depends on the recombination time-scales of the charge-transfer states, (5) in the figure below.

The POLYCOM project aims to control these recombination time-scales through control of the conjugated polymer microstructure and chemical make-up, with the aim of making the recombination as fast as possible.

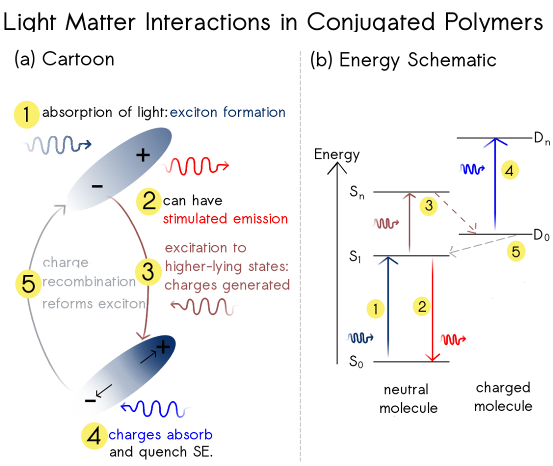

Figure: Schematic showing light-matter interactions in conjugated polymers. (a) Cartoon, (b) Energy Level Schematic demonstrating (1) absorption of light ($S_1 \leftarrow S_0$) and formation of exciton, (2) stimulated emission (SE), (3) re-excitation to S_n, to form charges (D_0) (4) absorption by the charges $D_n \leftarrow D_0$ (which overlaps spectrally with SE) and (5) recombination of the charges to form an exciton (S_1) and recovery of the stimulated emission.

Box 1: All-optical switching mechanism

Figure 2: Photograph of conjugated polymers in liquid, powder and thin film form. Conjugated polymers and oligomers are the main *active* materials used in the POLYCOM project.

doped systems and developed prototype fibres and device structures. This work has lead to several breakthroughs and produced quality publications and interest and discussion throughout research and industry.

2 Objectives

The main objectives of the project are:

1. the development of active organic photonic devices capable of all-optical ultrafast gain switching, and

2. the achievement of pure knowledge, related to the photophysical mechanism underlying the main application.

3 Contractors

The six contractors involved in the project have differing skills and are located across Europe. The co-ordinating group is at the **Politecnico di Milano** in Italy (email: guglielmo.lanzani@fisi.polimi.it) and they work mainly on the time-resolved spectroscopy aspect of the project, in particular characterizing the gain and switching spectral regions and time-constants in various materials and devices.

In order to produce homogeneous samples and POFs containing isolated conjugated polymers, a supramolecular approach is being attempted. This approach relies on producing co-polymers of the active material and PMMA. This is undertaken at the **Instituto Superior Tecnico** in Lisbon, Portugal. These materials, and others, are used to produce films and doped POFs. The doped POFs are produced using an adapted preform-drawing technique at **LUCEAT S.p.A.** (Italy). Examples of the some of the finished doped POFs are shown in Figure 3.

To determine the morphology and the excitonic properties of the materials in the POFs and films, work is done at the **University of Sheffield**, UK using techniques such as near-field scanning optical microscopy (SNOM), atomic force microscopy and single molecule spectroscopy. These are complemented by optical spectroscopy such as photoluminescence (PL), absorption, PL lifetime and PL quantum efficiency measurements.

Gain measurements and photochemical and photophysical stability measurements are performed at **Imperial College, London**, UK to determine the best dopants and photonic structures in terms of high gain in the correct wavelength region for data communications (520, 570 and 650 nm).

Doping the POFs with conjugated materials is bound to have some effect on the propagation of light through the fiber. This part of the project is studied at the **University of Applied Sciences in Wildau**, Germany. They look at changes in refractive indices upon doping, and perform loss measurements using various techniques.

Figure 3: POFs doped with various conjugated polymers and oligomers.

4 Results

4.1 New Materials

The new co-polymer materials synthesized at the Instituto Superior Tecnico (IST) have included different materials, shown in Figure 4. The first material (JM1) was based on the common polyfluorene poly(9,9-dioctylfluorene) (PFO) which is known for its gain and switching properties. The co-polymer material showed well-isolated active chains of material in the solid-state, stimulated emission and good switching properties. Addition of oligoether groups in the second generation of materials (JM2), resulted in much higher solubility of the polymer in liquid MMA (the monomer which makes up the POFs). To tune the spectrum towards the red, co-polymer materials containing thiophene units were successfully synthesized in the third generation. In addition, as photo-oxidation is often a problem in organic gain materials, co-polymers JM4 and JM5 were produced with spiro linkages rather than alkyl groups to reduce the possibility of ketone formation, making the materials more photo-stable. Finally, following work performed by other groups suggesting that the poly(9,9-dioctylfluorene-co-benzothiodiazole) (F8BT) was an ideal candidate for gain and switching purposes, IST made a series of materials including a low-molecular weight F8BT, a spiro-bt-spiro compound and a co-polymer of spiro-bt-spiro for incorporation in the POFs.

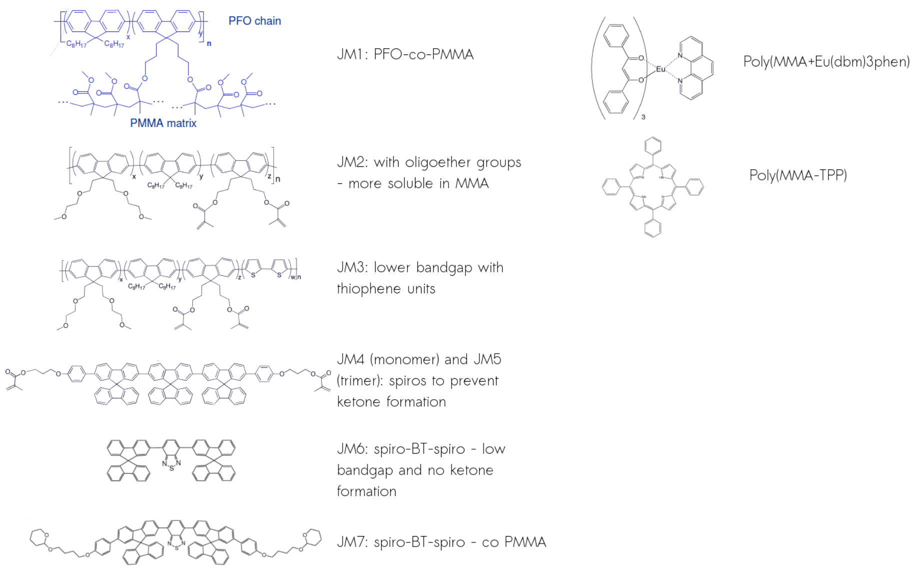

Figure 4: New materials produced during the POLYCOM project. The right-hand-side shows JM* materials - co-polymers of PMMA with active conjugated fluorene based polymers. The left-hand-side shows extra materials produced.

In addition, taking a different route, Europium and TPP compounds were synthesized. It was hoped that these small dye molecules could be used to produce amplifiers that can operate under CW excitation. Tests have shown that these materials show interesting temperature-dependent properties that might enable their use as temperature-sensors.

4.2 Photonic Devices Capable of Ultrafast Gain Switching

Four photonic devices were produced and characterized for gain, switching, losses and photo-stability. The four devices are shown in Figure 5.

Doped POFs are easily integratable within existing POF networks with low waveguiding losses and low coupling losses. They also show ultrafast gain switching throughout the blue and green spectral regions (430-530 nm). However, owing to solubility issues of the dopant and low photo-damage thresholds, the gain and maximal switching rate currently achieved is relatively low [2, 3].

An example of ultrafast gain switching in a doped POF is shown in Figure 6. The mechanism is that described in Box 3. Note the good on/off ratio (>100%) and the ultrafast recovery of the stimulated emission (<200 fs).

Optofluidic channels are devices in which optics and microfluidics are used together to produce highly compact and integrated devices. Here we exploit the properties of a fluid (conjugated polymers in solution) inside a microfluidic channel to produce a compact photonic device. The devices show waveguiding properties and high gain as well as ultrafast gain-switching. Furthermore, they have higher damage thresholds than the solid-state devices and hold the promise of CW-pumped conjugated polymer amplifiers and lasers. However, coupling to the channel and

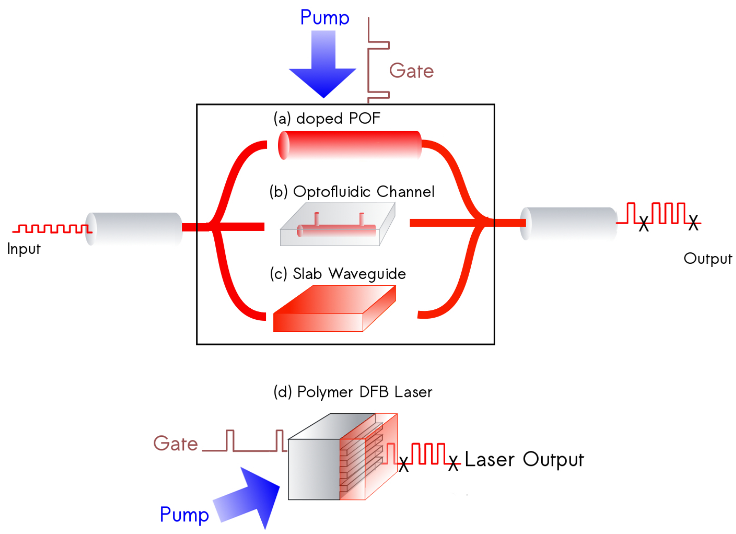

Figure 5: Schematic showing photonic devices using ultrafast switching (a) doped plastic optical fiber (POF), (b) optofluidic channel, (c) slab waveguide and (d) polymer distributed feedback (DFB) laser.

waveguide losses are high and the organic solvents used are often toxic [4].

Slab waveguides are cheap, easy and compact, they show high gain co-efficients as well as ultrafast gain switching in the correct circumstances. However, coupling and waveguide losses are large and the low damage threshold of the active material means that maximum repetition rates are capped at ∼GHz, despite the ultrafast response [5].

Finally, **polymer lasers** can be modulated using a gating pulse of the same wavelength as that used in telecommunication networks, thereby producing a simple, cheap and compact device for converting from telecom in long-haul networks to the datacom signals in local area networks. Again the low damage threshold of these devices is a problem [6, 7].

4.3 Towards Electrical Switching

The POLYCOM switching concept, which relies on the absorption losses induced by photo-generated charges for quenching stimulated emission, can in principle be realized by applied an external field. This may have some interest in applications where speed is not a crucial issue and the optoelectronic setting is convenient. An initial idea was to **ionize the singlet state** thus generating a short lived pair of charges on the chain. Unfortunately, this did not work.

The second idea was to use the **injection of charge carriers** from electrodes properly deposited on a thin structure comprising the active layer. This worked, and we demonstrated gain quenching through electrical switching. The deposition of the cathode onto the light amplifying layer is particularly critical, due to the well known quenching effects. POLYCOM has developed peculiar solutions to this problem.

This switching approach is limited in speed by the on-off ratio of the device,

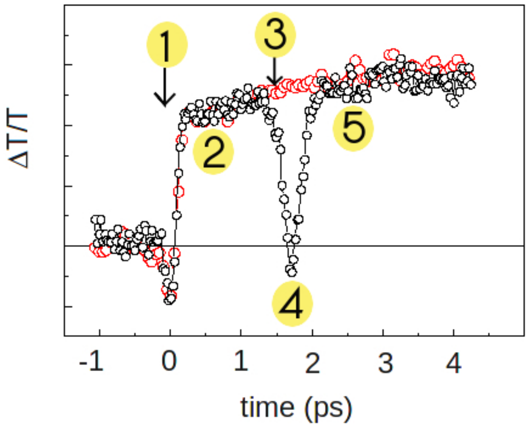

Figure 6: Ultrafast gain switch in a POF doped with fluorene heptamer. (1) arrival of pump, (2) positive signal is stimulated emission, (3) arrival of gating pulse (re-excitation to S_n, see Box 3), (4) charges absorb and completely quench stimulated emission, (5) charges recombine: full recovery of stimulated emission.

and requires long term stability under electrical currents. To date, organic LEDs have been demonstrated with modulation frequency in the 60 MHz region. With this successful experiment POLYCOM has introduced a new device concept and demonstrated its feasibility, extending its area of technological impact to optoelectronic.

In achieving the aim of electrical switching, we produced other breakthroughs. The combination of efficient light emission and high charge-carrier mobility has thus far proved elusive for polymer semiconductors, with high mobility typically achieved by cofacial pi-electron system to pi-electron system interactions that quench exciton luminescence. We report a new strategy, comprising the introduction of a limited number of more effective hopping sites between otherwise relatively isolated, and thus highly luminescent, polyfluorene chains. Our approach results in polymer films with large mobility ($\mu \sim$3-6$\times 10^{-2}$ cm^2 (Vs)$^{-1}$) and simultaneously excellent light-emission characteristics. These materials are expected to be of interest for light-emitting transistors, light-emitting diode sources for optical communications and may offer renewed hope for electrically pumped laser action. In the last context, optically pumped distributed feedback lasers comprising one dimensional etched silica grating structures coated with polymer have state-of-the-art excitation thresholds (as low as 30 Wcm^{-2}) and slope efficiencies (up to 11%) [8].

4.4 New Techniques

Two new measurement techniques were developed to enable the study of the relation of polymer blend microstructure with electronic properties. The first technique is **single molecule spectroscopy**, with a set-up developed at the University of Sheffield. The second uses a novel **femto-scope** which provides the spatial resolution of a confocal microscope (sub-μm) with the temporal resolution of femtosecond pump-probe spectroscopy (<150 fs).

4.4.1 Single Molecule Spectroscopy

Single molecule spectroscopy allows us to probe the electronic and optical properties of conjugated polymers at the single molecule level, thus ruling out effects such as intermolecular interactions. The active conjugated molecules are diluted at a concentration of 1 ngL^{-1} in an inert polymer matrix and deposited onto a substrate. By changing the properties of the inert matrix, the effect of the surroundings on the single molecule can be studied. Figure 7 shows an example image of single molecules emitting. The brighter spots may originate from more than one molecule.

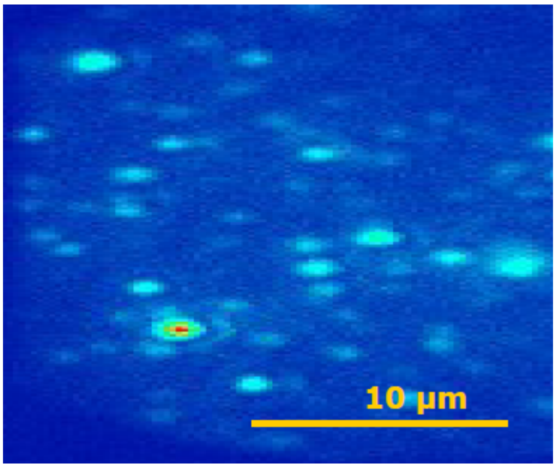

Figure 7: CCD image of fluorescence from a sample of active conjugated polymer diluted in an inert polymer matrix.

Using this technique we have successfully demonstrated that intrachain energy transfer is slower than interchain energy transfer [9].

This set-up and technique will in the future be used to map the excitonic properties of other single molecules, including more complicated conjugated polymers. It is becoming apparent that intermolecular interactions are fundamental for the photophysics and device physics of conjugated polymers. In order to understand their importance, work at the single molecule level is crucial, for, without knowing what happens at the single molecule level, it is difficult to untangle what happens when many molecules interact. Disorder, electron-phonon coupling and intermolecular interactions all play a role and to fully dis-entangle their individual roles, single molecule spectroscopy will be a very important tool.

4.4.2 Femto-scope

In order to image the electronic properties of the conjugated polymer blends used in POLYCOM, a femto-scope was developed which has the spatial resolution of a confocal microscope coupled with the temporal-resolution and power of pump-probe spectroscopy. This technique was successfully used to address the role of microstructure on the excitonic properties in polymer blends containing active polyfluorene and inert poly(methylmethacrylate) [10].

This 'femto-scope' will have many other uses in the future. In particular, it can be used in organic photovoltaic blends to spatially resolve features occurring at interfaces. Although the spatial resolution is not high enough to provide insight into processes such as exciton diffusion, it can nevertheless shed light on the different excitonic processes that occur in the bulk and at an interface. Such information has hitherto only been possible by using the crude method of comparing samples with many interfaces with those containing only bulk material. Interfaces are fundamentally important for photovoltaic and other organic electronic devices and it is believed that the interface states may dominate the device and photo physics. However, little is known about the photo-physics of these states and the femto-scope will allow us to gain greater insight into these states by selectively probing the excitonic properties of the interface with sub-μm resolution. In addition, it will be used to image photosynthetic cells to determine the energy transfer pathways within the cell membranes.

4.5 New Knowledge

Throughout the POLYCOM project, we aimed to achieve pure knowledge about the mechanisms underlying the main application. The main findings are shown below.

4.5.1 Charge-transfer States in Isolated Oligomers

During POLYCOM, we discovered that, surprisingly, even short isolated oligomers can support charge states which give rise to absorptions which overlap the stimulated emission [11]. This finding is important as it leads us to question the currently held view that charge generation in conjugated polymers occurs through exciton breaking and can only occur on long chains. It appears that charge generation can occur through *direct* excitation of a charge transfer state. This finding has repercussions for the fields of organic photonics as well as that of organic photovoltaic cells. Currently, the mechanisms behind charge photo-generation are not fully understood and these findings will help move towards completing the picture.

4.5.2 β-phase in Poly and Oligo-fluorenes

We have performed in depth studies as to the nature of the beta-phase in polyfluorenes and how it is formed. In particular it was found that (a) beta-phase can form even in oligomers thereby providing an estimate of the conjugation length of the polymer in beta-phase [12, 13] and (b) beta-phase can occur even when the conjugated polymer chains are isolated therefore demonstrating that it is an intrachain (rather than interchain) phase [14]. This is an important finding as beta-phase is known to show increased charge generation yield as well as interesting gain properties [15]. Understanding how to control and use this phase of polyfluorene is therefore important for photonic and optoelectronic applications.

4.5.3 Non-adiabatic Charge Recombination

Although it has recently been accepted by theoreticians that conical intersections and non-adiabatic relaxation are important processes in organic systems, it had never been demonstrated experimentally for conjugated polymers or oligomers. We demonstrated that charge recombination in fluorene oligomers occurs through a conical intersection [16]. This is an important finding for photovoltaic and photonic switching applications. Geminate recombination is a major loss mechanism in organic photovoltaic cells and understanding the processes of recombination are fundamental in understanding how to control them to avoid losses. In switching applications, the charge recombination determines the recovery time of the switch and is therefore important to understand.

4.5.4 Single Molecule Energy Transfer

Using single molecule spectroscopy, we have successfully demonstrated that intrachain energy transfer is slower than interchain energy transfer [9], an important finding for organic photonics as one of the quenching mechanisms for polymer lasers is exciton-exciton annihilation. If intrachain energy transfer is inefficient then isolating the conjugated polymers could lead to reduced exciton-exciton annihilation.

We have also used the results from the single-molecule spectroscopy on polythiophenes to help explain the time-resolved switching data on similar materials.

5 Impact

The work performed within POLYCOM is a breakthrough in all-optical switching for organic photonics as we demonstrate a *resonant* switching process with high on/off ratios and ultrafast response times. In the future, these findings may increase the data transmission rates in data communications, allow a move towards time-devision multiplexing (TDM) to increase bandwidth and could have implications for all-optical computing.

The values of gain achievable with our photonic devices are cutting edge values. Add to that their ultrafast all-optical switching capability and the POLYCOM project puts Europe in a position to lead the field of organic photonics.

We have produced a range of 'gain switcher' photonic devices, each with their own strengths and weaknesses, demonstrating the flexibility of the organic photonic approach. In addition, lifetime and environmental studies on our doped POFs demonstrate that they can withstand temperatures up to 300°C without degradation and are stable for months in ambient conditions. They therefore fit the needs of many of today's photonic applications, from ICT to bio-medical, which require low-cost, flexible, light-weight and robust devices.

The ultimate outcome of the project will, we hope, be wealth creation through technology up-take of further end-users creating sustainable growth and consequently employment opportunities. It is believed that the breakthrough results from POLYCOM will put Europe in a prime position to effectively generate more industrial growth in the organic photonics related market. The project results, in particular the devices produced and the knowledge gained, should increase the European competitiveness in the field of organic optoelectronics, nanofabrication, nano-photonics and nano-electronics by providing novel solutions without technological gaps.

A Appendix I: Dissemination

A.1 Introduction

POLYCOM is an advanced research project aimed at developing future technology based on new concepts for all optical switching that are suitable for integration into Plastic Optical Fibers networks. POLYCOM results include demonstration of devices, at the proof of concept level, and knowledge on materials, processes and their photonics properties. Exploitable Knowledge and near to the market product do not pertain to POLYCOM. In the following we present the activity of knowledge dissemination undergone within three years of POLYCOM research. This involves presentations at conferences, seminars, workshops and outreach events, journal and other media articles, conference organization, exhibitions etc..

A.2 Dissemination of knowledge

A.2.1 Summary Table

Type	N^o	Audience	Countries	Size	Partner
Invited Presentations	12	A, R	WW	100-1000	All
Other Oral Presentations	22	A, R	WW	100-1000	All
Conference Organization (EOS)	1	A, R	WW	100-1000	All
Journal Publications	22	A, R	WW	1000s	All
Theses (PhD, Masters...)	3	A, R	EUR	100	IST/POLIMI
Exhibitions	1	R, I	WW	100s	LUCEAT
Posters	8	A, R, I, M	WW	100-1000	All
Articles in magazines	2	Gen Pop.	EUR	1000	All
Project Website	1	Gen Pop	WW	>5000	POLIMI
News on other websites	1	Gen Pop	EUR	100s	All
Outreach events	1	Gen Pop	EUR	100	All
Use in Future Projects	2	A, R	EUR	1000	All
Seminars/ workshops	8	A, R	WW	100s	All

Table 1: Summary of Dissemination of Knowledge during POLYCOM project, 2007-2010. Key for audiences: A = Academic, R = General Research, I = Industry, M = Media, Gen Pop = General Population interested in Science. Key for Location of impact/dissemination: WW = WorldWide, EUR = Europe.

A.2.2 Invited Presentations

Owing to the impact of the knowledge gained within POLYCOM, as well as the international reputation of the people involved, we have been invited to give a number of presentations at international conferences. These presentations offer the opportunity to further disseminate the knowledge to researchers and academics who are interested in the field. Below is a list of the invited presentations attended/soon to be attended at international conferences:

Attended

- Invited Talk at Jaotong University 25.2.2009, Beijing, China
- Invited Talk at The 8th International Symposium on Functional π-Electron Systems 21.7.2008 - 25.7.2008, Location: Graz / Austria
- Invited Talk at Frontiers in Optics 2008, Laser Science XXIV October 19-23, 2008 Rochester Riverside Convention Center
- Special Lecture (âĂIJPhotoactive PMMA -polyfluorene copolymersâĂİ) e 47th microsymposium of âĂIJAdvanced Polymer Materials for Photonics and ElectronicsâĂİ Prague, Czech Republic, 15-19 July 2007.
- Invited presentation at the âĂIJInternational Symposium on nano and ultrafast photonicsâĂİ, Beijing Technical University, China, 29 October âĂŞ 3 November, 2007.
- Invited talk at “ECOER2007”, Varenna (I), October 2007
- Invited talk and oral presentation at the Optical Probes, Turku Finland, 11-15 June, 2007.
- Invited talk at Be-More Meeting, November 22 âĂŞ 24, 2007, Prague, Czech Republic
- Invited talk at 9th International Conference on Frontiers of Polymers and Advanced Materials, July 8 âĂŞ 12, 2007, Cracow, Poland

Up-coming communications

- Invited communication at the RANK Award Workshop in UK, 22-25 June 2009
- Invited talk at the next SPIE Photonics of S. Diego (Ca-USA) 2-6 August 2009
- Invited talk at CLEO/Pacific rim conference in Shanghai (China) 30 August-4 September 2009

A.2.3 Other Oral Presentations

Oral presentations at international conferences provide the opportunity of showcasing the knowledge gained within the POLYCOM project and of opening up discussions with other members of the academic and research world. Below are a list of oral presentations presented or shortly to be presented.

Attended

- Presentations (7) in total in different symposia) at the European Optical Society Annual Meeting 2008, Paris France, Oct. 2008.
- Presentations (2) at the International Conference of Synthetic Metals (ICSM), Porto di Galinhas, Brazil, July 6-11, 2008.

- Presentations (2) at the European Material Research Society spring meeting in Strasbourg, France, May 26-30th 2008.
- Presentation at the Materials Research Society fall conference in Boston, USA, December 2007.
- Presentation at the 12th Optoelectronics and Communications Conference/16th International Conference on Integrated Optics and Optical Fiber Communication (OECC/IOOC2007), Pacifico Yokohama, Yokohama, Japan, 10-15, July 2007.
- Presentation âĂIJ16th International Conference on Polymer Optical FibersâĂİ Turin, Italy, 10-12th September 2007.
- Presentation at the 12th Optoelectronics and Communications Conference/16th International Conference on Integrated Optics and Optical Fiber Communication (OECC/IOOC2007), Pacifico Yokohama, Yokohama, Japan, 10-15, July 2007.
- Presentation at the E-MRS, Strasbourg, France, 28-31 May 2007.

Up-coming communications

- Presentation at the Optical Probes Bi-annual Conference, Beijing, China. 6-10, June, 2009.
- Presentation at the Portuguese Meeting on Chemical Physics of the Portuguese Chemical Society, Aveiro, Portugal, 15-16 June 2009.
- Presentation at Conftele2009 âĂŞ 7th Conference on Telecomunications, Santa Maria da Feira, Portugal, May 3-5, 2009.
- Presentation at ICMAT- International Conference on Materials for Advanced Technologies, Singapore, 28 June-3 July, 2009.
- Presentation at EUROMAT, Glasgow, UK, September 2009
- Presentation at EOS, Capri, Italy, September 2009

A.2.4 Conference Organization

The main contribution to knowledge dissemination has been the organization of a topical meeting at the bi-annual meeting of the **European Optical Society**, held in Paris, 29th September 2nd October 2008. This meeting contributed to raise awareness on the resurging field of organic photonics, it established a community of reference for the field and disseminated to a vast audience POLYCOM research issues. The POLYCOM consortium was part of the program board, while the meeting was chaired by the POLYCOM coordinator. The EOS Annual Meeting 2008 was a great success, with 10 % more attendees than in 2006 registered for the meeting, which in the meantime has become an important biannual event for the European optics and photonics community. In particular the topical meeting on Organic Photonics (TOM5) was a new entry in EOS conference and based on the good success it had it will probably be repeated at the next annual conference in 2010. Several EU project coordinators attended the conference and contribute to a lively discussion at the technical session. TOM5 contributed to enhance connections between research groups and making opportunities for new proposals at the next organic photonic call.

Statistics of EOS bi-annual meeting:
Number of attendees: 650
Number of oral presentations: 324
Number of poster presentations: 194
http://www.photonik.de/fileadmin/pdf/fachaufsaetze/photonik_intl_2008_1_006.pdf

Some information on the event are below:

Synopsis of TOM5. Organic semiconductors are a broad class of materials comprising small molecules, conjugated polymers and carbon-based nanostructures (e.g. carbon nanotubes). They all have in common p-electron delocalization, in low dimensional space, which yields a number of interesting properties for photonics such as large optical cross-sections and short response time, large nonlinear optical responses, energy and charge transport, together with mechanical qualities (film formation, deposition, high damage threshold, low cost technology). In addition, the interaction of organic and inorganic semiconductors leads to new and promising functions which appear in hybrid systems and devices. This topical meeting aims at providing a state-of-art review on organic and hybrid photonics, including its fundamentals, potential and applications. The programme format allows for open discussion among participants and fruitful exchange of experience.

TOM5 Topics

- Plastic optical fibers
- Polymer laser
- Photonic components (carbon nanotubes, photonics, amplifiers, etc.)
- OLED and optoelectronic
- Optical properties and spectroscopy
- Photovoltaics and photodetectors
- Organic microcavities
- Plasmonics
- Hybrid organic / inorganic systems

Chair: Guglielmo Lanzani, Politecnico di Milano, Italy
Programme Committee:

- Luca Bazzana, Luceat S.p.A., Brescia, Italy
- Donal Bradley, Imperial College London, United Kingdom
- Juan Cabanillas Gonzalez, Politecnico di Milano, Italy
- Franco Cacialli, University College London, United Kingdom

- David Lidzey, University of Sheffield, United States
- Larry Luer, Politecnico di Milano, Italy
- Jorge Morgado, Instituto Superior Tecnico, Lisboa, Portugal
- Alessandro Nocivelli, Luceat S.p.A., Brescia, Italy
- Sigurd Schrader, University of Applied Sciences Wildau, Germany
- Tersilla Virgili, Politecnico di Milano, Italy

Plenary Speaker

- Valy Vardeny, University of Utah, Salt Lake City, USA

Invited Speakers

- Gonçal Badenes ICFO-Institut de Ciencies Fotoniques, Spain
- Werner Blau, University of Dublin - Trinity College, Ireland
- Hans-Joachim Egelhaaf, Johannes-Kepler-University, Linz, Austria
- Giuseppe Gigli, University of Lecce, NNL, Italy
- Gustav Kalbe, European Commission, Brussels, Belgium
- David Lidzey, University of Sheffield, USA
- Rainer Mahrt, IBM Zurich Research Laboratory, Switzerland
- Michele Muccini, Institute for Nanostructured Materials CNR, Bologna, Italy
- Hans Poisel, Georg-Simon-Ohm Hochschule Nuernberg, Germany
- Ifor Samuel, University of St. Andrews, United Kingdom
- Henry Snaith, Jesus College Oxford, United Kingdom

A.2.5 Journal Publications

POLYCOM have produced results in several areas of fundamental science, such as material science, organic semiconductor photophysics and molecular photonics. A major dissemination action is the publication in per reviewed international journals.

Accepted publications

- Khalil et al, Journal of Chemical Physics, 130 044903 (2009)
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- Optical gain and switching in doped POF to be submitted to Advanced Materials
- Synthesis and optical characterization of active co-polymers

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A.2.6 Theses: PhD and Masters

Throughout the course of POLYCOM, students have been trained have contributed significantly to the project. This has produced three theses; two masters theses and a PhD thesis.

- Ana Luisa da Silva MendonÃğa, ISTL, Materials Engineering PhD thesis on "Plastic Optical Fibers doped with Conjugated Polymers Exhibiting Optical Gain", to be concluded in December 2009.

- Lorenzo Parachini, POLIMI, Physics Engineering Masters thesis on "Ultrafast Gain Switching in Plastic Optical Fibers."

- Giulia Granchi, POLIMI, Physics Engineering Masters thesis on "Time-resolved Confocal Microscopy of Polymer Blends."

A.2.7 Exhibitions

At the 16th International Conference on Polymer Optical Fibes, LUCEAT show-cased the doped POFs produced by POLYCOM. This resulted in interest from industry and researchers. In particular, others in the POF industry suggested alternative applications for the POFs and a collaboration with a Spanish group who specialise in POFs was started.

A.2.8 Posters

Poster presentations offer the members of POLYCOM the possibility to show-case the POLYCOM knowledge at conferences that are not specifically targeted to materials science or POFs. This allows the opportunity of disseminating the knowledge to a wider academic, industrial and media audience. For example, POLIMI attended the European Union 'Science Beyond Fiction' conference and was able to discuss the work with academics from a large number of fields as well as industrial representatives interested in moving their work towards organic photonics and the media who are interested in this cutting edge research.

- Poster Presentation at 'Science Beyond Fiction' (FET09) Prague, Czech Republic April 2009.
- Poster Presentation at the European Optical Society (EOS) Annual Meeting, Paris, 29 September-2 October 2008.
- Poster presentation at the Gordon Research Conference, Mount Hollyoak College, USA, July 20-25, 2008.
- Poster presentation Ultrafast Phenomena, Stresa, Italy, June 9-12 (2008).
- Poster presentation at the European Conference of Molecular Electronics, in Metz, France September 5-8, 2007.
- Poster presentation and Proceeding at the Materials Research Society spring conference in San Francisco, USA, March 2007.
- Poster presentations (2) at First Mediterranean Photonics Conference 2008, June 25th - 28th June 2008, Ischia, Italy
- Poster presentations (2) at Supramolecular and Plastic Electronics (SOLE) Summer School, 2 âĂŞ 5 April 2008, Stresa, Italy

A.2.9 Articles in Non-Academic Magazines

To disseminate the knowledge to the widest possible audience of the general population who are interested in science, several articles have been written in popular science magazines. Below is a list:

- Article in optics.org http://optics.org/cws/article/research/39132 describing the optofluidic chip photonic switching device.
- Article concerning the novel femto-scope developed during the POLYCOM project in a popular science magazine.

A.2.10 Project Website

The project website, redesigned in 2008, fulfills two roles. The first is to allow partners to access documents relating to POLYCOM easily and quickly from the restricted section. The second is to raise awareness of the POLYCOM project. The website therefore shows the principles behind the project as well as the objectives. It also offers references and links to the journal articles for the more interested readers. Any unpublished work is not shown on the website. The site has received more than 5000 visits since 2008.

A.2.11 News on Other Websites

The POLYCOM project is show-cased on various other websites, mainly run by the European Union or subsidiary. These the OPERA website.

A.2.12 Outreach Events

POLYCOM participated in a 'Researchers' Night.

A.2.13 Use of Knowledge in Future Projects

The knowledge gained through work performed during the POLYCOM project will be used in two projects submitted in the latest call, ITHACA and OPSOL. ITHACA is a STREP project in which the POLYCOM switching concept will be applied to new supramolecular materials in which chain isolation is obtained by sugar threading conjugated strands. OPSOL is a project in which the KNOW-HOW obtained by POLYCOM on doped POF is exploited for building new generation luminescent solar collectors capable of light harvesting and spectral conversion within POF.

A.2.14 Seminars/Workshops

POLYCOM has been invited to give seminars in various universities and institutions and has participated in the workshops listed below. This activity serves to raise the profile of the POLYCOM project and to enable discussions with leading academics around the world.

- Talk at Newnham College, Cambridge, UK
- Short seminar at University of Sheffield, UK
- POLYCOM was invited to the Workshop organized by the THREADMILL network project (2nd April âĂŞ 4th April 2008, Stresa, Italy)
- Invited talk at the Université de Montréal, Canada 18th July, 2008.
- Invited talk at Argonne National Labs, Chicago, USA, 28th July, 2008.
- POLYCOM was invited at the Summer School of the BIMORE project (26th May âĂŞ 2nd June 2007, San Benedetto Del Tronto, Italy).
- Invited to the NFN Winterschool On Organic Electronics, January 27th - February 2nd 2007, Planneralm, Donnersbach, Austria
- Invited to the Workshop on OrganPV_Net, 22 - 23 January 2007, Hahn-Meitner-Institute, Berlin, Germany

A.3 Use of knowledge

A.3.1 Possible applications of ultrafast photonic switch devices

Below we outline some of the possible applications from the outcome of 'POLYCOM'

Automotive Industry The automotive industry has, in the last few years, moved away from copper cables and towards plastic optical fibers to transfer data around the car. Figure 8 shows the trend in required data rate for this sector. The move from copper to POF has been necessary due to the ever-increasing need for data transmission speeds and for transmission media which are robust, cheap and easy to use. The required data rate for these applications is below 1 GHz, as can be seen from Figure 9. In particular, important optical data communication is required for

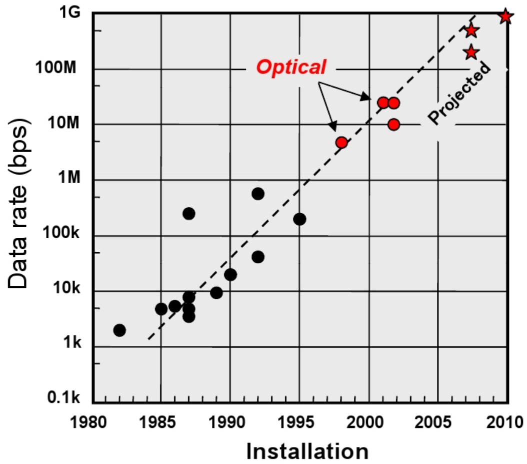

Figure 8: Trend graph taken from Ref. [17].

data rates in the kHz to MHz range, a window that can be filled with organic photonics. In addition, the need for *all-optical switching* has been outlined by Toyota in a recent technology conference [17]. The increase in data needs in the automotive industry is also expected to require POF amplifiers. We feel that conjugated polymers, and organic photonics in general, will meet this demand.

Time-Devision Multiplexing: TDM Wavelength-division multiplexing (WDM) is a technology which multiplexes multiple optical carrier signals on a single optical fiber by using different wavelengths of laser light to carry different signals. This allows for a multiplication in capacity, in addition to enabling bidirectional communications over one strand of fiber. Although early WDM systems were expensive and complicated to run, recent standardization and better understanding of the dynamics of WDM systems have made WDM less expensive to deploy. A WDM system uses a multiplexer at the transmitter to join the signals together, and a demultiplexer at the receiver to split them apart. It is generally easy to separate out signals using diffractive optics and therefore WDM has gained wide-spread popularity in telecommunications.

Time-Division Multiplexing (TDM) is a type of digital multiplexing in which two or more signals or bit streams are transferred apparently simultaneously as sub-channels in one communication channel, but are physically taking turns on the channel. The time domain is divided into several recurrent timeslots of fixed length, one for each sub-channel. A sample byte of sub-channel 1 is transmitted during timeslot 1, sub-channel 2 during timeslot 2, etc. One TDM frame consists of one timeslot per sub-channel. After the last sub-channel the cycle starts all over again with a new frame, starting with the second sample, byte or data block from sub-channel 1, etc. A problem with TDM is the detection of the different sub-channels. Using all-optical switching and amplification, however this becomes simple. Synchronising the gating pulse with the individual sub-channel it will be possible to simply and efficiently read out the data in each sub-channel.

Combining TDM with WDM increases the amount of data passing through a single fiber, by exploiting both the time and frequency domains of electro-magnetic

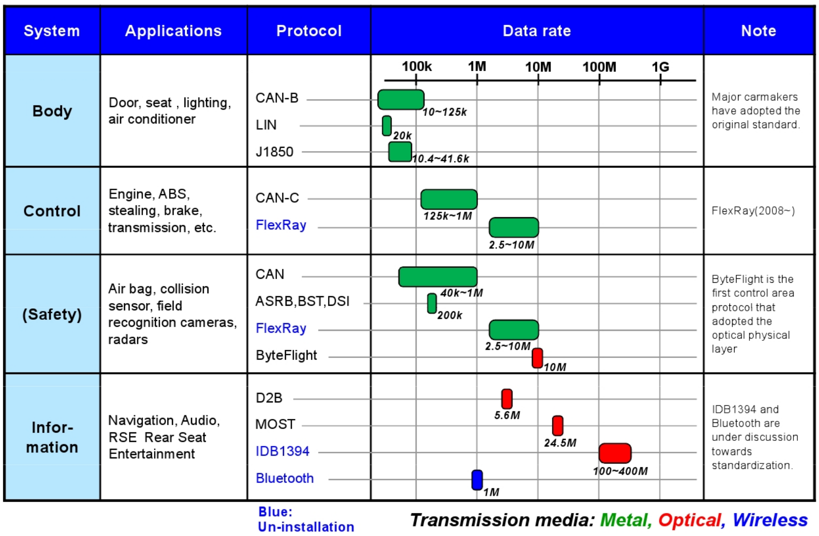

Figure 9: Trend graph taken from Ref. [17].

radiation.

All Optical Computing All-optical switching is a requisite for all-optical computing. The switch developed by the POLYCOM project can be used as a logical NOT gate, which is a fundamental logic piece for the development of all-optical computing.

A.3.2 Possible applications of doped plastic optical fibers other than switching

Much interest was generated by the doped plastic optical fibers produced by LUCEAT. As a result, many applications possible applications have been brought to light that are far from the initial gambit of POLYCOM. These include:

- sensing of humidity in textile materials (where the doped POF would be interwoven within the fabric));
- high-precision measurement of liquid levels within oil tanks;
- collision detection in cars (the doped fiber being integrated in the front and rear bumpers);
- selective filtering of wavelengths in wavelength division multiplexing POF-based optical transmission systems (in order to avoid using beam splitters or other passive elements);
- dynamically controllable variable attenuator in POF data links (in order to increase the acceptable distance range).
- spatially resolved pressure sensor, where the active POFs form a grid.

A.3.3 Use of acquired knowledge and techniques

During the POLYCOM project, different techniques were developed and these will be used in the future for various applications. In addition, fundamental knowledge gained through the POLYCOM project can have far reaching applications. These are outlined below.

Confocal Microscope In order to image the electronic properties of the conjugated polymer blends used in POLYCOM, a femto-scope was developed which has the spatial resolution of a confocal microscope coupled with the temporal-resolution and power of pump-probe spectroscopy. This technique was successfully used to address the role of microsctructure on the excitonic properties in polymer blends containing active polyfluorene and inert poly(methylmethacrylate).

This 'femto-scope' has many other uses, however. In particular, it can be used in organic photovoltaic blends to spatially resolve features occurring at interfaces. Although the spatial resolution is not high enough to provide insight into processes such as exciton diffusion, it can nevertheless shed light on the different excitonic processes that occur in the bulk and at an interface. Such information has hitherto only been possible by using the crude method of comparing samples with many interfaces with those containing only bulk material. Interfaces are fundamentally important for photovoltaic and other organic electronic devices and it is believed that the interface states may dominate the device and photo physics. However, little is known about the photo-physics of these states and the femto-scope will allow us to gain greater insight into these states by selectively probing the exictonic properties of the interface with sub-μm resolution.

M-line Technique The m-line measurement system developed to determine, with high accuracy, the refractive index of films of active materials within POLYCOM will continue to be used with other excitation sources for photonics applications involving small changes in refractive index. In addition, using a similar technique, coupling to plasmon resonances will be studied to determine the switching properties involved in small changes in refractive index of photo-excited conjugated polymer films.

Single Molecule Spectroscopy We have developed a single-molecule spectroscopy system, whereby molecules are âĂŸspreadâĂŹ out on a surface at low density, and then imaged using a conventional far-field optical technique. This has proved useful in understanding the role of matrix on the single molecule excitonic properties.

This set-up and technique will in the future be used to map the excitonic properties of other single molecules, including more complicated conjugated polymers. It is becoming apparent that intermolecular interactions are fundamental for the photophysics and device physics of conjugated polymers. In order to understand their importance, work at the single molecule level is crucial, for, without knowing what happens at the single molecule level, it is difficult to untangle what happens when many molecules interact. Disorder, electron-phonon coupling and intermolecular interactions all play a role and to fully dis-entangle their role, single molecule spectroscopy will be a very important tool.

New Materials As part of POLYCOM, many new materials were synthesized. These were originally designed as active materials for photonic applications in doped plastic optical fibers for data communications. POLYCOM showed that these materials worked well. However, they have been found to have numerous other characteristics which are important for various applications.

- **High photo-stability materials**: while designing materials for POLYCOM, high stability materials containing spiro compounds were produced. In particular a spiro-containing F8BT was shown to have good optical properties similar to the conjugated polymer but without the possibility of forming the unwanted keto-defect.

- **Heat sensors**. It was found that some of the new materials behave interestingly when heated. In particular they show *reversible* shifts with temperature of different bands of the photoluminescence spectra. This finding paves the way for organic heat sensors used, for example, to determine the heat produced by electronic devices etc.

- **Beta-phase in polyfluorenes**. While characterising the JM materials, much information was discovered as to the nature of the beta-phase in polyfluorenes. In particular it was found that (a) beta-phase can form even in oligomers thereby providing an estimate of the conjugation length of the polymer in beta-phase and (b) beta-phase can occur even when the conjugated polymer chains are isolated therefore demonstrating that it is an intrachain (rather than interchain) phase. This is an important finding as beta-phase is known to show increased charge generation yield as well as interesting gain properties. Understanding how to control and use this phase of polyfluorene is therefore important for photonic and optoelectronic applications.

CT in short oligomers During POLYCOM, we discovered that, surprisingly, even short isolated oligomers can support charge states which give rise to absorptions which overlap the stimulated emission. This finding is important as it leads us to question the currently held view that charge generation in conjugated polymers occurs through exciton breaking and can only occur on long chains. It appears that charge generation can occur through *direct* excitation of a charge transfer state. This finding has repercussions for the fields of organic photonics as well as that of organic photovoltaic cells. Currently, the mechanisms behind charge photo-generation are not fully understood and these findings will help move towards completing the picture.

Non-adiabatic Relaxation Although it has recently been accepted by theoreticians that conical intersections and non-adiabatic relaxation are important processes in organic systems, it had never been demonstrated experimentally for conjugated polymers or oligomers. We demonstrated that charge recombination in fluorene oligomers occurs through a conical intersection. This is an important finding for photovoltaic and photonic switching applications. Geminate recombination is a major loss mechanism in organic photovoltaic cells and understanding the processes of recombination are fundamental in understanding how to control them to avoid losses. In switching applications, the charge recombination determines the recovery time of the switch and is therefore important to understand.

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