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# Report on Properties & Shortcomings of Existing Materials



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## **0. Executive summary**

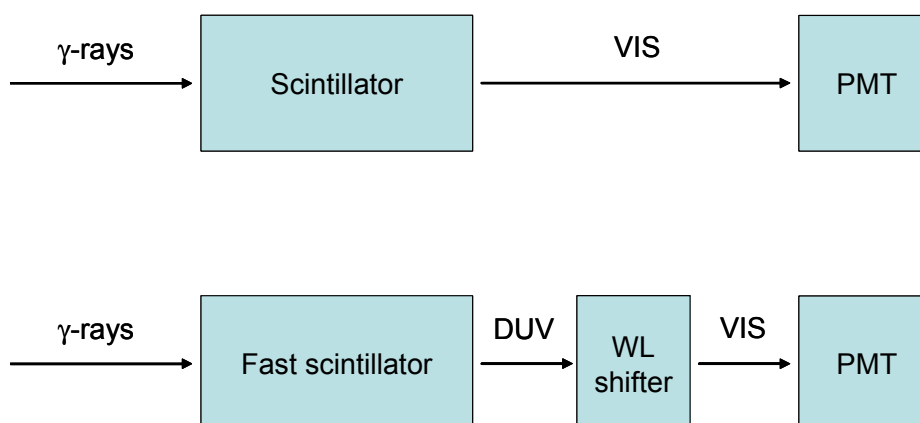
In the first 4 months of the project existing inorganic host matrices and luminescent organic dyes which seemed to be the most promising materials for the preparation of a ceramic thin film converter have been scrutinized. For this purpose an extensive literature search has been carried out to get a profound picture of the properties of state of the art materials. The outcome of these investigations was a quite clear understanding about certain shortcomings.

## 1. Introduction

In state-of-the-art PET scanners gadolinium silicate (GSO) or lutetium silicate (LSO) single crystals doped with light emitting  $\text{Ce}^{3+}$  ions are used as scintillator materials for coincidence detection of the high energy gamma photons ( $E = 511 \text{ KeV}$ ) [1]. Drawbacks of the presently used scintillator crystals are the relatively long lifetime of the  $\text{Ce}^{3+}$  emission ( $\tau > 30 \text{ ns}$ ), the low conversion efficiency of GSO ( $\eta < 10,000 \text{ photons / MeV}$ ) and the high cost price of the single crystals (more than 25% of the total PET scanner cost).

The spatial resolution and signal-to-noise ratio of PET scanners can be improved significantly by using scintillating materials doped with faster emitting lanthanide ions. Recent research has shown that the decay time of the d-f emission of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  is between 10 and 20 ns [2,3]. As a counterpart, the electronic structure of these latter rare-earth ions is such that the emission is situated in the deep UV (DUV) region, typically between 200 and 300 nm.  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  doped materials in which these ions show d-f emission have not been investigated widely w.r.t. to their applicability in scintillating materials. This very likely is due to the fact that materials with a large band gap are needed, to enable deep UV emission, which in turn limits the achievable light yield. This issue will be addressed in this project.

Since the fast photodetectors used in PET scanners have a low sensitivity in the deep UV spectral range, it becomes a necessity to shift the emission from the scintillator into the visible region, where the detector sensitivity is the highest. This task can be accomplished by developing an innovative device in which the scintillator crystals are replaced by scintillator stacks (scintverter) consisting of: (i) a fast scintillator, and (ii) a wavelength shifter, or converter (Figure 1).



**Figure 1.** Schematic of a traditional scintillator (top), and a scintverter (bottom).

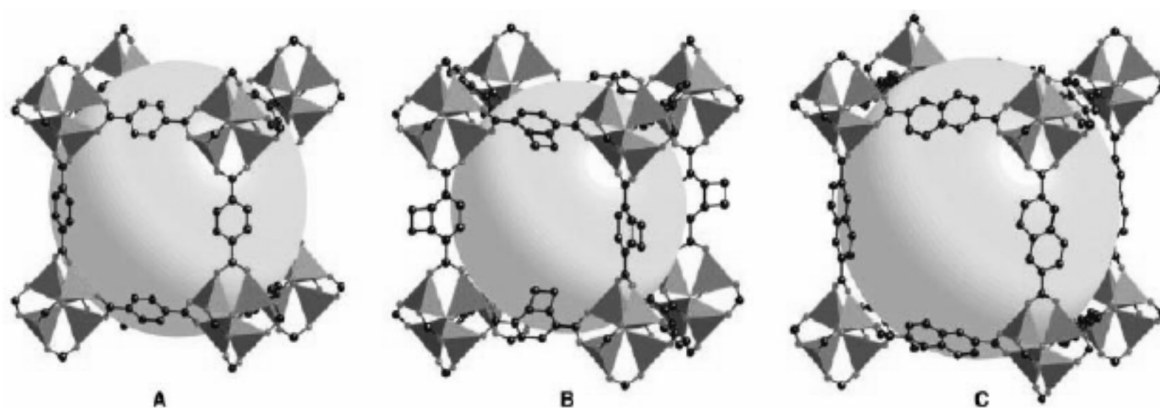
A similar approach has been applied since the 90's in the development of fast plastic scintillators [4,5], used as part of the detection systems for high energy relativistic particles from accelerators. The most common type of plastic scintillator consists in an aromatic plastic base (for example polystyrene, PS) doped with aromatic emitting dyes, called the primary fluors. When the energy from ionizing radiation is deposited into the plastic matrix, a non-radiative Förster-type energy transfer to the primary fluor occurs, with subsequent fluorescence emission, generally in the DUV region ( $200 < \lambda < 300 \text{ nm}$ ). To increase the emission-light bulk attenuation length, an additional fluorescent compound, called a wavelength shifter, is added. Now, a radiative energy transfer between the primary fluor and the shifter takes place, and the emission of the wavelength shifter in the visible ( $400 < \lambda < 600 \text{ nm}$ ) is detected. Although organic polymers are commonly used as a solid matrix for hosting organic molecules, they generally suffer from lack of photostability and optical quality [6]. This provides motivation for the successful introduction of active organic molecules into a more photostable inorganic glass.

In the STRING project a thin ceramic film wavelength shifter for spectral conversion from DUV to visible light will be designed based on fast and efficient luminescent organic dyes. The converter will be optimised to have a match between the DUV emission of the scintillator and the

absorption spectrum of the organic dye. To improve the stability under deep UV irradiation the organic molecules will be embedded in a ceramic matrix. Organic converting material embedded in an inorganic host matrix with the desired optical properties do not presently exist and the development of such fast, efficient and stable conversion layers is the challenge faced by the STRING project.

The realisation of this advanced technology rests on the development of multifunctional materials which simultaneously satisfy many functional requirements. The purpose of this report is to document the state-of-the-art of candidate host matrix materials and luminescent converting dyes at the time the project started.





**Figure 3.** Structures of MOF-5 (A), IRMOF-6 (B), and IRMOF-8 (C) illustrated for a single cube fragment of their respective cubic three-dimensional extended structure [9].

### 2.1.2 Mesoporous materials

Mesoporous materials are known since 1992 when researchers at Mobil Oil [10] demonstrated the synthesis of hexagonally packed silicate and aluminosilicates with uniform pore sizes, evenly distributed throughout the material. These materials were termed MCM-41. Their synthesis was achieved by the use of surfactant micelles as structure directing agents in a sol-gel process. Amphiphilic surfactants self assemble into cylindrical micelles, which are encapsulated by an inorganic material (silicate or aluminosilicate in this case), which balances the charge on the micellar surfaces. Calcination, a thermal processing technique, is then used to remove the organic surfactant, leaving a hexagonal arrangement of mesopores. Mesoporous materials have attracted much interest as they can be very useful as catalysts or adsorbents. With available pore sizes ranging from 2 to 10 nm, they have potential for other applications. For example, a small laser array can be fabricated using a patterned mesoporous silica film by incorporating dyes into the mesochannels. A solid electrolyte can be obtained by incorporating ion conductive materials, and a fluorescent film can be prepared by incorporating small silicon clusters.

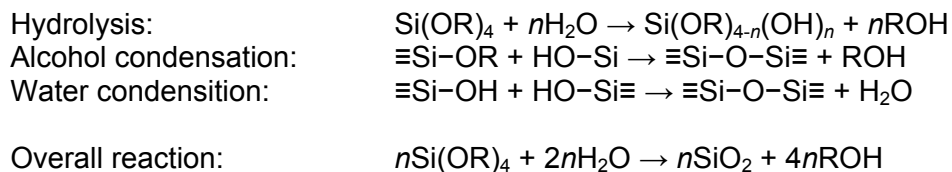
### 2.1.3 Macroporous materials

Macroporous materials with pore size between 50 and 100nm are not relevant to the STRING project, since the pore sizes are far bigger than required for guest molecules, i.e. organic dyes.

## 2.2 (Sol-gel) glass host

Hybrid scintillators that combine the fast organic dye-based emission centers with an inorganic glass host were known in literatures. For example, p-terphenyl has been doped into the low melting lead–tin–fluorophosphate glasses [11], which show a broad fluorescence emission band peaking at about 545 nm with a decay time of about 5 ns. These glasses were made by using classical technique from high temperature melt (~500 °C), which poses a serious obstacle to organic dyes having generally low thermal stability.

Another promising method to incorporate aromatic dye molecules into glass host is to use sol-gel process. This method allows high optical quality glasses to be made at much lower temperature. For example, tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) are hydrolysed to form a gel. After losing alcohol, the gels are dried to form the transparent glass. The chemical reactions can be written as follows:



where in the case of TMOS the alkyl group R is a methyl group.

In the early 80's, when the sol-gel process became a popular method for preparing glasses at room temperature, Avmir and Reisfeld demonstrated for the first time that an organic dye can be doped within an inorganic glass [12]. Since then, many groups around the world have introduced organic materials into a variety of inorganic matrices via the sol-gel process. Fluorescein and rhodamine 6G have recently been doped in the silicate glass with the sol-gel method [13] showing characteristic emission of the organic dyes.

### **2.3 Host matrix materials which might be considered in the project**

Except the zeolites, we shall explore the metal-organic frameworks, mesoporous and sol-gel glass-based materials as potential host matrix for organic dye molecules. Currently, there are already research activities in Leiden on MOFs. Although the research interest is focused on applications as catalysts or hydrogen storage materials, their potential use as inorganic host materials for organic dyes will be examined. As to the mesoporous materials, we shall concentrate our activity on the mesoporous silica films described by Canon Technology [14]. This technique allows the growth of silica films on a glass substrate with aligned tubular mesochannels of 3 nm in diameter. It requires a special surface treatment which aligns the surfactant molecule assemblies on the substrate. The film can then be formed by holding the glass substrate in an acidic reactant solution containing a surfactant and silica-oligomer within e.g. 3 days. Further, the sol-gel glasses are promising host materials for organic dye molecules. Due to the relatively low temperature required for the preparation of sol-gel matrices, it is particularly suitable for organic molecules with low thermal stability. In addition, dyes can be directly embedded in the glass matrices during the glass formation. Research activity on the photophysical characterization of rare-earth emitters hosted in sol-gel silica glasses is ongoing in Bologna [15].

### 3. Luminescent converting dyes

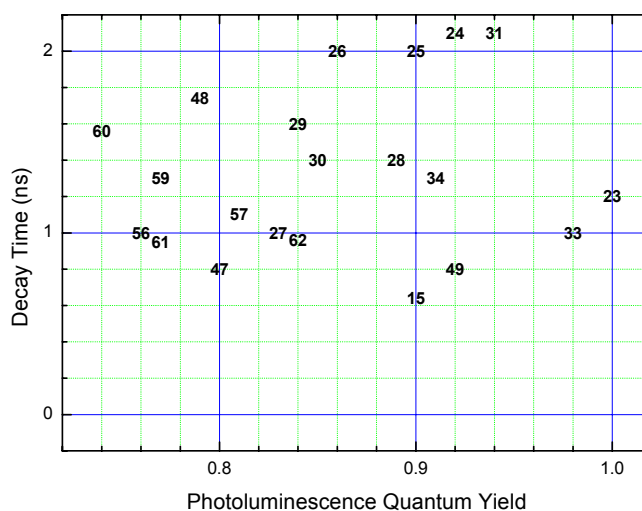
A variety of organic luminescent dyes exists. Molecules with  $\pi$ -conjugated electron systems have been the most widely studied organic optically active materials and show promising performances. In table 1 the photophysical properties of a selection of organic compounds showing high photoluminescent quantum yields ( $\Phi$ ) and short decay times ( $\tau$ ) are collected (data from ref. [16]).

#### 3.1 Desired features

Organic molecules that may be used as luminescent dyes in the converting layer must fulfil several conditions in order to be suitably processable and highly performing in the device. Desirable basic features are:

- i.* absorption matching the DUV emission of the fast scintillator;
- ii.* fluorescence emission matching the efficiency curve of the photomultiplier tube;
- iii.* large Stokes shift, to avoid self-absorption, but small enough to prevent thermal quenching (suitably around 2,500 – 3,000  $\text{cm}^{-1}$ );
- iv.* high light output, namely a good ability to absorb light (high extinction coefficient,  $\epsilon > 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) combined with a high fluorescent quantum yield,  $\Phi > 0.8$ ;
- v.* fast response time, i.e. luminescence decay time  $\tau < 2 \text{ ns}$ ;
- vi.* good photochemical stability to DUV radiation;
- vii.* acceptable cost.

The first three requirements are easily met, because most of the organic luminescent dyes with aromatic systems show (*i*) very intense ( $\epsilon > 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ )  $\pi$ - $\pi^*$  transitions in the DUV and UV regions, (*ii*) broad emission bands extending into the visible part of the spectrum, and (*iii*) Stokes shift in the range 1,500 – 3,500  $\text{cm}^{-1}$  (but typically larger than 2,000  $\text{cm}^{-1}$ ). Taking into account the high quantum yield and low lifetime constrains (*iv* and *v*) the number of organic wavelength shifters reduces considerably. The figure below shows how the requirement of a 2 ns decay time and a quantum efficiency of more than 80% results in a strong decrease in the number of applicable compounds. For what the photostability is concerned (point *vi*), the most part of the studies presented in the literature deal with red and infrared dye laser materials, and, as far as we know, no comparative or review article exist on this topic, and therefore this aspect will be addressed inside the project.



**Figure 4.** Plot of luminescent dyes combining high quantum yield and short decay time (the numbers refer to compounds listed in Table 1).

**Table 1.** Photophysical parameters of organic species

		$\lambda_{em}$ (nm)	$\Phi$	$\tau$ (ns)
1	9-amino-acridine	427	0.99	15.2
2	3,4,6,7,9,10-hexahydro-3,3,6,6-tetramethyl-1,8-acridinedione	–	0.91	5.2
3	3,4,6,7,9,10-hexahydro-3,3,6,6,10-pentamethyl-1,8-acridinedione	–	0.83	5.7
4	9-acridinone	413	0.97	10.8
5	10-methyl-9-acridinone	423	0.98	11.0
6	10-phenyl-9-acridinone	414	0.99	7.7
7	9-cyano-anthracene	403	0.93	15.6
8	9,10-dicyano-anthracene	421	0.90	11.7
9	9,10-dicyano-anthracene	427	0.87	15.1
10	9,10-dimethoxy-anthracene	404	0.87	14.7
11	9,10-dimethyl-anthracene	399	0.93	14.0
12	9,10-dimethyl-anthracene	403	0.89	11.0
13	9,10-diphenyl-anthracene	394	0.91	7.7
14	9,10-diphenyl-anthracene	392	0.95	8.2
15	1,4-bis(phenylethynyl)-benzene	344	0.90	0.6
16	benzo[k]fluoranthene	–	1.00	11.3
17	benz[f]indole	380	0.79	19.1
18	9,9'-bianthryl	394	0.95	10.6
19	1,1'-binaphthyl	325	0.77	3.0
20	7-(diethylamino)-4-(trifluoromethyl)-coumarin	–	1.00	4.1
21	1,7,-diazaperylene	443	0.97	6.2
22	fluorescein dianion	520	0.97	3.6
23	2,5-diphenyl-furan	343	1.00	1.2
24	indeno[2,1-a]indene	–	0.92	2.1
25	1,2-diphenyl-indole	329	0.90	2.0
26	2-phenyl-indole	331	0.86	2.0
27	2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole	330	0.83	1.0
28	2,5-diphenyl-1,3,4-oxadiazole	311	0.89	1.4
29	2,5-bis(4-biphenyl)-oxazole	–	0.84	1.6
30	2,5-diphenyl-oxazole	335	0.85	1.4
31	2-(1-naphthyl)-5-phenyl-oxazole	364	0.94	2.1
32	2-(1-naphthyl)-5-phenyl-oxazole	367	0.78	2.3
33	2,2'-(1,4-phenylene)bis(5-phenyl)-oxazole	380	0.98	1.0
34	2,2'-(1,4-phenylene)bis(5-phenyl)-oxazole	386	0.91	1.3
35	perylene	435	0.75	6.4
36	perylene	438	0.87	6.0
37	N,N'-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide)	522	1.00	4.9
38	N,N'-ditridecyl-3,4:9,10-perylenebis(dicarboximide)	520	0.94	–
39	N,N'-ditridecyl-3,4:9,10-perylenebis(dicarboximide)	525	0.96	–
40	magnesium(II) phthalocyanine	–	0.76	7.6
41	2-(dimethylamino)-purine	359	0.75	9.4
42	pyrromethene 546	498	0.99	5.6
43	pyrromethene 567	527	0.83	6.6
44	pyrromethene 597	541	0.77	4.2
45	pyrromethene 556	520	0.84	5.1
46	4-[1,1'-biphenyl]-4-yl-2,6-dimethyl-pyrylium	450	0.78	3.4
47	2,2':5',2'':5'',2'''-quaterfuran	387	0.80	0.8
48	2,2':5',2'':5'',2'''-quaterfuran	376	0.79	1.7
49	p-quaterphenyl	330	0.92	0.8
50	rhodamine, inner salt	520	0.88	4.4
51	N,N'-diethyl-rhodamine, inner salt	534	0.94	–
52	rhodamine 6G cation	546	0.86	3.8
53	rubrene	541	0.98	16.5
54	2-amino-(E)-stilbene	373	0.88	3.7
55	3-amino-(E)-stilbene	356	0.78	7.5
56	4,4'-diamino-(E)-stilbene	373	0.76	1.0
57	4,4'-diphenyl-(E)-stilbene	372	0.81	1.1
58	4,4'-diphenyl-(E)-stilbene	–	0.82	–
59	2,2':5',2'':5'',2'''-terfuran	350	0.77	1.3
60	2,2':5',2'':5'',2'''-terfuran	340	0.74	1.6
61	p-terphenyl	311	0.77	0.9
62	2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis-thiophene	370	0.84	1.0

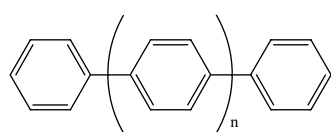
### 3.2 Organic dyes which might be considered in the project

The most interesting classes of luminophores are oligophenylenes, oxazoles, oxadiazoles, indoles, furans, stilbenes, and anthracenes (Chart 1), and will be considered first as candidate wavelength shifting materials. Commercially available organic luminescent dyes will be embedded in the above mentioned porous and sol-gel inorganic matrices and a thin film ceramic converter device will be prepared. Then, the photophysical properties (i.e.: absorption and emission spectrum, luminescence efficiency and decay time, and DUV stability) of the converters will be measured and compared.

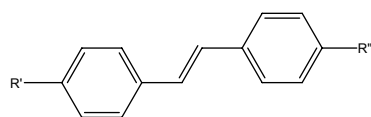
In the project there is capacity to look for new organic luminescent materials. Therefore, in a second step, quantum mechanical calculations will be used to identify suitable modifications of the organic luminescent dye molecules which fulfil the requirements mentioned above. Then, these materials will be prepared and characterised accordingly.

It is worth noting that at this time no material exist that possess all the desired properties at once.

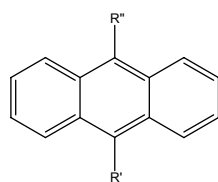
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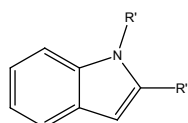
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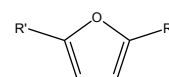
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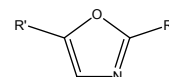
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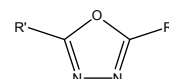
indoles



furans



oxazoles



oxadiazoles

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