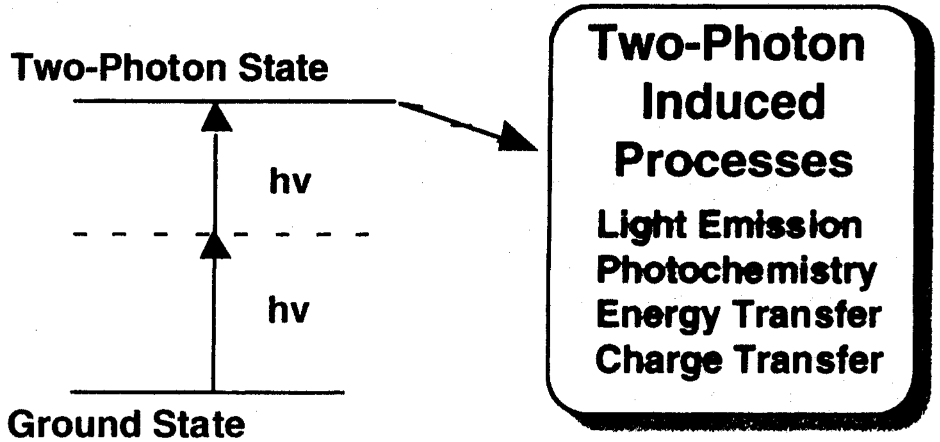
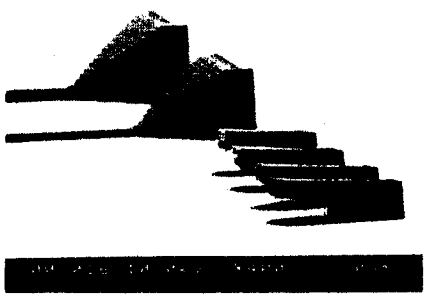
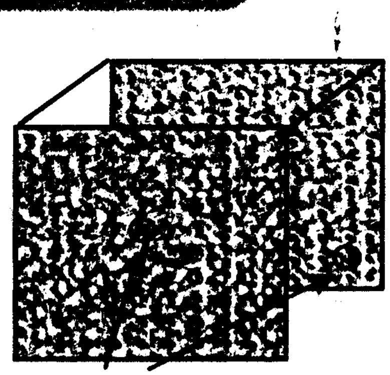
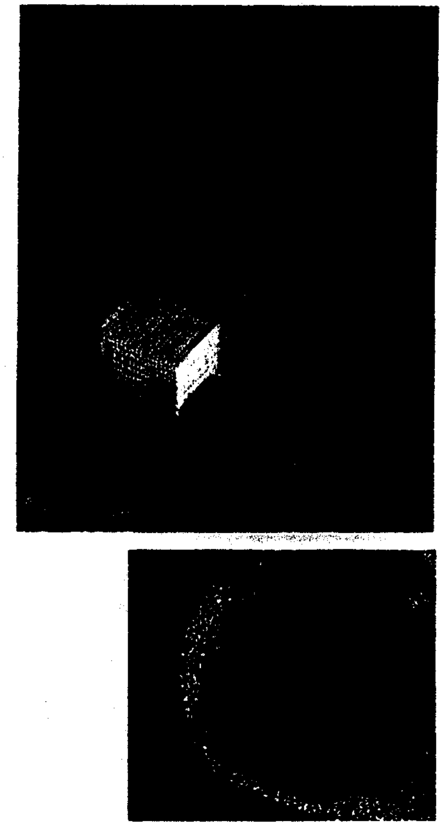
Two-Photon Absorbing Materials Impact a Wide Range of Applications









3-D Microfabrication
- Photonic Bandgap Materials
- Micro-optical Components
- MEMS

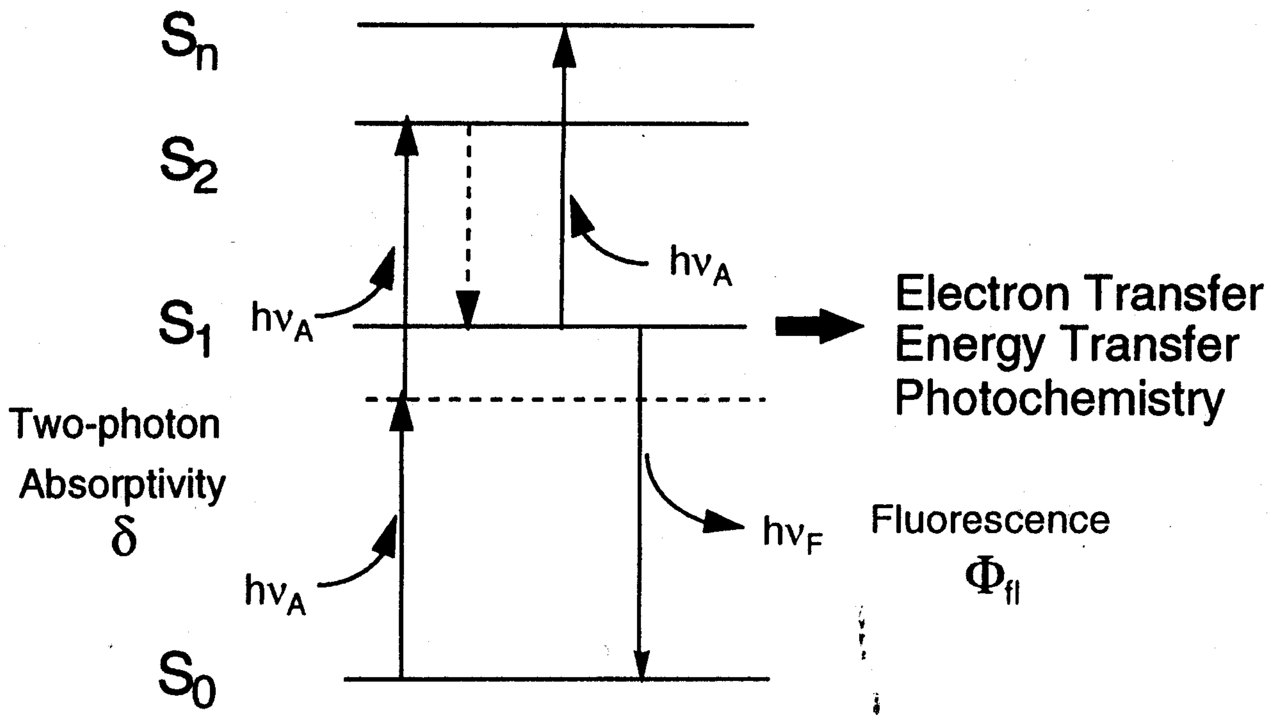
3-D Optical Memory
- Terabit Storage
- 3D ROM
- Fluorescent Memory

Biomedical Applications
- Imaging in Tissues
- Photodynamic Therapy
- Immunological Assays

Outline

- Two-photon absorption background
- Molecular design strategy
- Two-photon polymerization
- 3D microstructures
- Two-photon patterning of metals
- Biological imaging

Two-Photon Excited Processes



History of Two Photon Absorption

1931 — Two-photon absorption predicted by Maria Göppert-Mayer
Ann. Phys. 9, 273-295 (1931).

1960 — Invention of Laser

1961 — Two photon absorption is observed in CaF_2:Eu^{+2} crystal

W. Kaiser and C.G.B. Garrett. Phys. Rev. Lett. 7, 229-231(1961).

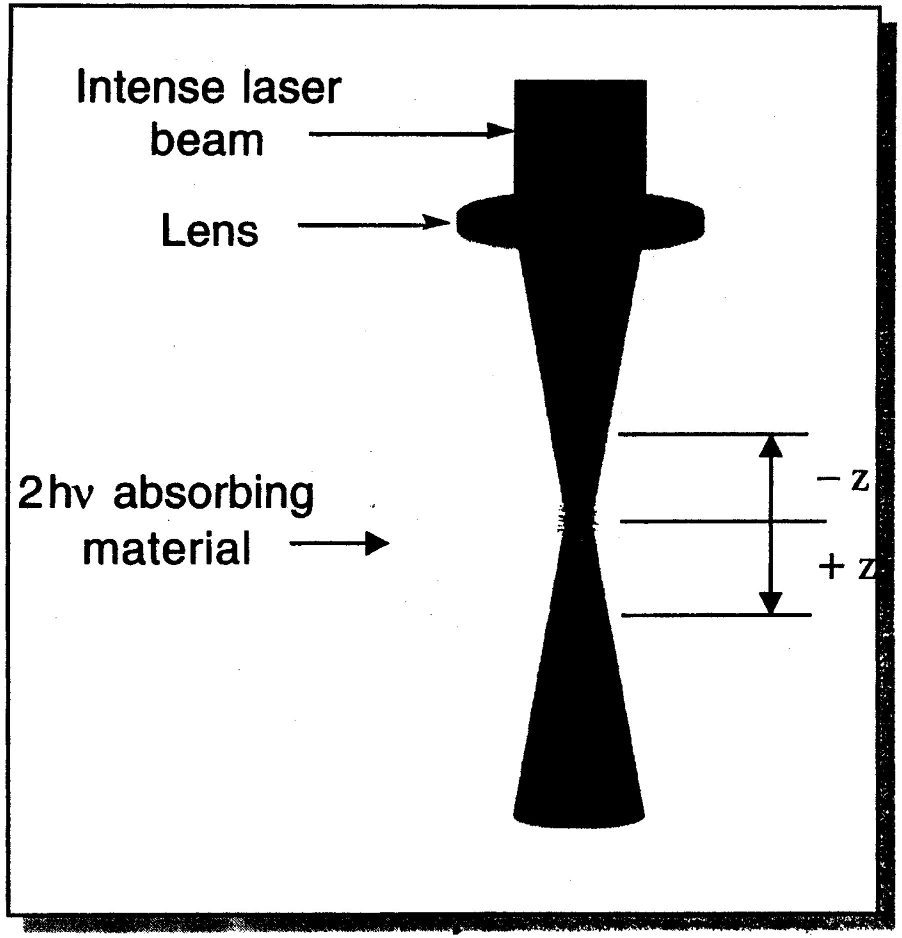
1975 — Two-photon used as molecular spectroscopic tool

1990 — Two Photon Fluorescence Microscopy and Optical Data Storage

W. Denk, J.H. Strickler, W.W. Webb, Science (1990).

P. Rentzepis et al Science (1990)

Two-Photon Absorption: 3D Resolved Pinpoint Excitation



- **3-D Confinement**

$TPA \propto I^2$

↓

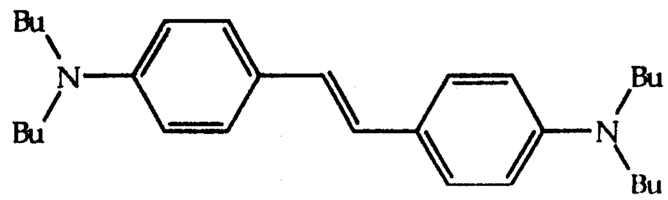
$I \propto z^{-2}$

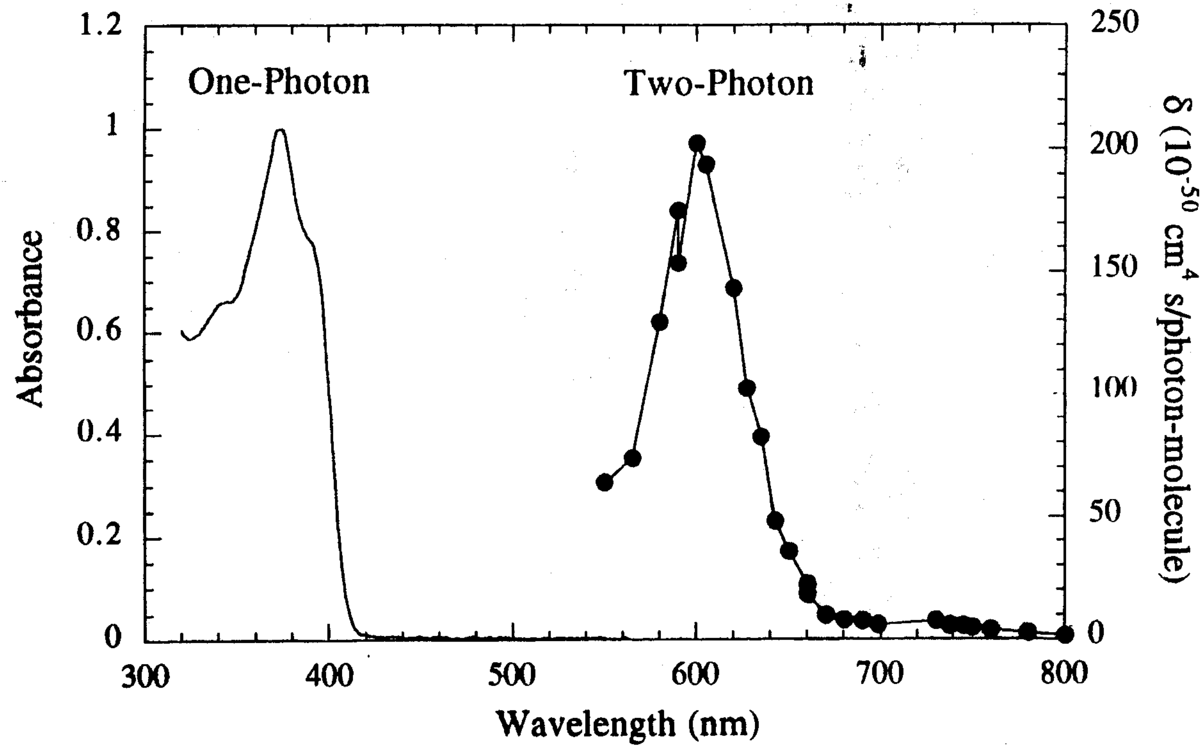
↓

$TPA \propto z^{-4}$

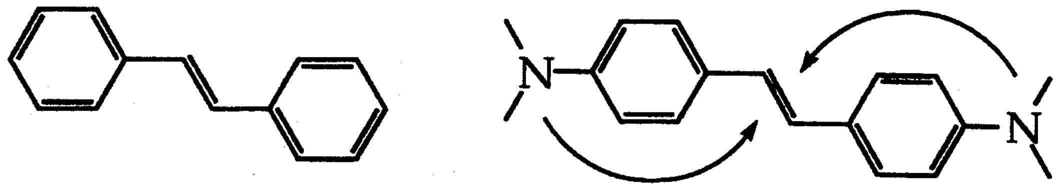
Excitation at ~ $2\lambda_{op}$ affords reduced linear absorption and scattering

One- and Two-Photon Absorption Spectra for *Bis*(dibutylamino)stilbene (BDAS)

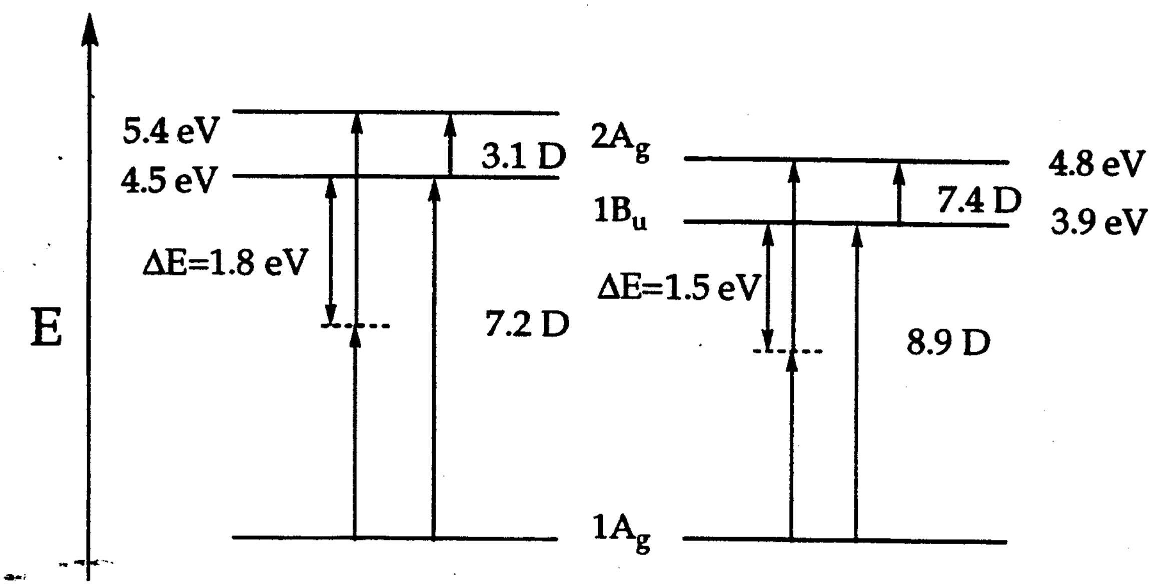


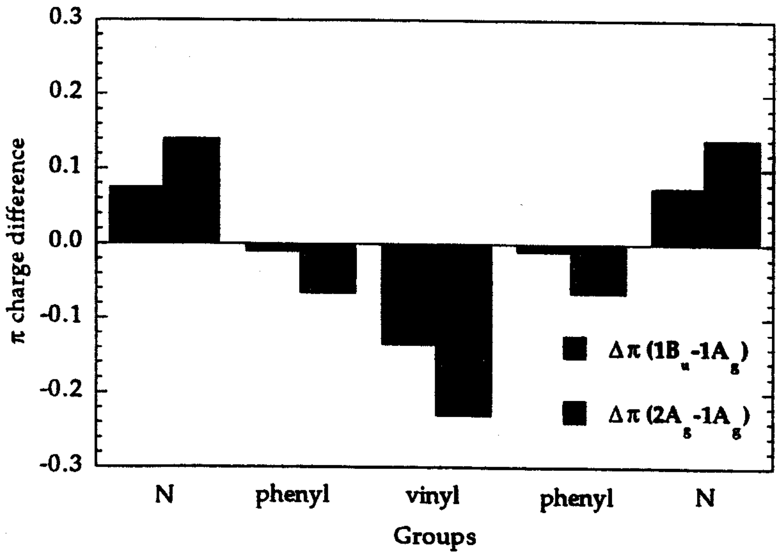


Effect of bis-Donor Substitution



$\delta \approx 10 \times 10^{-50}$ cm^4 s photon^{-1} $\delta \approx 200 \times 10^{-50}$ cm^4 s photon^{-1}



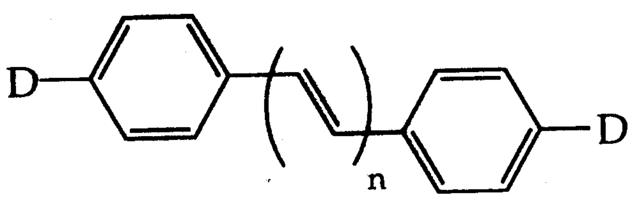


Semiempirical Calculations (Brédas et al. 1997)

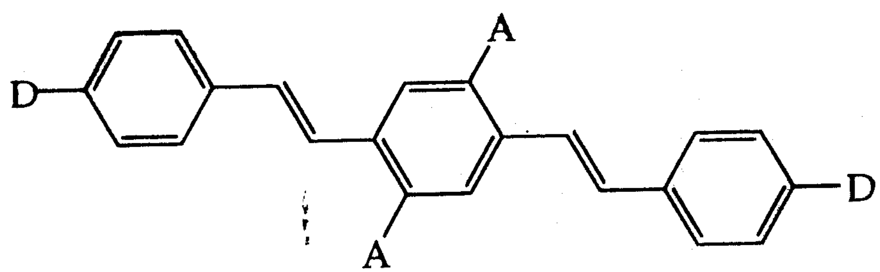
Strategies for the Design of New Materials

D-π-D

Increase conjugation length



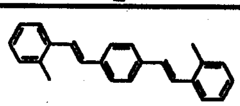
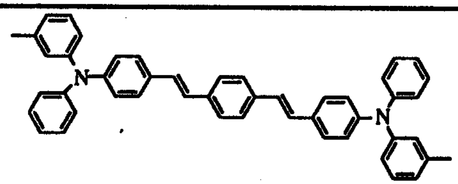
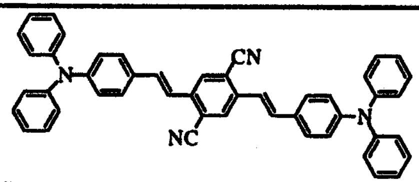
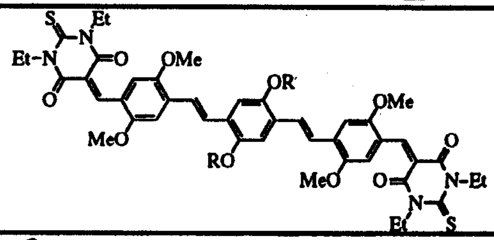
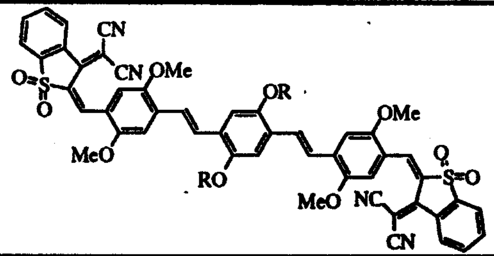
Add electron acceptors to the backbone



D–π–A–π–D

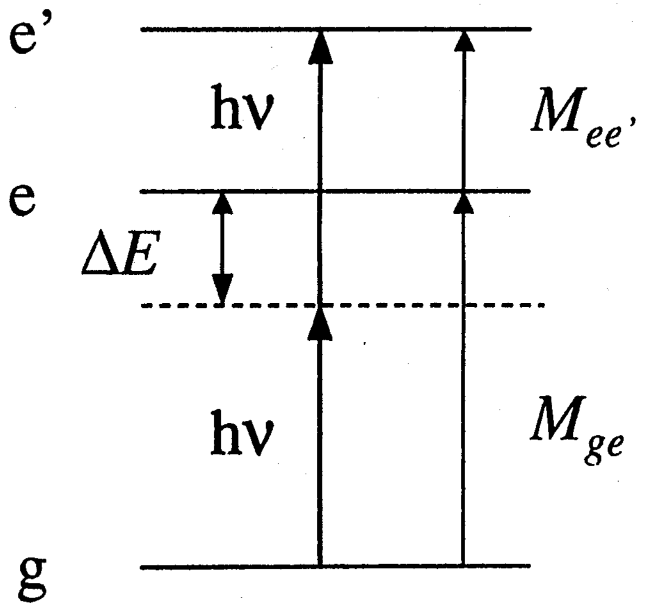
Also: **A–π–D–π–A**

D-A-D and A-D-A Molecules

Compound	$\lambda^{(2)}_{max}$ (nm)	δ_{max} (GM)	Φ_{fl}
	568	55	0.95
	745	805	0.93
	835	1940	0.86
	970	1750	0.06
	975	4400	0.0085

- ~ 100 times increase in δ

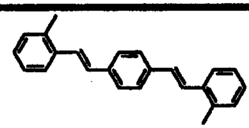
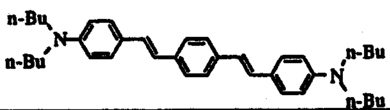
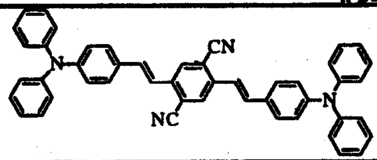
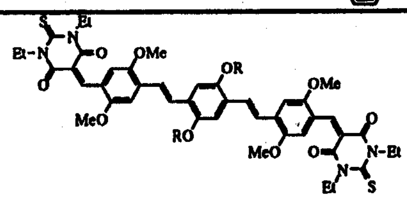
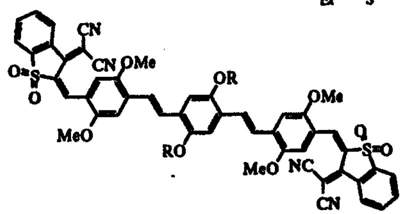
Two-Photon Absorption



$$\delta \propto \frac{M_{ge}^2 \, M_{ee'}^2}{\Delta E}$$

Effect of D/A Substitution

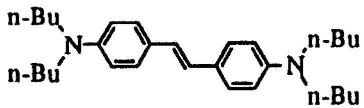
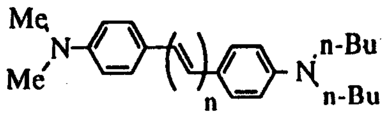
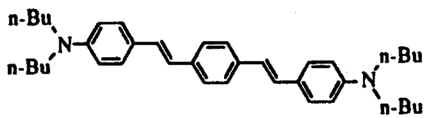
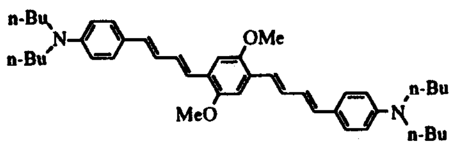
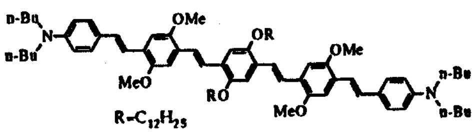
$$\delta_{ge'} \propto M_{ge}^2 \, M_{ee'}^2 \, \Delta E^{-2}$$

Compound	δ (GM)	ΔE (eV)	M_{ge} (D)	$M_{ee'}$ (D)
	55	1.41	8.9	2.9
	995	1.34	10.8	12.0
	1940	1.16	11.1	16.2
	1750	0.96	13.5	12.1
	4400	0.73	11.6	17.1

- **Increase in $M_{ee'}$**
- **Decrease in $\Delta E = E_{ge} - \hbar\omega$**

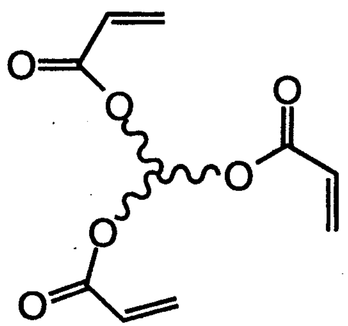
Effect of Increased Chain Length

$\delta_{ge'} \propto M_{ge}^2 M_{ee'}^2 \Delta E^{-2}$

Compound	δ (GM)	ΔE (eV)	M_{ge} (D)	$M_{ee'}$ (D)
	210	1.26	7.7	6.0
 n=4	360	1.16	12.44	5.3
	995	1.34	10.8	12.0
	1250	1.14	11.9	10.9
	1420	1.17	14.5	10.7

- **Increase in $M_{ge'}$**
- **Decrease in $\Delta E = E_{ge} - \hbar\omega$**

Two-Photon Photopolymer Systems



$\xrightarrow[\text{D-}\pi\text{-D TPA dye}]{2h\nu}$ **Cross-linked polymer**

- **Polymerization of triacrylates in liquids and solid photopolymer films**
- **Polymerization takes place in methanol--radical mechanism**

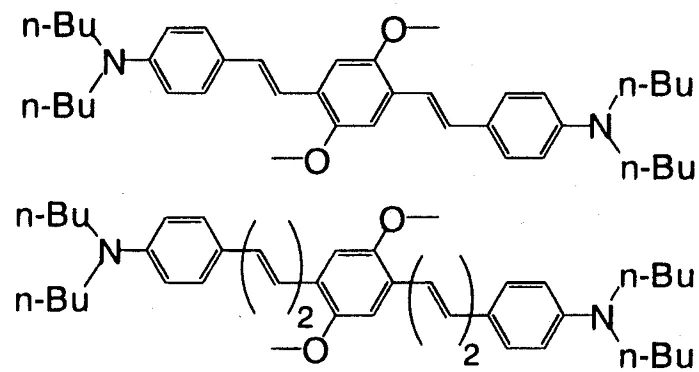
Two-photon cross-linking of acrylates forms the basis of our current photopolymer systems

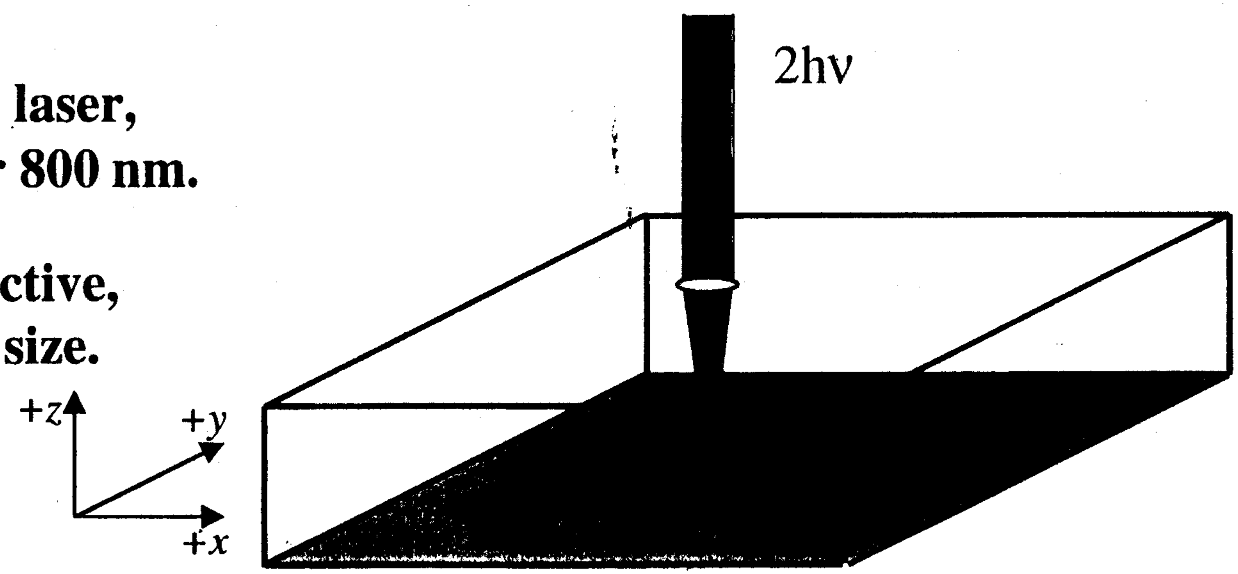
3D Microfabrication in Two-Photon Photopolymer Films

- **Photopolymer: 70% crosslinkable acrylate monomer, 30% polymer binder, 0.1% two-photon initiator. Cast as 100-140 μm thick film.**

- **Laser: Ti:Sapphire laser, 150 fs pulses, 730 or 800 nm.**

- **Optics: 1.4 NA objective, 0.35 μm radial spot size.**

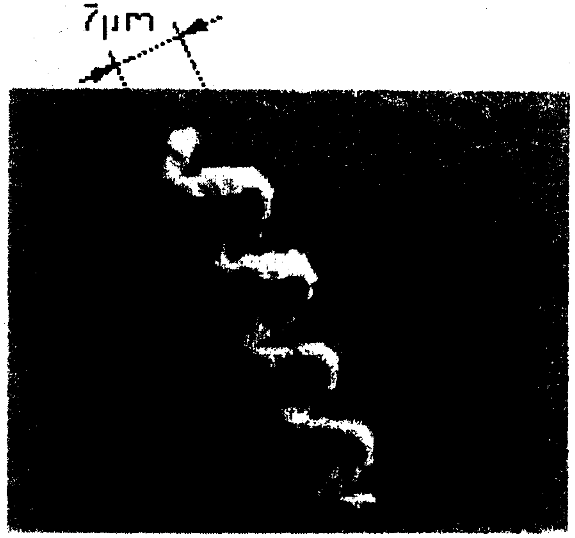




Two-Photon 3D Micro-fabrication ca. 1995

Strickler & Webb SPIE **1398**, 107 (1990)

Writing conditions:
100 fs pulses, 5 mW, 10 ms dwell time (0.2 ms threshold)

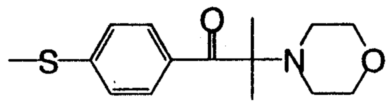
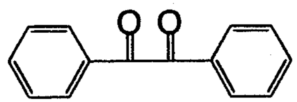
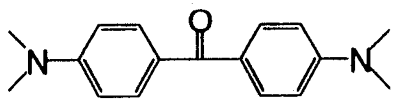
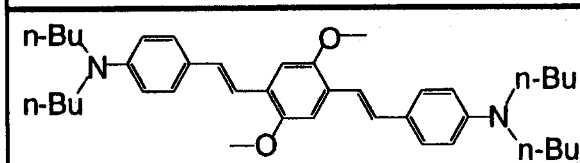
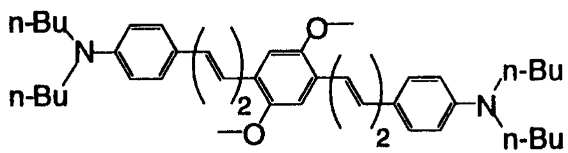


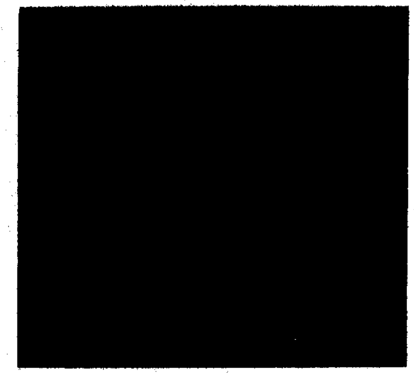
Maruo & Kawata Opt. Lett. **22**, 132 (1997)

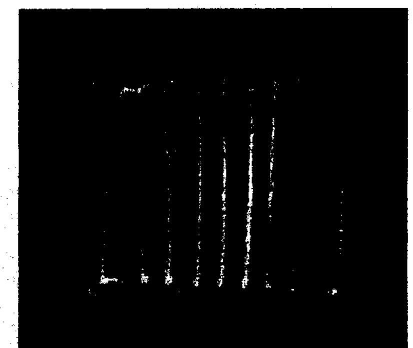
Writing conditions:
200 fs pulses, 20 mW, 8 ms dwell time

Early work employed commercially available UV photoinitiators which have small two-photon absorptivities

New Dyes Provide Improved Sensitivity for Two-Photon Polymerization

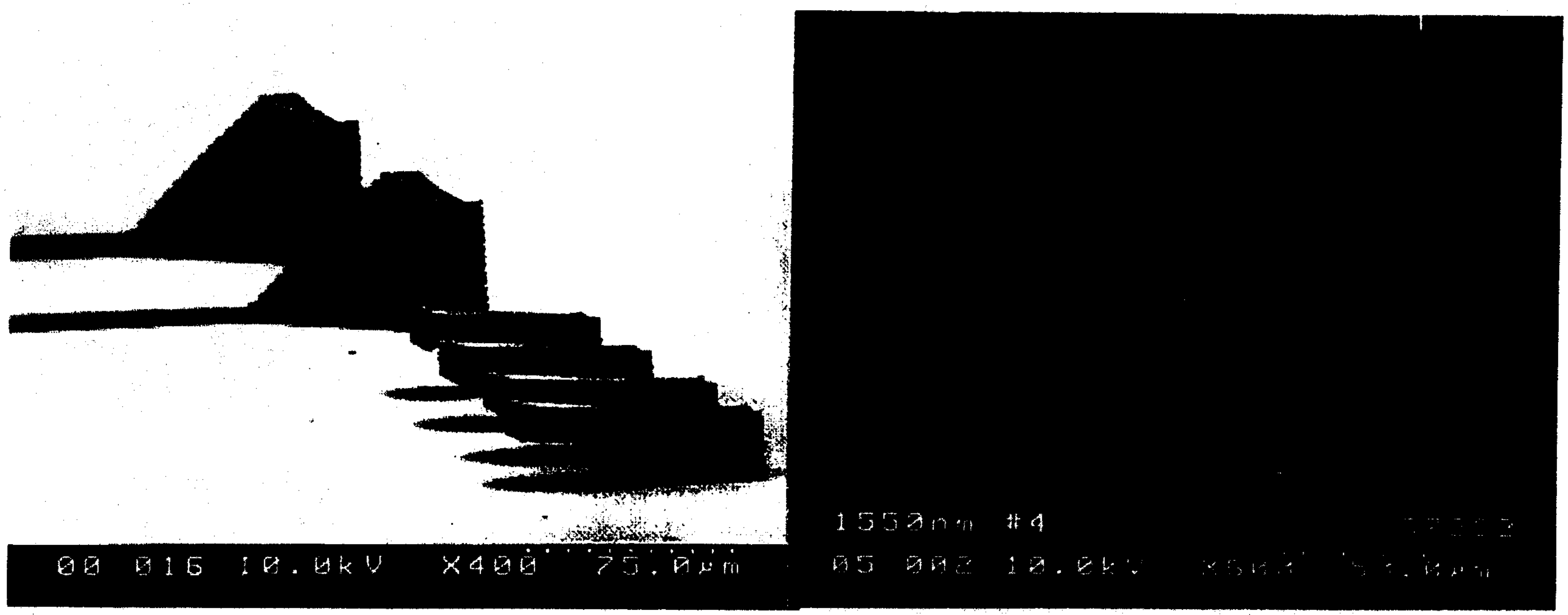
	Initiator	Writing Threshold (mW)	Writing Power range
		~10	1
		~10	1
		4	2.5
New Dyes		0.2	50
		0.3 (800 nm)	33





Data for 120 fs Pulses at 730 nm, 20 ms dwell time

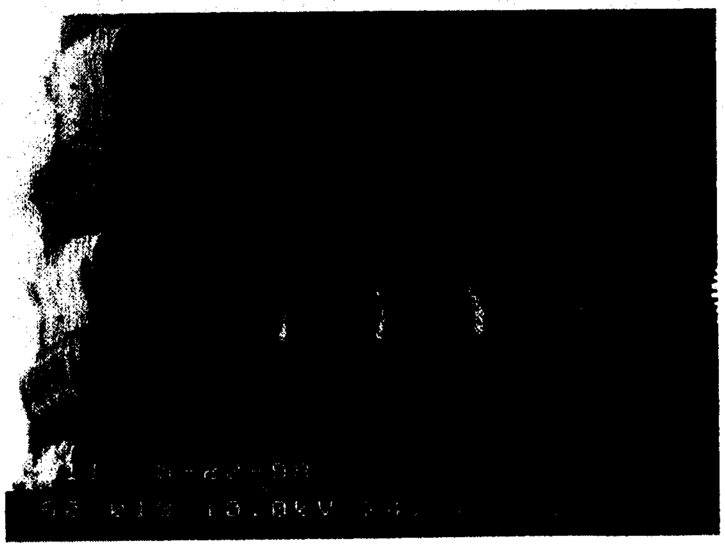
Micro-Optics and MEMS by Two-Photon Polymerization

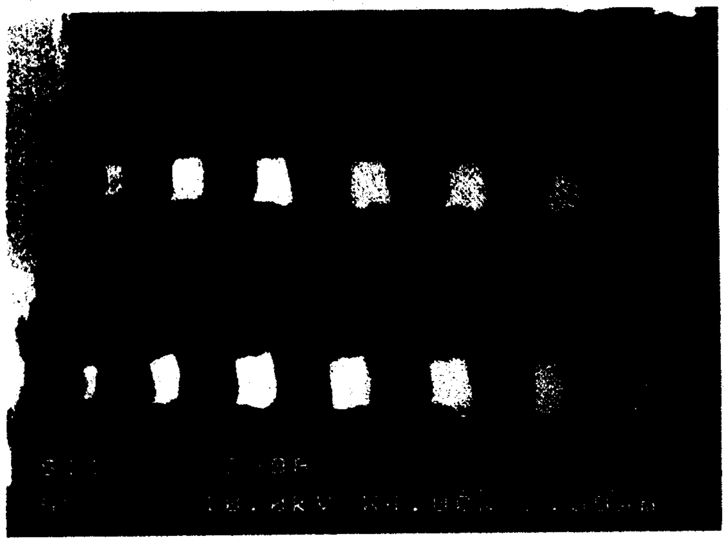


Two-photon photopolymers provide capability to fabricate complex 3D microstructures

Photonic Bandgap Structures

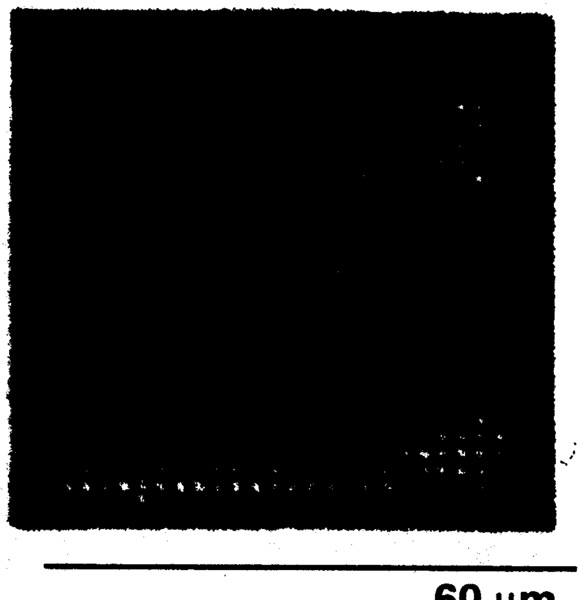
- **3D periodic structures -- Infrared filters, waveguides, & camouflage.**
- **"Stack-of-logs" with 5 μm periodicity; useful in the IR; fabricated in a single step.**
- **Structure can be coated or filled for higher dielectric contrast.**



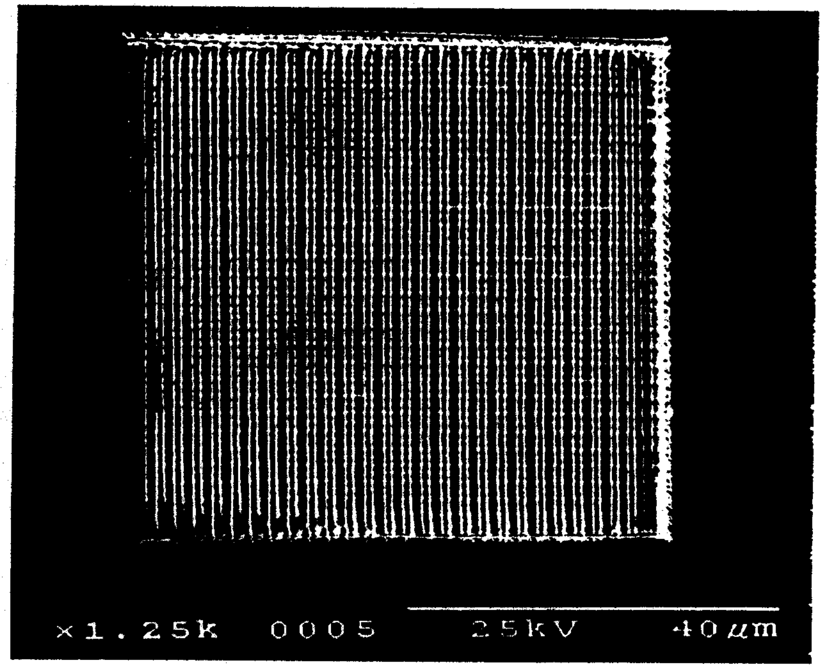


Photonic Bandgap Structure

~1 μm period



Optical microscope image

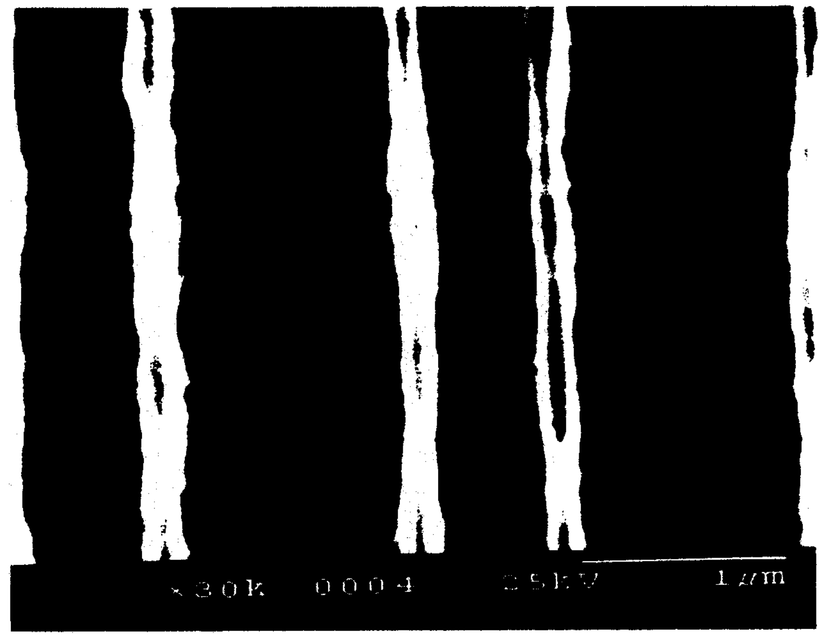


Scanning electron micrograph

Photonic Bandgap Structure

~1 μm period

Scanning electron micrograph

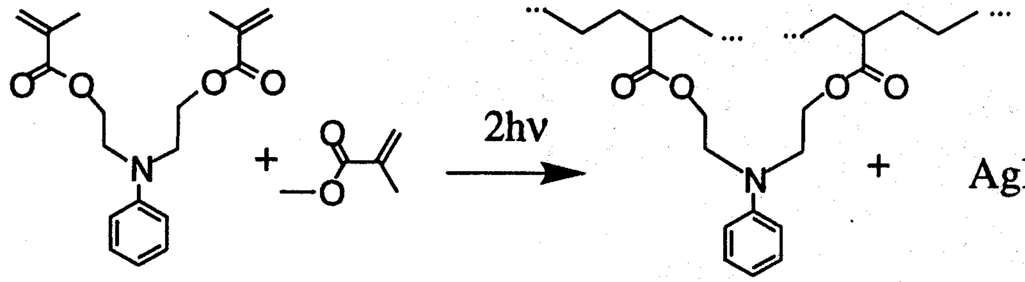


Scanning electron micrograph.

~200 nm linewidth

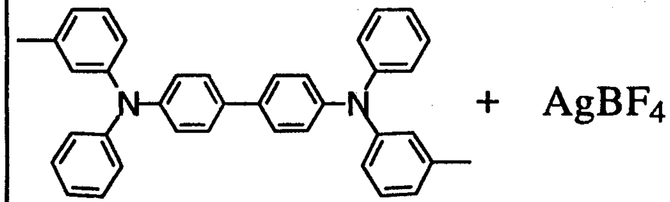
Methods for Two-Photon Photodeposition of Ag Metal

Method 1



+ $AgBF_4$ ⟶ **Ag^0 coated surface**

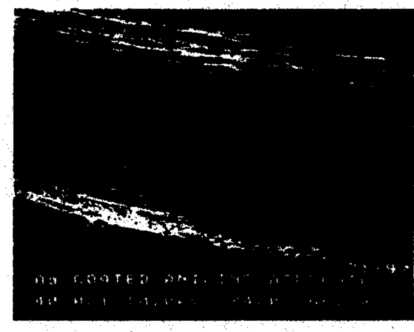
Method 2



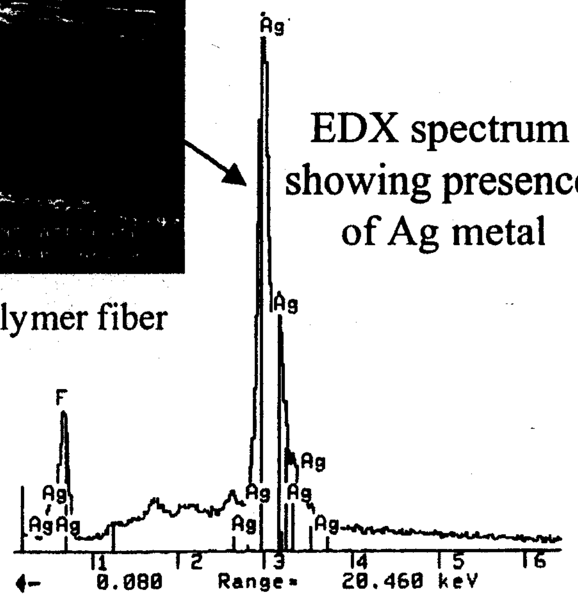
+ $AgBF_4$

2hν ⟶ **Ag^0 nanoparticles**

Cellulose acetate gel

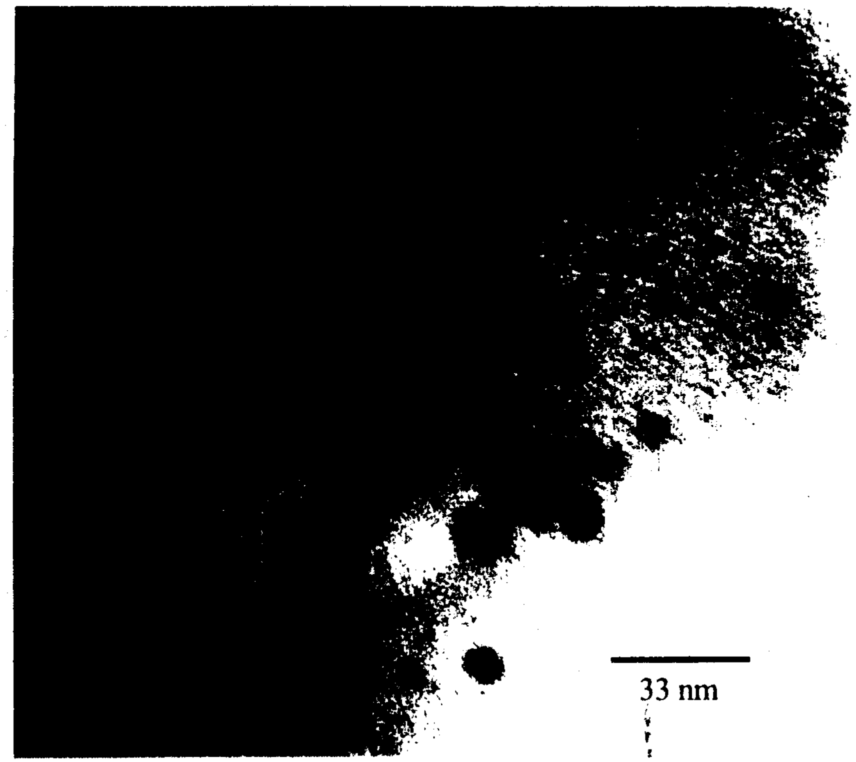


Ag coated polymer fiber



EDX spectrum showing presence of Ag metal

Photochemically Produced Ag Nanoparticles



TEM Image