Organic Semiconductor Centre

► Light-emitting dendrimers for OLEDs
► Photophysics – fs to μs luminescence
► Exciton diffusion/solar cells
► Lasers and optical amplifiers
► A new light source for medicine

50th anniversary
Outline: Part I

- Introduction – towards polymer photonics
- Review of laser physics
- Gain measurements
- Feedback structures
- Distributed feedback lasers
- Exercise (for you!)
Organic Semiconductors

- Conjugated molecules
- Novel semiconductors
- Easy to process
- Can tune properties
- Can emit light
- Flexible
OLED Displays

SONY ultra-thin 13" display

Kodak Viewfinder

Epson Widescreen Display

MED Ltd
Plastic Photonics

Passive

Active
Laser Physics

Light Amplification by Stimulated Emission of Radiation

**Generic LASER:**
optical amplification with feedback

Excitation

mirrors

Output
Laser Rate Equations

\[
\frac{dN}{dt} = \Lambda - \frac{N}{\tau} - \frac{N\sigma I}{h\nu}
\]

- **Excitation**
- **Spontaneous emission**
- **Stimulated emission**

\[
\frac{dp}{dt} = \frac{\sigma cl}{L} N(p+1) - \frac{p}{\tau_{\text{cav}}}
\]

- **Amplification**
- **Decay**

\[N = N_2 - N_1\]

\[\tau_{\text{cav}} = \frac{2L}{\beta c}\]
Steady-state Lasing Characteristics

- Population inversion (spontaneous emission) clamped at threshold level by stimulated emission
- Power rises linearly with pumping
- Increased spectral and spatial coherence
  - Narrowing of emission spectrum
  - Directional output beam
Threshold and Slope Efficiency

Threshold: ►Gain exceeds loss  \( \text{gain} = 2\sigma Nl > \beta \)

►Photon mode concept
  ►10⁶-10¹⁰ spatial and spectral photon modes
  ►Above threshold all energy stimulated into one mode (or at least very few modes)

Efficiency:  
\[
P_{out} = \frac{\beta_o}{\beta} \frac{\nu_l}{\nu_p} \eta_R \left( P_{IN} - P_{TH} \right)
\]

- Fraction of useful losses
- Photon energies
- Radiative efficiency
- Pump rate above threshold
Pulsed Operation

- Dynamic solution of rate equations

- Gain medium has fluorescence lifetime $\tau$ to build population inversion
  - If $t_\Lambda < \tau$ - pump energy density important
  - If $t_\Lambda > \tau$ - pump intensity important

- Pulse build-up time
  - Time required for pulse to be macroscopically amplified
  - 1 photon ($= 3 \times 10^{-19}$ J) to 1 nJ pulse - 100 dB gain required
  - Build-up time must be less than excited state lifetime/pump duration
  - Short cavities required
Pulsed Operation: A Femtosecond Polymer Laser

2D DFB laser with MEH-PPV as active medium

Pumped by 100 fs pulses

Pulse width decreases at high excitation density

Minimum pulse width of 700 fs
Potential for Polymer Lasers + Amplifiers

- Absorption and emission separated - 4 level system
- Strong absorption $\sim 10^5$ cm$^{-1}$ - Enormous gain
- Little concentration quenching
- Broad spectra - broad bandwidth
- Compatible with polymer fibre transmission windows (500–560 and $\sim 660$ nm),
- Scope for low cost manufacture
- Possibility of electrical pumping

Chemical Reviews 107 1272 (2007)
Organic Semiconductor Laser Materials

- Conjugated polymers
  - solution processed
  - wide range of materials

- Dye doped Alq₃
  - co-evaporated
  - conventional laser dyes in energy transfer host

- Dendrimers
- Spiro molecules
- Truxenes
  - Small solution processed molecules
Organic Laser Energy states

\[ |S_N\rangle \quad |T_N\rangle \quad |S_1\rangle \quad |T_1\rangle \quad |S_0\rangle \]

\[
\begin{array}{c}
0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
3.0 & 2.5 & 2.0 & 1.5 \\
400 & 500 & 600 & 700 & 800 \\
\end{array}
\]

Wavelength (nm)

Absorbance / Photoluminescence (arb.)

Energy (eV)
Measuring Gain 1: Transient Absorption

- Excite sample with short laser pulse
- Measure change in transmission with time-delayed probe
- Gain (if present) will increase in transmission
Probing Optical Gain (Stimulated Emission) in Materials

- Excite with short pulse to $S_1$ state.
- Send a probe pulse resonant with PL.
- Probe is amplified by stimulated emission

$$\frac{\Delta T}{T} \sim N_1(\sigma_{SE} - \sigma_{ESA}) - N_p \sigma_p$$
Transient Absorption of PPV (1992)

With F. Raksi and R.H. Friend
Transient Absorption ~1997

- Snapshot of absorption $\Delta A$ induced by pump pulse
- Photo-induced absorption at low energies
- Gain (-ve absorption) mirrors PL spectrum
- Gain present for a few hundred picoseconds

Data from Arvydas Ruseckas
Measuring Gain 2: Waveguide Amplifiers

- Polymer film (100-400 nm) forms optical waveguide
- Pump \( \lambda \) absorbed in \(~100\) nm
- Total internal reflection confines light in polymer film
- Signal amplified by 1000 times in 1 mm propagation through film

Measuring Gain 3: ASE

- Excite stripe on film and observe emission from edge

- Above characteristic energy:
  - Super-linear increase in output intensity
  - Dramatic narrowing of spectrum
  - Signatures of gain narrowing via amplified spontaneous emission

Measuring Gain 3: ASE

- Net gain and waveguide losses can be inferred from the SLN measurements.

- Gain: output related to stripe length
  \[ I(\lambda) \propto \frac{I_p}{g(\lambda)} \left[ e^{g(\lambda)l} - 1 \right] \]

- Loss: measured by varying length of unpumped region
  \[ I(\lambda) \propto e^{-\alpha(\lambda)z} \]
Measuring Gain 3: ASE

- Net gains of 10 cm\(^{-1}\), 21 cm\(^{-1}\) and 30 cm\(^{-1}\) (up to 130 dBcm\(^{-1}\)) for different pump densities

- Loss coefficient: 3 cm\(^{-1}\) in unpumped waveguide

Lasing in MEH-PPV Solution (1991-92)

High quantum efficiency luminescence from a conducting polymer in solution: A novel polymer laser dye

Daniel Moses
Institute for Polymers and Organic Solids, University of California, Santa Barbara, California 93106

(Received 17 December 1991; accepted for publication 13 April 1992)

A novel dye laser based on the soluble conducting polymer poly[2-methoxy, 5-(2’ ethyl-hexyloxy)-p-phenylenevinylene], MEH-PPV, has been demonstrated. Laser action has been tested in a transverse cavity configuration where the conducting polymer laser was pumped by light pulses generated from the second harmonic radiation of a Q-switched Nd:YAG laser. The performance of MEH-PPV in solution as a laser dye was compared to that of rhodamine 6G in solution under identical conditions. The results indicate that the quantum yield of MEH-PPV laser is comparable to that of rhodamine 6G.
Polymer Laser Resonator Geometries

- Solution processing - high quality waveguides
- Sub-micron structures - laser microresonators
- Strong absorption – transverse pumping possible

- microcavity
- microring
- microsphere
- 1-D DFB
- 2-D DFB / photonic bandgap
- random scatterers
Typical Experimental Configuration

- Pump laser
- Variable grey filter
- Lens
- Energy meter/beam profiler
- Polymer laser in vacuum chamber
- CCD spectrograph
Polymer Microcavity Lasers

- Resonant wavelengths: $m\lambda_m = 2d$
- Few spectral modes
- At high pump energies emission is stimulated preferentially into one spectral mode

Surface-emitting Distributed Feedback Lasers

Pulsed pump laser excitation

1st order scattering provides surface output coupling

2nd order scattering provides distributed feedback

Angle-Dependence of Bragg scattering

\[ \lambda = n_{\text{eff}} \Lambda \]

\[ \lambda < n_{\text{eff}} \Lambda \]

\[ \lambda > n_{\text{eff}} \Lambda \]
Angle Dependent Photoluminescence

- Photoluminescence dominated by Bragg-scattered emission from waveguide modes
- Photonic stopband evident at normal incidence
Wavelength scale corrugations cause Bragg scattering

Counter-propagating waveguide modes couple together at $\lambda_B$

$$m\lambda_B = 2n_{\text{eff}} \Lambda$$
Questions – For You to Answer

You wish to make an MEH-PPV DFB laser operating at 640 nm. The refractive index of the waveguide mode is 1.6.

(a) Write down the Bragg condition for the lasing modes

(b) For the first two diffracted orders
   (i) Calculate the grating period required
   (ii) Determine whether the laser is surface or edge-emitting

What are the advantages and disadvantages of each configuration?

(c) What would the emitted beam look like for
   (i) A one-dimensional grating?
   (ii) A two-dimensional grating?
1-D and 2-D DFB Laser Structures
Emission Pattern of 1-D and 2-D DFB Lasers
1-D versus 2-D feedback

Blue lasing in PFO
- 2-D mode confinement leads to lower threshold lasing and improved slope efficiency

Outline: Part II

► Tuning polymer lasers, simple fabrication
► Reducing size of pump – towards practical lasers
► Indirect electrical pumping
► Sensing explosives
► Polymer optical amplifiers
► Optical switching of lasers and amplifiers
Tuning a Polymer Laser by Microstructure

Array of 15 grating periods from 350 to 420 nm

95 nm grating depth, unity mark to space ratio

Atomic force microscope image of grating
Tuning of Laser Emission

- Laser wavelength tuned by translating the substrate
- Stopband wavelength changes linearly with grating period
- Laser emission on band edge ~4nm longer in wavelength
- 20 nm tuning range using a single substrate (1 mm translation)
Simple Fabrication of Polymer Nanostructures

- Hot embossing
- Solvent assisted micro-moulding
- UV-nanoimprint lithography

120 seconds

AFM image of 400 nm period, 90 nm deep eggbox corrugation

Appl Phys Lett 81, 1955 (2002); Appl Phys Lett 82, 4023 (2003);
Shrinking Polymer Laser systems

1995 Regenerative amplifier (Tessler)

~2000 Q-switched Nd:YAG

2003 Microchip laser

2006 Diode pumped

2008 LED pumped

Compact Polymer Lasers

- Pulsed microchip pump laser
- 1 ns pulses at 532 or 355 nm
- Up to 100 nJ to 1 µJ pulse energy
- 5 kHz rep rate
Diode laser pumped polymer lasers

- GaN diode laser
  - $\lambda = 407$ nm
  - $E_{\text{pulse}} = 0.7$ nJ
  - $t_{\text{pulse}} \sim 1.2$ nsec

- DBR microcavity with a few resonant modes
- Above threshold (8$\mu$J/cm$^2$), lasing peak grows rapidly
- Single lasing peak dominates spectrum at higher pump powers


Electrically Pumped Organic Lasers?

Main Challenges
► High projected threshold current density (> 100s A/cm²)
► Low carrier mobilities
► Losses from metal contacts
  (10X to 100X intrinsic waveguide loss)
► Polaron and triplet absorption losses

Why?
Novel, tuneable, simple to fabricate, (flexible) lasers
Without need for expensive (and bulky) separate pump lasers

How to recognize lasing
Ifor D. W. Samuel, Ebinazar B. Namdas and Graham A. Turnbull

The race to demonstrate new lasers, including electrically pumped polymer lasers, makes it a good time to reflect on the measurements that must be undertaken to support a claim of lasing.

Main Challenges
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http://en.wikipedia.org/wiki/Laser

Alternative: Indirect Electrical Pumping
Try a Nitride LED as the Pump

Advantages
► Exploits high mobility of InGaN
► Separates charge injection from gain medium
► Much lower cost than laser pumped system
► Very compact, electrically controlled

All the benefits from direct electrical pumping

Challenges
► Incoherent light source hard to focus
► CW intensities < 30 W/cm²
Lumiled K2 emitter  cw spec: (475mW @ 1A at 455 nm)
Under ns pulsed operation:
- 47 ns pulses
- Up to 255 W/cm$^2$ (275 nJ) for 160 A drive current (8 kAcm$^{-2}$)

Yang et al., App Phys Lett 92, 163306 (2008);
Polymer Gain Medium

Requirement for gain medium
- Absorption matches LED emission
- Long exciton lifetime

ADS 233YE
F8_{0.9} BT_{0.1}

PLQY: 80%
lifetime: 3.4 ns

Yang et al., App Phys Lett 92, 163306 (2008);
1D Distributed feedback resonator
355 nm period grating
In-plane feedback and surface output coupling

Polymer DFB Lasers

Pumped with 450 nm from 4 ns OPO
DFB lasing in TE₀ and TM₀ transverse modes
Low Threshold Polymer DFB Lasers

- Dependence on pump beam area
- Threshold intensity falls with increasing excitation area
- Saturates for areas above ~1 mm²

- Minimum threshold ~200 W/cm²
- Threshold reduced to 160 W/cm² by double-passing pump light

Graphs showing:
- Threshold intensity vs. pump beam area
- Output vs. pump intensity
- Pump energy vs. pump intensity
- Wavelength vs. output (inset graph)

Wavelength: 568 nm
Pumped by OPO at 450 nm
LED Pumped Polymer Lasers

- Light emitting area: 1.5 mm by 1.5 mm
- InGaN LED
- Laser Output
- Pulsed current source
- CYTOP ADS233YE Silica
- Pump filter

LED Pumped Polymer Laser

Hybrid organic semiconductor-GaN-CMOS smart pixel arrays
(St Andrews, Strathclyde, Edinburgh, Imperial College)

Optical Concentrators for Organic Lasers

Aim: increase power density from LED

- Use luminescent optical concentrators as used in solar panels
- Miniaturised version designed for concentrating LED power density

5-fold reduction in lasing threshold for optimised concentrators

Yang et al., Adv Mat 21, 3205 (2009)
Fluorescent explosives detection

- Many common explosives include TNT, DNT etc
- Nitroaromatic compounds are strong electron acceptors

Introduction of nitroaromatic molecule leads to dissociation of exciton and quenches emission

Swager et al., Chem Rev 107, 1339 (2007)  Richardson et al., APL 95 063305 (2009)
Sensitivity enhancement with polymers

- Reversible binding of nitroaromatic molecule with fluorophore
- Only fluorescence from the bound molecules is quenched

Toal et al., J Mater Chem, 16, 2871

- Conjugated polymer - series of connected fluorescent sites
- One nitroaromatic molecule can quench emission from whole chain

Toal et al., J Mater Chem, 16, 2871
Fluorescence sensing with polyfluorene

- Polyfluorene film exposed to ~10ppb dinitrobenzene vapour in air
- 15% drop in fluorescence
- Fluorescence recovers to original value when purged in nitrogen
Polyfluorene Laser Explosives Sensor

Polyfluorene DFB laser exposed to ~10ppb DNB vapour in air
- 85% drop in emission
- Factor 3 change in slope efficiency
- Lasing recovers to original performance when purged in N₂

Lasers could 'sense' vapours released by explosives

By Katia Moskworth
Science reporter, BBC News

Scientists believe robots might soon replace people in the search for landmines. UK scientists claim to have developed laser technology able to sense hidden explosives.

The technology could help to detect landmines and roadside bombs and to improve airport security.

The team from University of St Andrews produced a laser by ‘pumping’ a type of plastic called polyfluorene with photons from another light source.

They found the laser reacted with vapours from explosives such as TNT.

The work was published in the journal Advanced Functional Materials.

Graham Turnbull, a physicist at the University of St Andrew's in Fife, UK, is one of the authors of the study.
Some Future Applications

► Integrated tunable lasers sources for spectroscopy

► Intrinsic chemical sensing

► Optical amplifiers/modulators

A. Rose et al., Nature 434, 876 (2005)

Amarasinghe et al., APL 92, 083305 (2008)
Advanced Polymer Photonics: Optical Amplifiers

Need for low cost amplifiers e.g. compensate splitting losses
Compatibility with polymer optical fibre, planar lightwave circuits
Scope for very broad amplification bandwidth
Solution Polymer Optical Amplifier

Amplify a weak light pulse to a strong one

First demonstrated in solution

Tuneable Oscillator 580–630 nm

Polymer Optical Amplifier

Nitrogen Laser 337 nm (0.5 ns)
Solution Polymer Amplifier: High Gain, Broadband

Gain over 30 dB in 1 cm
Bandwidth >50 nm
or 50 THz

APL 80, 3036 (2002) and 85, 6122 (2004)
Solid State Polymer Amplifiers

Gain up to 21 db: signal amplified 100 times
Wide wavelength range
A Polymer Optical Amplifier Using F8BT: Amplification of a Pulse Sequence with 70 ps Spacing

Gain characteristics of multiple pulses
$\sigma = 6 \times 10^{-17} \text{ cm}^2$

Three pulses in a 140 ps window.
Amplification $> 20$ dB.
Repetition rate 5 kHz.
Pulse shape not affected.
Optical Switching of Gain

Input

Output from amplifier

Push pulse

1 2 3 4 5

500 nm

800 nm
Optical Switching of Gain in a Co-polymer

\[
\begin{align*}
\tau_1 &= 0.05 \text{ ps} \quad (a_1 = 0.86) \\
\tau_2 &= 1 \text{ ps} \quad (a_2 = 0.14)
\end{align*}
\]

\[\Delta T/T \text{ (arb units)} \]

Time (ps)

C$_{8}$H$_{17}$ C$_{8}$H$_{17}$ \( x = 0.9 \)

\( y = 0.1 \)

Optical Switching of Copolymer Amplifier

Amplified

Push blocked- amplified again

Switched off by push pulse

Input

Organic Semiconductor Lasers and Optical Amplifiers: Conclusion

► Organic Semiconductor Lasers:
► Compact, tuneable visible lasers
► Simple fabrication
► Direct pumping by InGaN LED demonstrated

► Polymer Optical Amplifiers
► Strong gain >20 dB/mm over broad bandwidth
► Potential compatibility with POF

► Optical Switching
► All-optical switching of gain and lasing demonstrated
► Promising building blocks for polymer photonics

Further Reading

► Samuel and Turnbull Chem. Rev. 2007
► Yang, Turnbull, Samuel APL 2008
► Lupton Nature 2008
► Samuel, Namdas, Turnbull, Nature Photonics 2009