AFRL-AFOSR-UK-TR-2021-0002

Development of linear and non-linear optical materials based on sol-gels doped with functional materials

Gvishi, Raz
SOREQ - NAHAL SOREQ NUCLEAR RESEARCH CENTER
SOREQ
YAVNE, , 81800
IL

03/08/2021
Final Technical Report

Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515 Box 14, APO AE 09421

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
08-03-2021

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
15 Mar 2016 - 20 Mar 2020

4. TITLE AND SUBTITLE
Development of linear and non-linear optical materials based on sol-gels doped with functional materials

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-16-1-0201

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Raz Gvishi

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
SOREQ - NAHAL SOREQ NUCLEAR RESEARCH CENTER
SOREQ
YAVNE, 81800
IL

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
EOARD
UNIT 4515
APO AE 09421-4515

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR IOE

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-UK-TR-2021-0002

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The purpose of the project was to study routes for doping functional materials in Sol-Gel matrices. Sol-Gel materials were produced and doped with functional materials such as carbon nanotubes (CNT) and 2 photon absorption (2PA) chromophores. The dye : Sol-Gel solution was cast and optical filters were fabricated. The obtained filters were polished, and their spectral properties studied. The samples were sent to Dr. Thomas Cooper, Air Force Research Laboratory (AFRL), Wright-Patterson Air Force Base OH, for additional nonlinear spectroscopic studies.
The following routes for doping functional materials in Sol-Gel matrices were studied: Sol-Gel doped with CNT and 2PA chromophores; Sol-Gel doped with 2PA platinum complex (E1-BTAF-OH) chromophore supplied by AFRL; Enhancing NLO properties by controlling the singlet-triplet transition of E1-BTAF-OH doped in Sol-Gel. The main achievement was succeeding to control the singlet-triplet intersystem-crossing (ISC) of AFRL 2PA chromophore, E1-BTAF-OH, doped in fast Sol-Gel (FSG) matrix. We succeed by modifying the FSG, to a more aromatic matrix, to convert the 2PA chromophore from its singlet-state form to its triplet-state form. The Sol-Gel matrix modification was achieved by adding tri-methoxy-phenyl-silane (TMPS) precursors to the Sol-Gel production process. A high optical quality Sol-Gel disc with triplet-state chromophore form was obtained. The sample was sent to Thomas Cooper at AFRL for additional NLO characterization to test the enhancement of the NLO properties.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			JASON FOLEY
U	U	U	SAR	17	**19b. TELEPHONE NUMBER** *(Include area code)* 555-555-5555

Standard Form 298 (Rev.8/98)
Prescribed by ANSI Std. Z39.18

AFOSR/EOARD Final report: Development of Linear and Non-Linear Optical Materials Based on Sol-Gels Doped with Functional Materials

By
Raz Gvishi, Ilan Sokolov and Galit Bar

<u>AFOSR/EOARD project</u>
Grant Number: FA955o-16-i-0201
PI: Raz Gvishi
Institution: Applied Physics Division, Soreq
EOARD IPO: **Dr. Jason Foley (jason.foley.1@us.af.mil)**

November 2019

Abstract

(less than 250 words.)

The purpose of the project was to study routes for doping functional materials in Sol-Gel matrices. Sol-Gel materials were produced and doped with functional materials such as carbon nanotubes (CNT) and 2 photon absorption (2PA) chromophores. The dye : Sol-Gel solution was cast and optical filters were fabricated. The obtained filters were polished, and their spectral properties studied. The samples were sent to Dr. Thomas Cooper, Air Force Research Laboratory (AFRL), Wright-Patterson Air Force Base OH, for additional nonlinear spectroscopic studies.

The following routes for doping functional materials in Sol-Gel matrices were studied: Sol-Gel doped with CNT and 2PA chromophores; Sol-Gel doped with 2PA platinum complex (E1-BTAF-OH) chromophore supplied by AFRL; Enhancing NLO properties by controlling the singlet-triplet transition of E1-BTAF-OH doped in Sol-Gel. The main achievement was succeeding to control the singlet-triplet intersystem-crossing (ISC) of AFRL 2PA chromophore, E1-BTAF-OH, doped in fast Sol-Gel (FSG) matrix. We succeed by modifying the FSG, to a more aromatic matrix, to convert the 2PA chromophore from its singlet-state form to its triplet-state form. The Sol-Gel matrix modification was achieved by adding tri-methoxy-phenyl-silane (TMPS) precursors to the Sol-Gel production process. A high optical quality Sol-Gel disc with triplet-state chromophore form was obtained. The sample was sent to Thomas Cooper at AFRL for additional NLO characterization to test the enhancement of the NLO properties.

In addition, we proposed a continuation project for 2020, entitled: "Additive manufacturing with Sol-Gel - 3D-printing gradient-index (GRIN) optical devices based on UV-cured Sol-Gel materials".

Keywords

Optical filters, Sol-Gel, 2-photon absorption (2PA), carbon nanotubes (CNT). Singlet-Triplet intersystem crossing (ISC), Platinum complex chromophores, Donor – Acceptor system, Fluorescence emission and Phosphorescence emission.

Objective:

Research and development of optical filters by doping functional materials in Sol-Gel matrices.

Introduction

The two-photon absorption (2PA) mechanism is a well-known method used in nonlinear optical filters for controlling the exposed light intensity; so called optical limiters [1]. Two-photon absorbing (2PA) materials have been studied extensively in the past decades [2]. The possibility to achieve significant 2PA cross-section is dependent on materials with an unsymmetrical cloud of electrons which have locally high electrons density. Commonly studied families of 2PA materials are; organic chromophores (composed of donor (D) – acceptor (A) system) [3,4] and carbon-based materials (CNT, fullerenes, graphene) [5] which are effectively in the visible region, while semiconductors (such as ZnSe) [6] are effective in the infra-red (IR) region. However, most of the studied works of organic chromophores and carbon-based materials were done in liquid solvent matrices. Nevertheless, liquid solvent matrices are not appropriate for most optical applications. Another common approach uses organic polymeric matrices which suffer from limitations in their mechanical and optical properties and therefore are also not appropriate for optical applications. Much more appropriate for optical applications are matrices based of inorganic polymers or hybrid ceramics materials. A well-known method for fabrication of such inorganic optical matrices is the sol-gel technology [7]. The Sol-gel process allows fabrication of inorganic or hybrid inorganic-organic optical materials at low temperature while adding a variety of dopants and resulting in tailored structures. Especially, we developed at Soreq a fast sol-gel process which allows fabrication of hybrid glassy monolith without shrinkage and cracks, and possessing good mechanical and optical properties [8,9].

At our photonics group at Soreq we have long term experience in studying both 2PA materials and sol-gel materials. We have studied in the past (with P. Prasad at SUNY Buffalo) nonlinear properties of organic chromophores such as BBTDOT (thiazole-thiophene-thiazole, A-D-A structure) in solution [10], DDPPH/DDOPPH (polyphenyl-didecyl- polyphenyl, A-D-A structure) in solution and in sol-gel matrix [11], ASPI/ASPT (Pyridinium-Amino, A-π-D structure) [12], C_{60} (fullerenes) and BBTDOT doped both in sol-gel matrix [13]. More recently we studied tetraketo (TK) chromophores (Benzo-hydrindacene-Benzo, D-A-D structure) in solution as 2PA florescence probes [14] and Carbazol-derived chromophores (carbazolyl-biphenyl- carbazolyl, D-A-D structure) as UV-trigger for resonance energy transfer (RET) to photochromic dyes [15].With the NLO group at CREOL we studied Fluorene-based molecules (Phenyl-Styryl–Fluorene-Styryl-Phenyl, A-π-Fl-π-A or D-π-Fl-π-D structures) in solution [16]. Lately we demonstrated other nonlinear processes in solid-state matrices-based sol-gel technology. We demonstrated a nonlinear solid-state filter based on photochromism induced by 2-photon absorption in a dye-doped sol-gel (with NLO group at CREOL) [17] and studied nonlinearity of carbon nanotubes (CNT) in sol-gel filters [18,19]. The fast sol-gel (FSG) process which was developed at Soreq can be a "toolkit" for fabrication of optical materials and elements. The advantages of FSG are: Rapid manufacturing process, solidification without shrinkage and without formation of cracks [20], dual thermal or UV-curable materials with low organic content [21], high optical transparency [22], high adhesive strength and high temperature stability [23], High laser damage threshold, adaptable opto-mechanical properties (refractive index, dn/dT) [24].

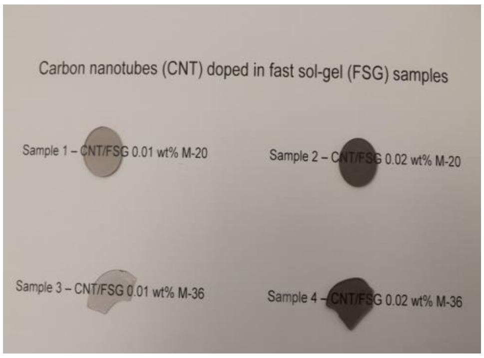
Results and discussion

In this section we present the research work which was done during the current project. We studied routes for doping functional materials in Sol-Gel matrices. Sol-Gel materials were produced and functional materials such as carbon nanotubes (CNT) and 2-photon absorption (2PA) chromophores were doped in them. The dye : Sol-Gel solution was cast and optical filters were fabricated. The obtained filters were polished and studied for spectral properties. The samples were sent to Dr. Thomas Cooper, Air Force Research Laboratory (AFRL), Wright-Patterson Air Force Base OH, for additional nonlinear spectroscopic studies. In the First Year Sol-Gel matrices doped with CNT were studied; In the Second Year, Sol-Gels doped with 2PA platinum complex (E1-BTAF-OH) chromophore supplied by AFRL were studied; In the Third Year a modified aromatic Sol-Gel matrix was developed, allowing to convert the 2PA chromophore from its singlet-state form to its triplet-state form. The Sol-Gel matrix modification was achieved by adding tri-methoxy-phenyl-silane (TMPS) precursors to the Sol-Gel production process. A high optical quality Sol-Gel disc with triplet-state chromophore form was obtained. The sample was sent to Thomas Cooper at AFRL for additional NLO characterization to test the enhancement of the NLO properties.

Year-1

As a continuation to our previous work on Carbon Nanotubes (CNT) doped in Sol-Gel matrices [18,19) we prepared and characterized a set of CNT:Sol-Gel filters. The set of 4 CNT:Sol-Gel discs are presented in Figure 1.

(a) All samples –

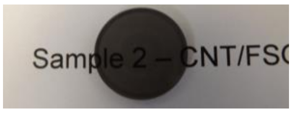


(b) Sample 1 – CNT/FSG 0.01 wt% M-20

h = 1.31 mm ± 0.01 mm

d = 21.7 mm ± 0.2 mm

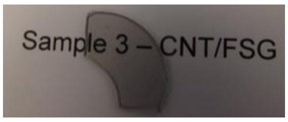
(c) Sample 2 – CNT/FSG 0.02 wt% M-20



h = 1.55 mm ± 0.01 mm

d = 21.0 mm ± 0.2 mm

(d) Sample 3 – CNT/FSG 0.01 wt% M-36



h = 0.82 mm ± 0.01 mm

d ~ 14 mm X 28 mm

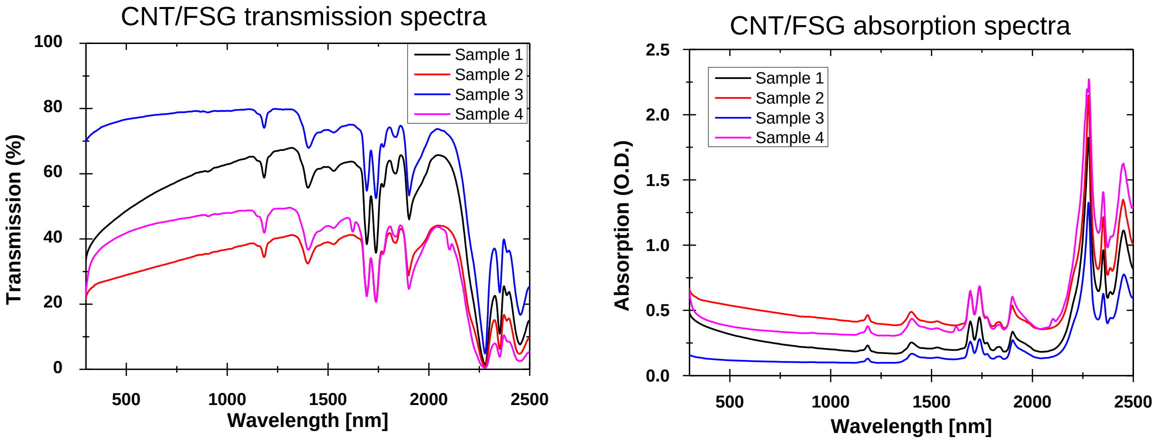
(e) Sample 4 – CNT/FSG 0. 02 wt% M-36

h = 1.90 mm ± 0.01 mm

d ~ 20 mm X 20 mm

Fig 1: CNT:Sol-Gel filters – set of 4 samples: photos and disc properties height (h) and dimeter (d). (a) all samples, (b) Sample 1 – CNT/FSG 0.01 wt% M-20, (c) Sample 2 – CNT/FSG 0.02 wt% M-20, (d) Sample 3 – CNT/FSG 0.01 wt% M-36, (e) Sample 4 – CNT/FSG 0. 02 wt% M-36

The set of 4 CNT:Sol-Gel discs were characterized for their optical propertied. Refractive index of $n = 1.430 \pm 0.005$ was measured for the samples using an AR-4D-type Kruss refractometer measured at $\lambda = 589$ nm (resolution ± 0.001). The optical spectrum was measured using a Jasco model V-570 spectrometer over the 300-2500 nm range with a 2 nm resolution. The transmission (a) and absorption (b) spectra are presented in Figure 2. In the wavelengths range 300-1100 nm the samples present good optical transparency which is reduced due to CNT concentration; Transmission of ~70% for 0.01 wt% CNT concertation and ~40% for 0.02 wt% CNT concertation. In the wavelengths range 1100-2500 nm there are absorption peaks due to the Sol-Gel structures as discussed in ref 22.



(a) (b)

Fig 2: CNT:Sol-Gel filters – transmission (a) and absorption (b) spectra.

These 4 samples were sent to Dr. Thomas Cooper, Air force research laboratory (AFRL), Wright-Patterson Air Force Base OH, for additional nonlinear spectroscopic studies. However, unfortunately it was found that the CNT dispersion in these Sol-Gel discs is not so good and aggregates are present which made the samples not appropriate for nonlinear spectroscopic measurements.

Year-2

The nonlinear materials group of Dr. Thomas Cooper at AFRL is focusing on studding nonlinear materials based on Platinum Acetylide as 2-photon chromophores for already decade (25-28). These bis(phenyl-ethynyl)bis(tri-butyl-phosphine)platinum(II) complexes feature highly π -conjugated ligands substituted with π-donor or π-acceptor moieties. The ligands have strong effective 2PA cross-sections, while the heavy metal platinum centers give rise to efficient intersystem crossing to long-lived triplet-states [25]. In solution the Platinum Acetylide chromophores present 2PA from singlet transitions of the order of 30-300 GM (1 GM = 10^{-50} cm^4/s) while for triplet transitions enhanced 2PA of the order of >1000 GM is obtained [26]. In addition, it was found that nonpolar media lead to a breaking of the ground-state symmetry and increase the intersystem crossing transition (ICT) to triplet-state [28].

We received from Dr. Thomas Cooper the Pt complex 2PA chromophore with two benzo-thiazolyl-fluorene units, molecule 1 in ref 25, but with the addition of OH moieties at both ends and called therefore E1-BTAF-OH, shown in Figure 3. The energy level diagram of Pt complex 2PA chromophore, E1-BTAF (molecule 1 in ref 25), presents an intersystem crossing from singlet to triplet states, τ_{isc}, shown in Figure 4a. This E1-BTAF chromophore present absorption and emission spectra in benzene solution which exhibit fluorescence (in air-saturated environment) at ~450 nm and phosphorescence (in deoxygenated environment) at ~600 nm, shown in Figure 4b for molecule 1 [25]. The E1-BTAF-OH Pt complex chromophore was already doped in Sol-Gel matrix [27] based of combination of silanes precursors with addition of gold nanoparticles (AuNP) for enhancement of plasmonic transition.

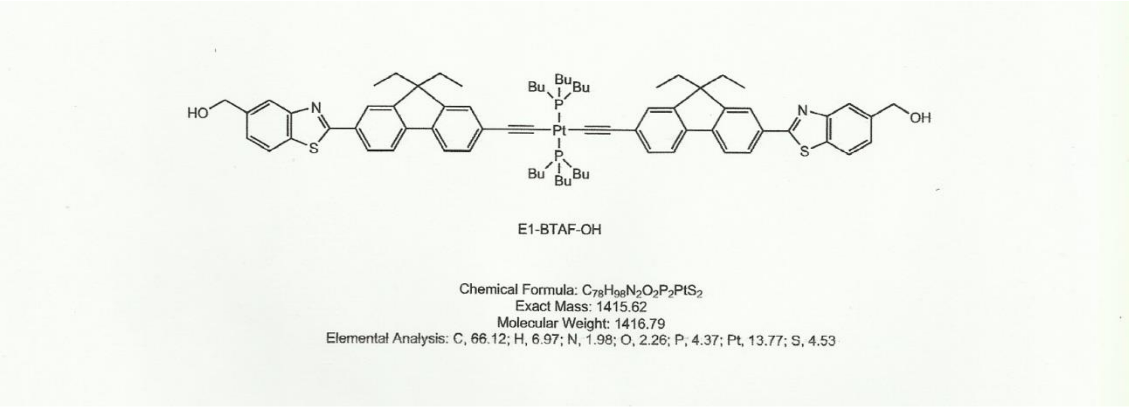
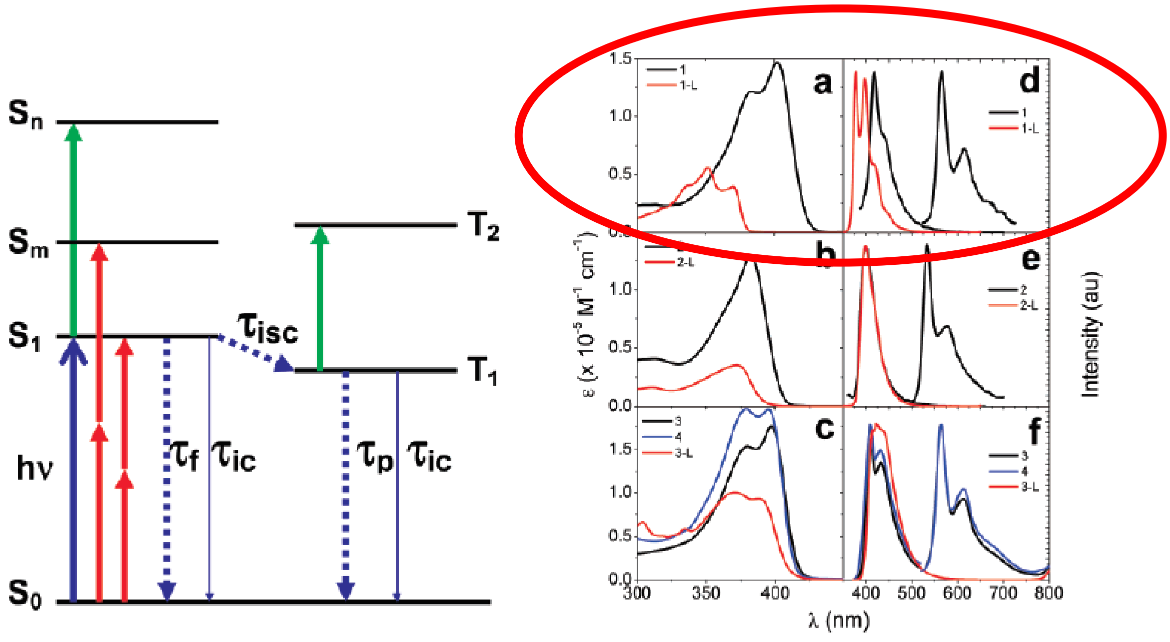


Fig 3: Platinum Acetylide 2PA chromophore with two benzo-thiazolyl-fluorene units, molecule 1 in ref 25, but with the addition of OH moieties at both ends and called therefore E1-BTAF-OH. It was supplied by Dr. Thomas Cooper from AFRL.

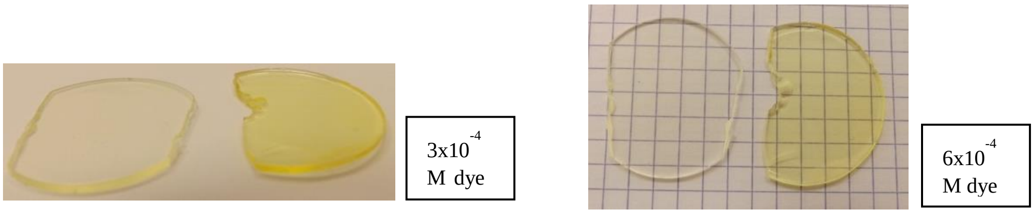


(a) (b)

Fig 4: Pt complex 2PA chromophore, E1-BTAF, molecule 1 in ref 25: (a) Energy level diagram presents an intersystem crossing from singlet to triplet states, τ_{isc}. (b)Absorption and emission spectra in benzene solution which exhibit fluorescence measured in air-saturated environment) and phosphorescence measured in deoxygenated environment, molecule 1 [25].

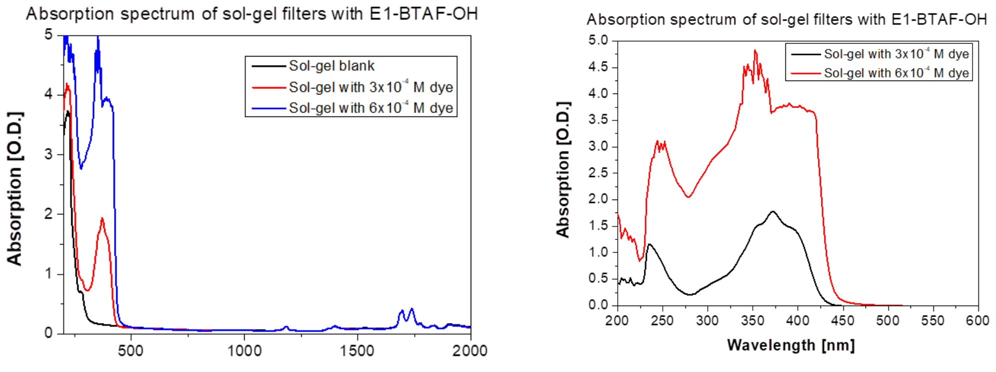
During the second year of the current research project we prepared Sol-Gel filters doped with the Pt 2PA chromophore E1-BTAF-OH using our standard procedure for fabrication of fast-sol-gel (FSG) materials. The concept of the FSG process is to complete the reaction of all the precursors and evacuation of the unnecessary products (alcohol and water) before gelation occurs. The process starts without adding any additional alcohol solvent and since the first stage is performed in a closed vial, the alcohol which is produced in the reaction acts as a common solvent. Briefly [8,9], the procedure consists of mixing of alkoxide and organically modified alkoxide precursors, such as Tetramethoxysilane (TMOS) Methyltrimethoxysilane (MTMS) and Dimethoxydimethylsilane (DMDMS), in a reaction vessel. An example of fast sol–gel starting combination is a mixture containing TMOS:MTMS:H_2O in molar ratio 0.2:1:2, respectively. The system is kept closed, allowing the temperature and pressure to increase without boiling above the standard boiling temperature of the alcohol, until all the hydrolysis of the precursors is completed. Then, a rapid evacuation of the unnecessary products (alcohol and water) is performed by releasing the pressure and pumping the system below atmospheric pressure. The process is stopped before gelation occurs, where the gel contains about 4% residual liquid and the material is still in a solution state. The product at this stage is a viscous resin which can be poured into a mold or diluted for long shelf life storage. In our case the viscous resin was diluted with THF in weight ratio 1:1. The Pt 2PA chromophore E1-BTAF-OH was also dissolved in THF solution and was added to the Sol-Gel:THF solution. Then, the THF was evaporated using a thermal heat treatment at 60ºC on a hotplate, resulting with the viscous resin doped with E1-BTAF-OH chromophore. This is followed, by pouring the viscous resin into Petri dishes, which are used as molds for achieving discs. The samples were left for a couple of days at 60ºC in an oven for completing thermal curing. Then the Sol-Gel discs were extracted from the mold and were polished for flatness and optical quality.

Two series of Sol-Gel filters doped with AFRL Pt 2PA chromophore E1-BTAF-OH were prepared and sent to Dr. Thomas Cooper, AFRL, for additional nonlinear spectroscopic studies. In Case of series 1 – two Sol-Gel filter discs with Pt complex 2PA chromophore, E1-BTAF-OH with 2 concentrations $3\text{x}10^{-4}$ M and $6\text{x}10^{-4}$ M were prepared and shown in Figure 5. The Absorption spectra of these samples are shown in Figure 6, were the absorption in the range 200-2000 nm is compared to blank Sol-Gel disc (4a) and the spectra in the range 200-600 nm (4b) presenting the peaks belonging to E1-BTAF-OH, where there is an increase in the absorption due to the concentration. Series 2 samples were improved Sol-Gel filter discs with Pt complex 2PA chromophore, E1-BTAF-OH with 2 concentrations $3\text{x}10^{-4}$ M and $9\text{x}10^{-4}$ M, shown in Figure 7. For these samples we measured the absorption (Figure 8a) and emission (Figure 8b) spectra. The samples present an absorption peak at 400 nm and fluorescence peak at 450 nm, while there can also be seen the existence of a small shoulder at ~600 nm which can be related to phosphorescence as presented in Figure 4b. The samples from series 2 were sent to Dr. Thomas Cooper, AFRL, for additional nonlinear spectroscopic studies.



(a) (b)

Fig 5: Series 1 - Sol-Gel filter discs with Pt complex 2PA chromophore, E1-BTAF-OH with 2 concentrations $3x10^{-4}$ *M and* $6x10^{-4}$ *M: (a) Side view photo. (b) Top view photo.*



(a) (b)

Fig 6: Series 1 – Spectroscopic characterization of Sol-Gel filter disc with Pt complex 2PA chromophore, E1-BTAF-OH with 2 concentrations $3x10^{-4}$*M and* $6x10^{-4}$ *M: (a) Absorption in the range 200-2000 nm compared to blank Sol-Gel disc. (b) Absorption in the range 200-600 nm presenting the peaks belonging to E1-BTAF-OH.*

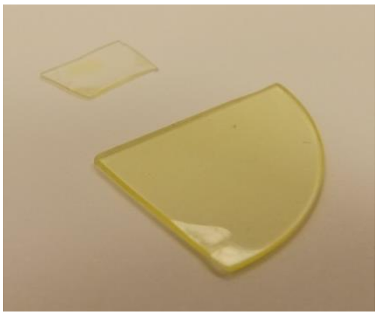


Fig 7: Series 2 - Sol-Gel filter discs with Pt complex 2PA chromophore, E1-BTAF-OH with 2 concentrations $3x10^{-4}$*M and* $9x10^{-4}$*M.*

At AFRL, Sol-Gel filter disc with Pt complex 2PA chromophore, E1-BTAF-OH with concentration $9x10^{-4}$ M was characterized for the life-time measurement of the triplet-state emission. Figure 9 presents the absorption spectrum at initial stage of the measurement (9a), the change in absorption spectrum under excitation with 430 nm laser excitation as function of excitation time (9b) and the triplet-state emission decay graph (9c). From the decay graph were calculated 2 lifetimes, 1.6 & 3.4 μs. It should be noted that although the amount of the chromophore molecules which are caged in triplet-state is low, it was able possible to achieve significant signal from the triplet-state emission.

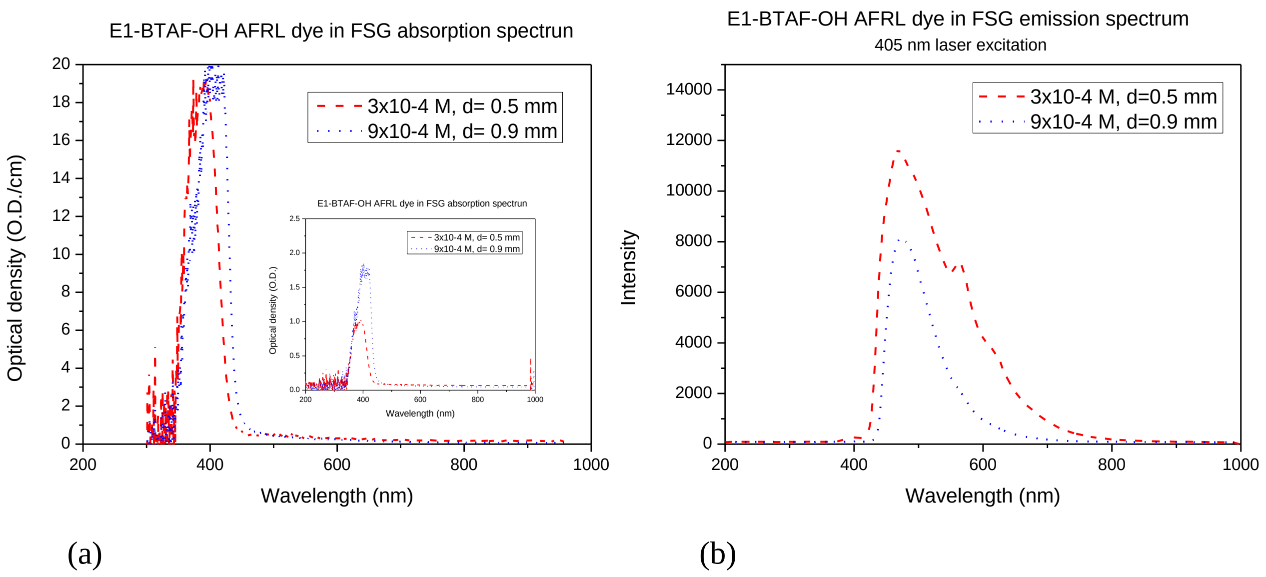
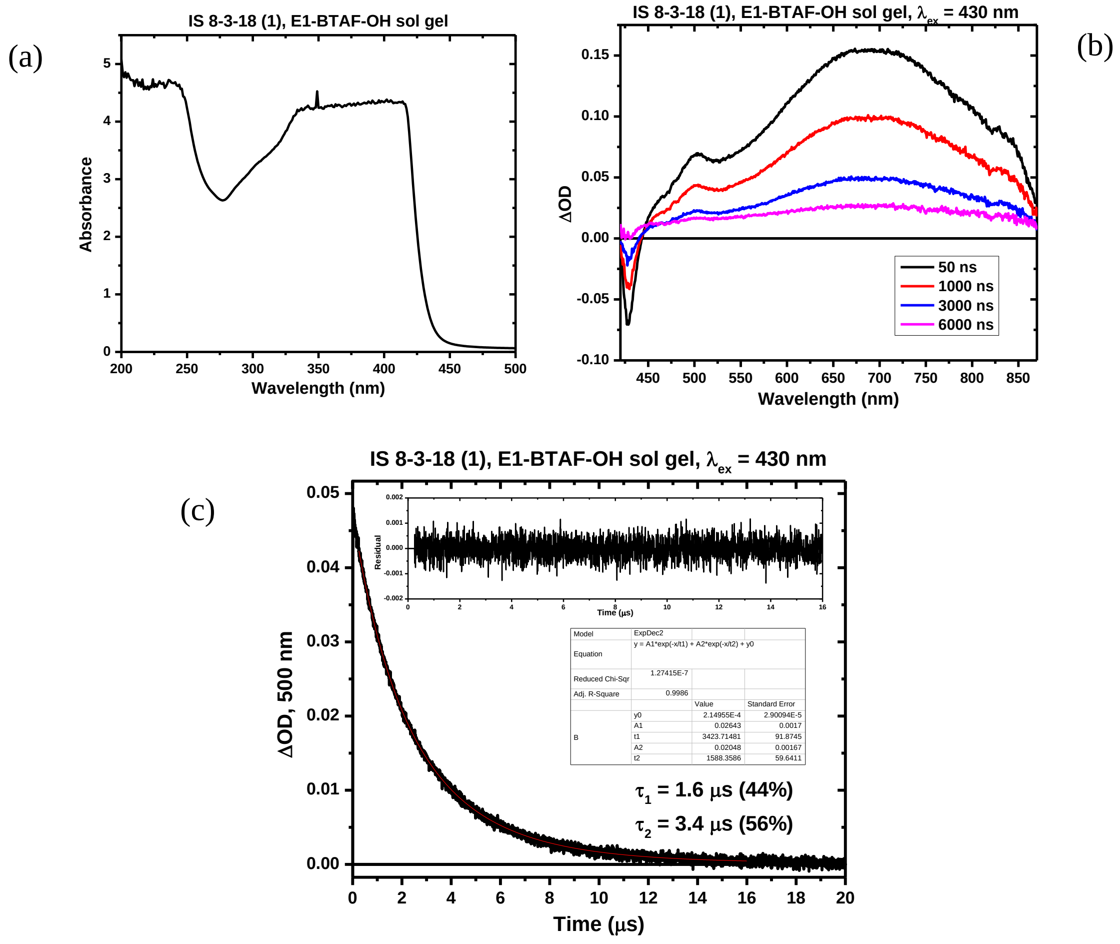


Fig 8: Series 2 – Spectroscopic characterization of Sol-Gel filter disc with Pt complex 2PA chromophore, E1-BTAF-OH with 2 concentrations 3x10^{-4} M and 9x10^{-4} M: (a) Normalized absorption/thickness in the range 200-2000 nm, while the insert is the absorption spectra in O.D. units. (b) Emission in the range 200-600 nm excited by 405 nm laser.



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	1.27415E-7		
Adj. R-Square	0.9986		
		Value	Standard Error
B	y0	2.14955E-4	2.90094E-5
	A1	0.02643	0.0017
	t1	3423.71481	91.8745
	A2	0.02048	0.00167
	t2	1588.3586	59.6411

Fig 9: Series 2 - Life-time measurement at AFRL of the triplet-state emission of Sol-Gel filter disc with Pt complex 2PA chromophore, E1-BTAF-OH with concentrations 9x10^{-4} M. (a) Absorption spectrum at initial stage. (b)The change in absorption spectrum under excitation with 430 nm laser excitation as a function of excitation time. (c) The triplet-state emission decay graph and calculated life time.

Year-3

The last year of the project was focused on enhancing NLO properties by controlling the singlet-triplet intersystem crossing transition (ICT) of AFRL 2PA chromophore, E1-BTAF-OH, doped in fast Sol-Gel (FSG) matrix. Since it was already found by Cooper et al., that nonpolar media lead to a breaking of the ground-state symmetry and increase the intersystem crossing transition (ICT) to triplet-state [28], our route was to develop a nonpolar Sol-Gel matrix and to succeed to cage in it the Pt 2PA chromophore in its triplet-state. The concept was to modify the FSG to a more aromatic matrix by adding tri-methoxy-phenyl-silane (TMPS) precursors to the Sol-Gel production process. Using this concept, we succeeded to produce a high optical quality Sol-Gel disc with chromophore E1-BTAF-OH caged in its triplet-state form. The sample was sent to Thomas Cooper at AFRL for additional NLO characterization.

The fabrication process started with a mixture of the precursors consisting of TMOS, MTMS and additional TMPS in order to achieve aromatic nonpolar Sol-Gel matrix - the molecular structures of the precursors is shown in Figure 10. The amount of TMPS was determined in order to achieve 50 wt% phenyl moieties in the final Sol-Gel material. After mixing the precursors, heat was applied and pressure in the closed vial was obtained. Then, the pressure was released, and vapors were evacuated until a viscous resin was obtained. The resin was diluted with THF including 3 wt% AFRL dye (E1-BTAF-OH). In order to fabricate a Sol-Gel disc the THF was evaporated using a thermal heat treatment at 60ºC on a hotplate, until a viscous sol-gel was achieved. This was followed by pouring the viscous resin into Petri dishes, which are used as molds for achieving discs. The samples were left for 7 days at 40ºC in an oven for completing thermal curing. The Sol-Gel discs were then extracted from the mold and were polished for flatness and optical quality. For the final Sol-Gel disc a refractive index of n=~1.54 at λ= 589 nm was measured using Atago Multi-Wavelengths Abbe Refractometer DR-M2/1550 (resolution ± 0.001). The elevated refractive index is due to the large amount of phenyl moieties in the final Sol-Gel material. In Figure 11 presents measurement of the dispersion in the visible range of refractive index as function of wavelength (483, 546, 589, 633 nm) for the Aromatic FSG (▲) and the Standard FSG (♦) compared to commercial refence glasses, a BK standard 1.5163 (■) and Fused silica (●). In all cases obtained a similar dependence of small change, dispersion, in the refractive index typical for glasses.

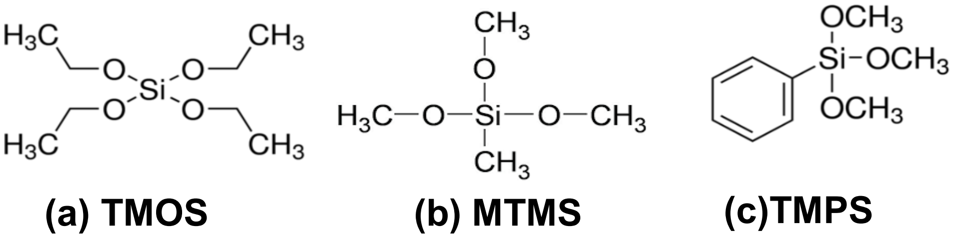


Fig 10: Molecular structures of the precursors used for fabrication of aromatic Sol-Gel matrix: (a)Tetra-methoxy-silane (TMOS), (b)Methyl-tri-methoxy-silane (MTMS), (c) tri-methoxy-phenyl-silane (TMPS).

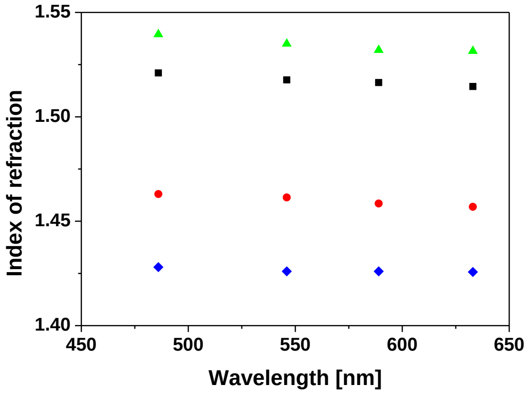


Fig 11: Refractive index of glasses as function of wavelength, dispersion (measured at 483, 546, 589, 633 nm) for BK standard 1.5163 (■), Fused silica (●), Standard FSG (♦), Aromatic FSG (▲)

The aromatic Sol-Gel filter disc with Pt complex 2PA chromophore were characterized for the spectroscopic behavior of both the aromatic Sol-Gel matrix and the Pt complex 2PA chromophore dopant. The aromatic Sol-Gel absorption spectrum at the NIR-IR range (900-2500 nm) was compared to the spectra of other Sol-Gel materials, shown in Figure 12. The other Sol-Gel materials are: Standard FSG (TMOS:MTMS), UV-cured FSG (TMOS:MTMS+MAPTMS) and Elastic FSG (TMOS:MTMS+DMDMS), called respectively T,N & G in ref 22.

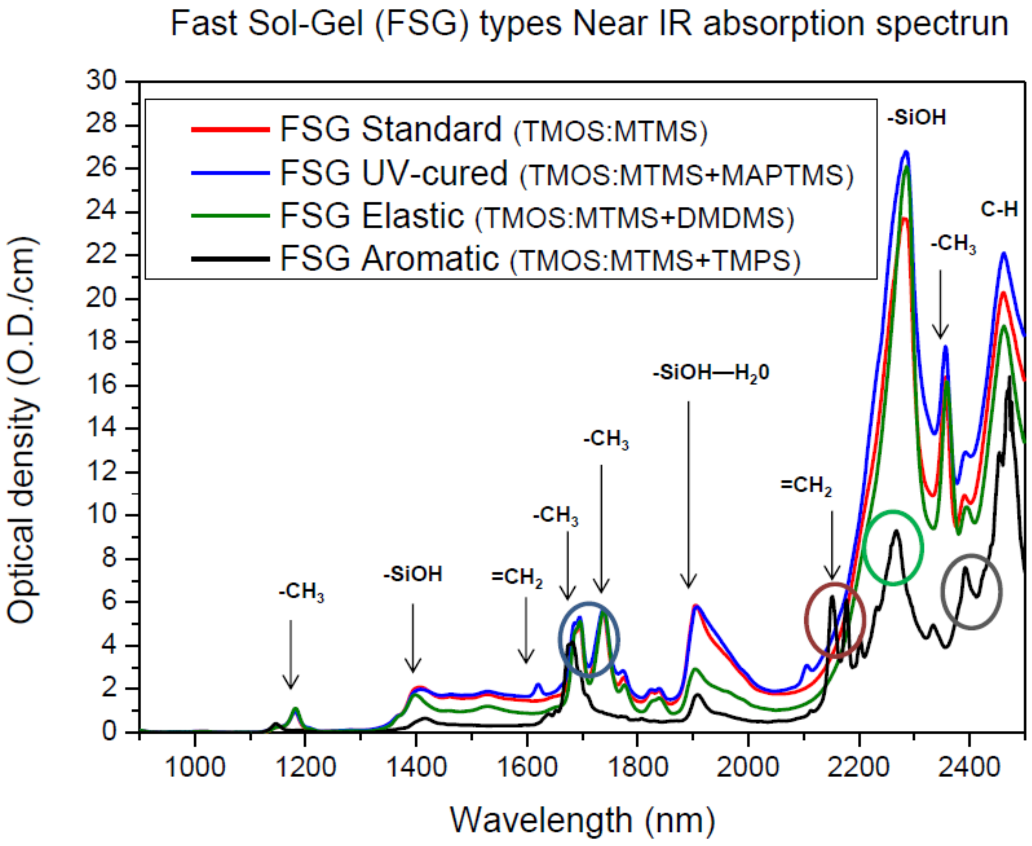


Fig 12: Absorption spectrum in the NIR-IR range (900-2500 nm) of 4 types of fast-sol-gel (FSG) materials: Standard FSG (TMOS:MTMS), UV-cured FSG (TMOS:MTMS+MAPTMS), Elastic FSG (TMOS:MTMS+DMDMS) and Aromatic FSG (TMOS:MTMS+TMPS).

From the spectra in Figure 12 two main effects can be seen: (1) We first focus on the SiOH-H_2O absorption at ~1900 nm indicating the affinity to adsorb water. The standard and the UV-cured FSG are hydrophilic and the elastic and aromatic FSG have more hydrophobic characteristic. (2) Secondly, while for the first three FSG materials (Standard, UV-cured and Elastic) the curves are very similar, the aromatic FSG differs with peaks exhibiting decrease in Si bonds (~2250 nm) and increase in carbon double bonds (~2150 nm) related to phenolic peaks.

The influence of the aromatic matrix on the spectroscopy of Pt-complex 2PA chromophore, E1-BTAF-OH, was studied using absorption and emission spectroscopy. As it was already found by Cooper et al., that nonpolar media lead to a breaking the ground-state symmetry and increase the intersystem crossing transition (ICT) to triplet-state [28], our expectations were that the aromatic Sol-Gel environment will transform the chromophore from its singlet-state to the triplet state. This issue was checked by preparing 2 kinds of aromatic Sol-Gel matrices, one with a low aromatic load in the chromophore will essentially be in its singlet-state, and the second with high aromatic load (~50 wt%) which driving the chromophore into its triplet-state. Figure 13 presents the absorption spectra for both kinds of aromatic Sol-Gel matrices; for the two cases there is no significant difference in absorption spectra. However, the emission spectra are completely different as shown in Figure 14. While the chromophore doped in the low aromatic load Sol-Gel exhibits mainly fluorescence emission with peak at ~450 nm, the chromophore doped in the high aromatic load exhibits mainly phosphorescence emission with peak at ~600 nm - similar to the case of benzene solution in deoxygenated environment (Figure 4b for molecule 1 [25]). Figure 15 presents together the absorption and emission spectrum of Pt-complex 2PA chromophore, E1-BTAF-OH ~$3\text{x}10^{-4}$ M in the high aromatic load (~50 wt%) Sol-Gel which drives the chromophore into its triplet-state. Furthermore, it should be clearly noted that in our case, the measurement was done in standard air-environment and the caged chromophore in the Sol-Gel disc is stable in its triplet-state. This fact makes our samples appropriate candidates for use in optical systems.

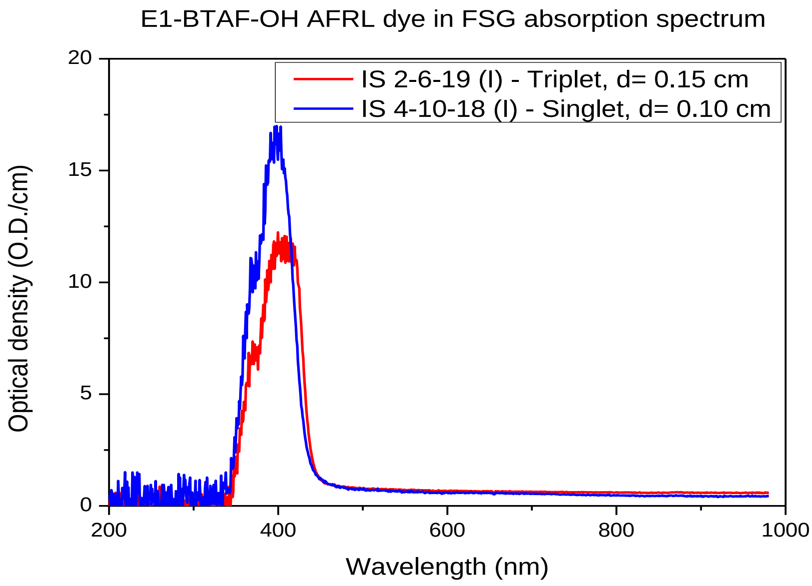


Fig 13: Absorption spectra of Pt-complex 2PA chromophore, E1-BTAF-OH ~3x10^{-4} M in 2 kinds of aromatic Sol-Gel matrices; low aromatic load with the chromophore in its singlet-state and high aromatic load (~50 wt%) with the chromophore in its triplet-state.

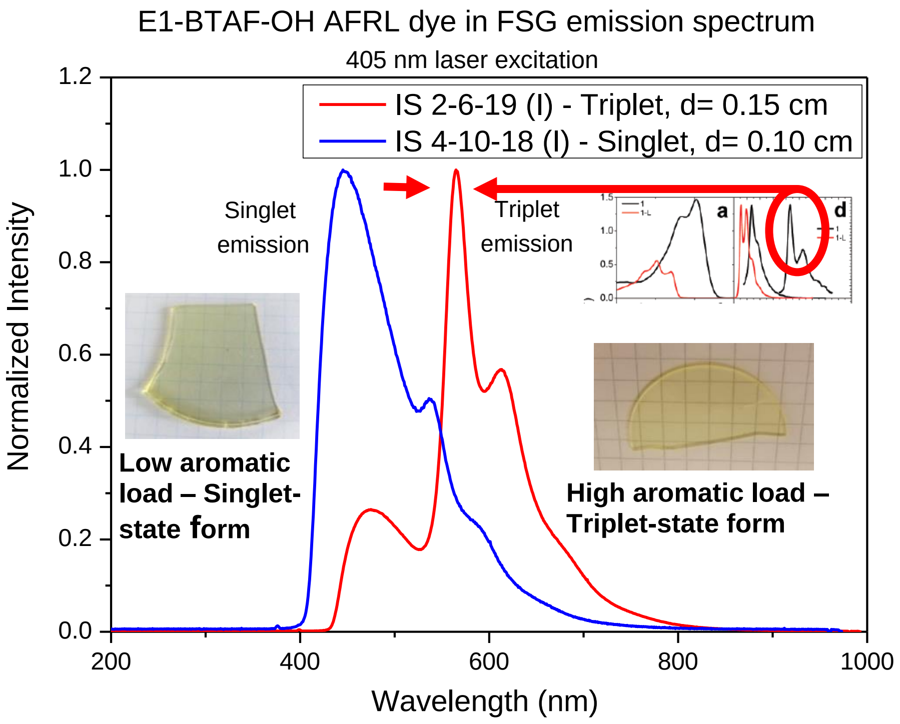


Fig 14: Emission spectrum of Pt-complex 2PA chromophore, E1-BTAF-OH ~3x10^{-4} M in 2 kinds of aromatic Sol-Gel matrices; low aromatic load with the chromophore in its singlet-state and high aromatic load (~50 wt%) with the chromophore in its triplet-state. The emission was excited with 405 nm laser.

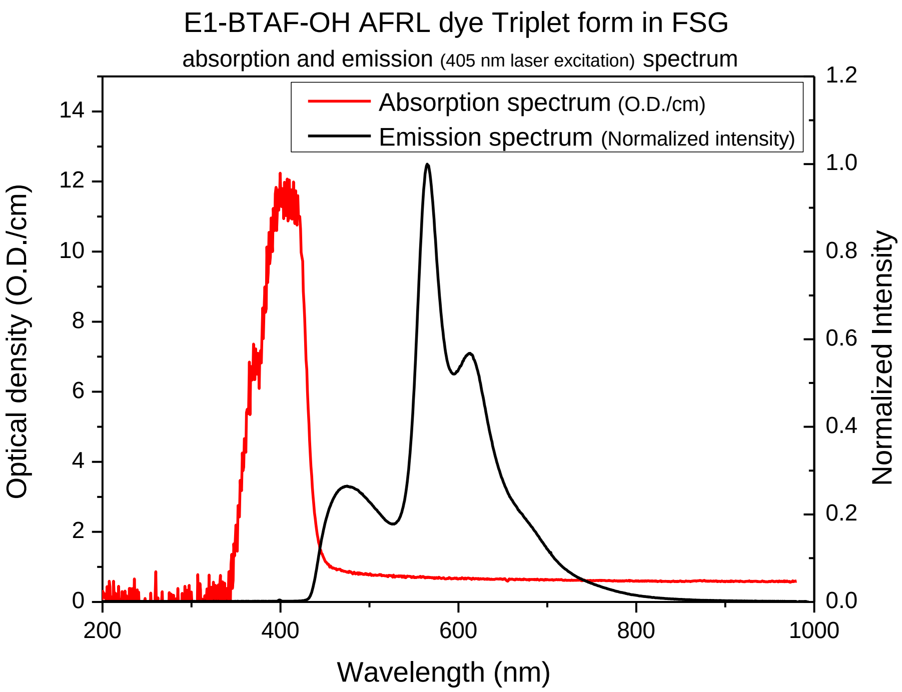


Fig 15: Absorption and emission spectrum of Pt-complex 2PA chromophore, E1-BTAF-OH ~3x10^{-4} M in high aromatic load (~50 wt%) Sol-Gel which drives the chromophore into its triplet-state. The emission was excited with 405 nm laser.

Conclusions and future plans

The purpose of the project was to study routes for doping functional materials in Sol-Gel matrices. The main goal of the project was to achieve doping in a solid Sol-Gel matrix of a Pt-complex 2PA chromophore, E1-BTAF-OH in its triplet-state, which enhances its NLO properties. The Pt-complex 2PA chromophore was received from Dr. Thomas Cooper, Air Force Research Laboratory (AFRL), Wright-Patterson Air Force Base OH. Following Cooper et al's assumption that nonpolar media lead to a breaking the ground-state symmetry and increase the intersystem crossing transition (ICT) to the triplet-state [28], our route was to develop a nonpolar Sol-Gel matrix and to succeed to cage in it the Pt 2PA chromophore in its triplet-state. Therefore, we developed a process to modify the FSG to a more aromatic matrix by adding tri-methoxy-phenyl-silane (TMPS) precursors to the Sol-Gel production process. We succeeded to produce high optical quality filters of high aromatic load (~50 wt%) Sol-Gel disc with chromophore E1-BTAF-OH caged in its triplet-state form. The emission spectrum of Pt-complex 2PA chromophore, E1-BTAF-OH exhibits mainly phosphorescence with peak at ~600 nm indicating triplet-state similar to what was shown in the case of benzene solution in deoxygenated environment (Figure 4b for molecule 1 [25]). Furthermore, it should be clearly noted that in our case, the measurement was done under standard air-environment and the caged chromophore in the Sol-Gel disc is stable in its triplet-state. This fact makes our samples appropriate candidates for use in optical systems. The sample was sent to Thomas Cooper at AFRL for additional NLO characterization. We are looking forward for the results of the NLO measurements at AFRL, which hopefully will indicate an enhancement in the NLO properties.

In addition, we proposed a continuation project for 2020, titled: "Additive manufacturing with Sol-Gel - 3D-printing gradient-index (GRIN) optical devices based on UV-cured Sol-Gel materials". In a white paper we submitted, we proposed development of a new class of UV-cured sol-gel materials based on silica (SiO_2) with elevated refractive index by introducing additives such as zirconia (ZrO_2) and titania (TiO_2), while keeping the UV-curable properties. The new class of materials will be used for fabrication of optical devices by additive manufacturing 3D-printing. The research will focus on developing UV-curable glassy materials with desired mechanical and optical properties and demonstration of the ability to use them for 3D-printing. The goal of the research will be to achieve gradient-index (GRIN) optical devices by 3D-printing. Currently, we started our study for developing Fast Sol-Gel (FSG) materials with elevated refractive index (compared the current refractive index of silica n=1.458). In the current report Sol-Gel with refractive index of n=1.54 was presented, due to addition of phenyl aromatic moieties, and by adding zirconia we are able to achieve UV-curable Sol-gel with refractive index above n>1.6. In parallel, we succeeded to demonstrate 3D-printing with UV-curable Sol-Gel using digital light processing (DLP) printer.

Publications

Emphasizing and referencing the archival publications that were written with support of this grant.

Until now no publication was written with support of this grant. However, there is a possibility for three publications to be written in the near future:

1. “3D Sol-Gel printing & Sol-Gel bonding for fabrication of Macro- and Micro/Nano-structured photonic devices”.
2. “Modification of Fast Sol-Gel for controlling polarity environment and refractive index”.
3. “Enhancement of NLO properties of Pt-complex 2PA chromophore doped in aromatic Sol-Gel matrix due to the increase of ISC to triplet-state”. Publication of this paper depends on the results of the measurements at AFRL and will published with AFRL.

Reference

1. Prasad, P. N.; Williams, D. J. "Introduction to Nonlinear Optical Effects in Molecules and Polymers"; Wiley: New York, 1991.
2. Qiong Zhang, Xiaohe Tian, Hongping Zhou, Jieying Wu and Yupeng Tian, "Lighting the Way to See Inside Two-Photon Absorption Materials: Structure–Property Relationship and Biological Imaging, *Materials* 2017, 10, 223
3. M. Albota, D. Beljonne, J-L Bredas, J.E. Ehrlich, J-Y Fu, A. A. Heikal, S. E. Hess, T. Kogej, M.D. Levin, S. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramanian, W. W. Webb, X-L Wu and C. Xu., *Science* 281, 1653, 1998.
4. E.M. Breitung, C.F. Shu, R.J. McMahon, "Thiazole and Thiophene analogues of Donor-Acceptors Stilbenes: molecular hyperpolarizabilities and structure – property relationships", *JACS* 2000, 122, 1154.
5. Justus, B. L.; Kafafi, Z. H.; Huston, A. L. *Opt. Lett*. 1993, 18, 1603.
6. M. Sheik-Bahae, A.A. Said, A. Wei, D.J. Hagan, E.W. Van Styrland, IEEE J. of Quantum Electronics, 26, 760,1990.
7. Brinker, C. J. and Scherer, G. W. (eds) [Sol-Gel Science], "The Physics and Chemistry of Sol-Gel Processing", Academic Press Inc, New York, (1990).
8. R. Gvishi, "Fast Sol-Gel technology – from fabrication to applications*" J. Sol-Gel Sci. and Tech.* **50 (2009)** 241.
9. Gvishi R., "Monolith Sol-Gel Materials", chapter 10 in "The Sol-Gel Handbook", Eds: Levy D. and Zayat M., Wiley-VCH, September (2015).
10. R. Gvishi, J. Swiatkiewicz, P. N. Prasad, B. A. Reinhardt and A. G. Dillard, "Dynamics of third-order nonlinearty of thiophene derivative by the homodyne and heterodyne phase-tuned femtosecond optical Kerr gate. Nonlinear Optics, 12 107 (1995).
11. R. Gvishi, P. N. Prasad, B. A. Reinhardt and J. C. Bhatt, "Third-order optical nonlinear studies of heptamers doped sol-gel processed silica : polymer composite by degenerate four-wave mixing and optical Kerr gate measurements". Journal of Sol-Gel Science and Technology, special issue on "Sol-gel preparation of nonlinear optical materials". 9, 157 (1997).
12. C. F. Zhao, R. Gvishi, U. Narang, G. Ruland, and P. N. Prasad, "Structures, spectra and lasing properties of new hemicyanine laser dyes". J. Phys. Chem., 100 4526 (1996).
13. R. Gvishi, J. Bhalwaker, D. N. Kumar, G. Ruland, U. Narang, P. N. Prasad and B. A. Reinhardt, "Multiphasic nanostructured composites for photonics: fullerene-doped monolith glass". Chemistry of Materials, 7 2199 (1995).
14. R. Gvishi, G. Berkovic, Z. Kotler, P. Krief, L. Shapiro, J.T. Klug, J. Skorka and V. Khodorkovsky, "Studies of new two-photon fluorescent probe for multiphoton microscopy in biological setting", Proc. SPIE 5211 82 (2003).
15. R. Gvishi, Z. Kotler, G. Berkovic, P. Krief, M. Sigalov L. Shapiro, D. Huppert, V. Khodorkovsky, V. Lokshin and A. Samat, "Resonance Energy Transfer in a novel two-component system: Two-Photon fluorophore and a photo-chromic acceptor molecule. Proc. SPIE 5724 13 (2005).

16. Gvishi, R., Tank, H., McMillian, Hagan, D.J., Van Stryland, E.W., Katherine, J., Schafer, Yao, S., Belfield, K.D., “Nonlinear absorption and refraction measurements of Fluorene-based molecules via Picosecond Z-scans", SPIE 5934 (2005).
17. Raz Gvishi, Peng Zhao, Honghua Hu, Galit Strum, Amir Tal, Shmuel Grinvald, Galit Bar, Laura Bekere, Vladimir Lokshin, Vladimir Khodorkovsky, Mark Sigalov, David Hagan, Eric Van Stryland, "Nonlinear solid-state filter based on photochromism induced by 2-photon absorption in a dye-doped sol-gel", SPIE vol. 9181, 9181OJ.
18. Mariana Pokrass, Zeev Burshtein and Raz Gvishi, "Non-linear optical and electrical conductivity properties of Carbon Nanotubes (CNT) doped in Sol-Gel matrices", SPIE vol. 9168, 916807, (July 2014).
19. R. Dror, Z. Burshtein, M. Pokrass, and R. Gvishi, "Transition from saturable to reverse saturable absorption in multi-walled carbon nanotubes doped sol-gel hybrid glasses", J. Opt. Soc. Am. B 32(10), 2198-2206 (**2015**).
20. Tamara Hanuhov, Eric Asolin, Raz Gvishi, "Evaluation of opto-mechanical properties of UV-cured and thermally-cured sol-gel hybrids monoliths as a function of organic content and curing process", *Journal of non-Crystalline Solids*, 471, 301 (2017).
21. R. Gvishi, G. Strum, A. Englander, "UV-curable glassy material for the manufacture of bulk and nanostructured elements", J. Europ. Opt. Soc. Rap. Public. 7, 12002 (2012).
22. Mariana Pokrass, Irina Gouzman, Galit Bar, Raz Gvishi, "Infrared and X-ray photoelectron spectroscopy studies of hybrid organic/inorganic fast sol–gel glasses", Optical Materials 34 341–346 (2011).
23. R. Gvishi, M. Pokrass, G. Strum, "Optical bonding with fast sol-gel", Journal of European Optical Society, Rapid Publications 4, 09026 (2009).
24. M. Pokrass, Z. Burshtein and R. Gvishi, "Thermo-optics coefficient in some hybrid organic/inorganic fast sol-gel glasses", Optical Materials 32 975 (2010).
25. J.E. Rogers, J.E. Slagle, D.M. Krein, A.R. Burke, B.C. Hall, A. Fratini, D.G. McLean, P.A. Fleitz, T.M. Cooper, M. Drobizhev, N.S. Makarov, A. Rebane, K-Y Kim, R Farley, and K.S. Schanze, “Platinum Acetylide Two-Photon Chromophores”, Inorg. Chem., 46 , 6483−6494 (**2007**).
26. A. Reban, M. Drobizhev, N. S. Makrov, G. Wicks, P. Wunk, Y. Steaneko, J.E. Haley, D.M. Krein, J.L. Fore, A.R. Burke, J.E. Slage, D.G. McLean, T.M. Cooper, ”Symmetry breaking in Platinum Acetylide chromophores studied by femtosecond two-photon absorption spectroscopy”, *The Journal of Physical Chemistry A.*, 2014, 118, 3749.
27. D. Chateau, A. Liotta, H. Lunden, F. Lerouge, F. Chaput, D.M. Krein, T.M. Cooper, C. Lopes, A.A.G. El-Amay, M. Lindgren, S. Parola, ”Long distance enhanchment of nonlinear optical properties using low concentration of plasmonic nanostrctures in dye doped monolithic Sol-Gel materials”, *Adv. Func. Mater*, 2016.
28. T.M. Cooper, J.E. Haley, D.M. Krein, A.R. Burke, J.E. Slagle, A. Mikhailov, A. Reban, ”Two-photon spectroscopy of a series of Platinum Acetylide chromophores: conformation-induced ground-state symmetry breaking”, *The Journal of Physical Chemistry A.*, 2017, 121, 5442.