NEW ORGANIC SCINTILLATORS WITH LARGE STOKES' SHIFTS(*)

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ABSTRACT

Four new scintillators were synthesized on the basis of PMP in order to obtain a series of dopants with large Stokes' shift for application in ionizing particle counting. Absorption and emission spectra, light yield, quantum efficiency, decadic extinction coefficients and absorption lengths of their toluene solutions were measured and compared to p-terphenyl (+ POPOP), PMP, and 3-HF, which have already been applied for particle detection.

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1. INTRODUCTION

Particle detectors based on scintillating substances have been used since the early days of nuclear and particle physics. Within the last few decades, the introduction of photomultiplier tubes multiplied the applications of this technique. At present, large detector dimensions as for voluminous liquid scintillators to trace solar and cosmic neutrinos [1] or for scintillating fibres to achieve spatial particle tracking [2] call for efficient light transmission over optical paths of several metres. Therefore, it is desirable to apply scintillator compounds, which combine sufficient light yield with low self-absorption, in order to transmit a large number of photons to the photo cathode for efficient detection.

Since particle detectors at accelerators require high counting rate capabilities, only organic compounds with fluorescence lifetimes shorter than 5 ns are interesting in our considerations. The π-electrons of aromatic compounds produce the absorption and fluorescence phenomena: By energy transfer from an appropriate liquid solvent or polymer matrix, the dissolved scintillator molecules are excited into their higher singlet states where they occupy mostly the upper rotational or vibrational levels. Before returning to their ground states, they lose vibrational energy via direct interactions with neighbouring molecules, and the radiative ground state transition starts from the lower vibrational levels of the excited singlet. Therefore, excitation (absorption) involves more energy than the subsequent fluorescence emission. The energy difference between the resulting absorption and emission bands is commonly called the Stokes' shift [3]. The residual overlap between these two bands causes self-absorption of the fluorescence light and is mainly responsible for the reduced intensity of transmitted light.

We will report here on the measured decadic extinction coefficients, in particular within the overlap regions, on the resulting absorption lengths, and on the light yields of different new aromatic compounds (listed in table 1), which were dissolved in toluene. This solvent has been chosen because its chemical composition is similar to that of polystyrene and polyvinyl-toluene, the most important polymers for solid bulk and fibre scintillators. Most of the scintillator compounds have chemical structures similar to that of PMP (1-phenyl-3-mesityl-2-pyrazoline), some photophysical properties of which have already been reported by Güsten et al [4].

2. EXPERIMENTAL SECTION

2.1 Substances

Among the organic scintillators listed in table 1 and 2 3-HF (3-hydroxyflavone), p-terphenyl and POPOP [1,4-di-2-(5-phenyloxazolyl) benzene] are of commercial origin (Aldrich; Merck, Darmstadt). PMP and the four PMP derivatives were prepared by standard
procedures [5], i.e. either by condensation of the appropriately substituted Mannich bases with appropriately substituted phenylhydrazines or by condensation of mesityl vinyl ketone with the appropriately substituted phenylhydrazines. The PMP derivatives are purified by several recrystallizations from ethanol. All new compounds furnished correct data for elemental analysis and were further characterized by their fluorescence spectra, NMR spectra as well as by their mass spectroscopic fragmentation [6]: 1-phenyl–3–mesityl–2–pyrazoline, mp 96°C (PMP 420); 1–p–tolyl–3–mesityl–2–pyrazoline, mp 105–106°C (PMP 430); 1–p–tolyl–3–(2', 6’–dimethoxyphenyl)–2–pyrazoline, mp 182–183°C (PMP 440); 1–p–anisyl–3–mesityl–2–pyrazoline, mp 88–89°C (PMP 450); 1–p–anisyl–3–(2', 6’–dimethoxyphenyl)–2–pyrazoline, mp 187–188°C (PMP 460). All photophysical data of the scintillators investigated were measured in toluene.

2.2 Instrumentation and techniques

The fluorescence quantum yields were determined at room temperature relative to quinine bisulfate in 1 N H₂SO₄ (Qₓ = 0.55 at 25°C [7]) as the fluorescence standard according to the method of Parker and Rees [8] by measurement of the integral intensities of the absolute fluorescence spectra. Details of the procedure and the self-correcting spectrofluorimeter have been described in [9] and [10]. All fluorescence quantum yield measurements were performed in non-degassed toluene in the concentration range of 1–3 × 10⁻⁵ mole l⁻¹ solutions. The fluorescence decay times were determined in the concentration range of 3–8 × 10⁻⁴ mole l⁻¹ solutions by impulse fluorimetry using the sampling technique. A nitrogen laser was used as excitation source. Details of the impulse fluorimeter and the technique have been reported [9] and [10].

For all measurements reported in table 2 and in figs 2–8, realistic standard concentrations of the scintillator solutions, i.e. of 0.025 mole l⁻¹ in toluene, were used, with the exception of PMP 460, which is only soluble at 0.0125 mole l⁻¹. Concentrations of organic scintillators of about 0.025 mole l⁻¹ have proved to yield the highest light output in liquid scintillation counting [11]. POPOP was dissolved at 2.5 × 10⁻³ mole l⁻¹ only, since it has a much higher extinction coefficient across the overlap region of absorption and fluorescence.

The spectral light absorptions were measured with a double beam spectrophotometer (Lambda 6, Perkin Elmer, Norwalk, USA). The solutions were in quartz cuvettes (Hellma, D–7840 Müllheim, Germany) with optical path lengths d ranging from 0.01 mm to 100 mm depending on the absorption region of the samples. The reference beam I₀ was transmitted through the same cells as used for the sampling beam, but they contained pure toluene. The recorded fractions I/I₀ (λ) of light intensities were transformed into decadic molar extinction coefficients:
\[ \varepsilon(\lambda) = \frac{0.4343}{cd} \ln \left( \frac{I}{I_0} \right)_\lambda \; [ \text{l mole}^{-1}\text{cm}^{-1}] \]  

and into the corresponding absorption lengths, \( \Lambda \) which reduces the original light intensity to \( 1/e \):

\[ \Lambda(\lambda) = \frac{0.4343}{\varepsilon c} = \frac{d}{\ln \left( \frac{I}{I_0} \right)_\lambda} . \]  

To evaluate the lower measuring limit of the decadic extinction coefficient, we repeatedly compared the absorbances \( A \) of two identical 100 mm long quartz cuvettes filled with pure toluene and placed in the sampling and reference beam of the spectrophotometer. The statistical variations of the recorded absorbance differences \( \Delta A \) amounted to less than:

\[ \Delta A = \Delta \log(I/I_0) \leq 5 \times 10^{-4}. \]  

Accordingly, we obtain for the lower measuring limit of \( \varepsilon(\lambda) \) with 100 mm optical path \( d \) and 0.025 mole \( l^{-1} \) scintillator concentration \( c \):

\[ \varepsilon_{\text{min}}(\lambda) = \frac{\Delta A}{dc} \leq 2 \times 10^{-3} \; \text{l mole}^{-1}\text{cm}^{-1} \]  

and for the corresponding upper measuring limit of the absorption length:

\[ \Lambda_{\text{max}}(\lambda) = \frac{0.4343}{c \cdot \varepsilon_{\text{min}}} \geq 87 \; \text{m} . \]  

The fluorescence emissions from the scintillator solutions were excited and analyzed with a self–correcting spectrofluorimeter (Mod. 8000, SLM Instruments Inc., Urbana IL 61801, USA): Light from a 450 W Xenon lamp is filtered with 8 nm bandwidth through a double grating excitation monochromator and split into the excitation beam and the reference beam for automatic corrections of intensity variations. A single grating emission monochromator analyzes at 4 nm bandwidth the fluorescence emission, which passes, at the rear of its entrance slit, a linear polarizer (aligned parallel to the grating) in order to minimize optical aberrations. The analyzed light as well as the excitation reference beam are detected via uv–extended photomultiplier tubes (R928, Hamamatsu Photonics, Toyooka–village, Japan). Their radiant sensitivity varies by \( \pm 5\% \) between 350 nm and 550 nm wavelength.

In order to measure the fluorescence yield without self–absorption we arranged the cuvettes filled with the relevant scintillator solutions as indicated in fig. 1. This arrangement is called "surface excitation", since at 270 nm the exciting light penetrates only about 5 \( \mu \)m into the solution before being fully absorbed by toluene. At this penetration depth the scintillator solutes contribute only by a few per cent to the light absorption, i.e. most of the
light is absorbed by the toluene and the energy is transferred to the scintillator in a similar way as the energy loss of ionizing particles. To evaluate directly the self–absorption of different scintillator solutions, we inserted cuvettes of different absorption paths, but with solutions identical to those of the excited liquids, into the fluorescence path in front of the analyzer (fig. 1).

3. RESULTS AND DISCUSSION

3.1 Photophysical properties

The photophysical data of the dilute toluene solutions of the organic scintillators, such as the maxima of the electronic absorption and fluorescence, the Stokes' shift, the fluorescence quantum yield $Q_F$, and the fluorescence decay time $\tau$ are summarized in table 1.

Since no fine structure can be observed in the absorption and fluorescence spectra of the scintillators investigated (figs 2 and 3) at room temperature, the 0–0 transition is difficult to determine and, therefore, the energy difference of the absorption and emission maxima is taken as a measure of the Stokes' shift. PMP and its derivatives combine very good photophysical properties such as high fluorescence quantum yields and short fluorescence decay times with a high solubility. Due to the absence of oxygen quenching, the fluorescence quantum yield for PMP 420 is by about 15% higher in degassed toluene while the fluorescence decay time is longer by about this percentage [13]. Generally, practical scintillation counting of organic solutions occurs in air saturated solvents. It is not clear from the literature (ref. [12]) whether or not the photophysical data for p–terphenyl and POPOP have been measured in degassed toluene. The most striking difference of the PMP derivatives in comparison with the common scintillators p–terphenyl and POPOP is the exceptionally large Stokes' shift of more than 10,000 cm$^{-1}$ (see table 1). The advantage of the large Stokes' shift of the PMP derivatives is that they can be used without wavelength shifter in scintillation counting [14,15]. Thus, contrary to the classical combination of primary and secondary solutes used in scintillation counting for more than 35 years, secondary solutes are no longer necessary when PMP is used. This is particularly important for large–volume scintillators as well as in scintillating fibres of tracking detectors [16]. The importance of reducing the reabsorption effects in scintillators by employing solutes with large Stokes' shifts was stressed recently by Renschler and Harra [17]. They favoured as scintillator 3–HF with a large Stokes' shift. Thus, this scintillator has also been investigated and compared with the new scintillators.
3.2 Light attenuation

The intensity of the scintillation photons is related to the solute concentration. Since the optimum concentration of organic scintillators is higher than $10^{-2}$ mole $1^{-1}$, reabsorption effects can diminish the counting efficiency. Thus, in the "fight for every photon" the transmission of the scintillator solution in the wavelength range over 400 nm is of importance.

The absorption and emission curves measured for pure toluene and for the various scintillator solutions are plotted in figs 2 and 3. Since for the reference samples we inserted the identical cuvettes filled with pure toluene, figs 2, 3 and 4 present the extinction coefficients for the pure scintillator compounds. Note the different scales in fig. 2.

The decadic molar extinction coefficients $\varepsilon(\lambda)$ for all scintillators within their emission regions are displayed on a logarithmic scale in fig. 4. The corresponding absorption lengths for 0.025 molar scintillator solutions are shown in fig. 5.

The effect of self–absorption is demonstrated in fig. 6. It shows how the short wavelength flank of the PMP 420 and the POPOP emission bands change with the absorber thickness introduced between the excited liquid surface and the entrance slit of the analyzer. The POPOP concentration had to be 10 times smaller because of its strong self–absorption in the overlap region. These distortions were measured with the arrangement shown in fig. 1. The reduction of the light yield by self–absorption within the most critical region of the first 50 mm absorption path is plotted for the various scintillator solutions in fig. 7. Note the 10 times smaller POPOP concentration and the low light yield of 3–HF (table 2).

The results obtained for the investigated scintillators at high concentrations are compiled in table 2. Apart from some basic information it shows the Stokes' shift, the light yield normalized to PMP 420 for "surface emission" and the range of the absorption lengths $\lambda$ for a 0.025 molar solution of the scintillator across the full width at half maximum of its emission band.

It is interesting to compare the spectroscopic properties of the PMP derivatives in table 1 with those of table 2. While the absorption maxima measured with dilute ($5 \times 10^{-5}$ M) and with high ($> 10^{-2}$ M) concentrations coincide within the error margins, the fluorescence maxima of the high concentrations are shifted by 3 to 5 nm to shorter wavelengths. The reason may be due to the different excitation wavelengths: All dilute solutions (table 1) were excited at 313 nm within the absorption bands of the PMP derivatives, whereas the high concentrations (table 2) were excited at 240 nm within the toluene absorption band.

We observe also a distinct difference between the absolute fluorescence quantum yields of the PMP derivatives in dilute solutions of air saturated toluene (table 1) and the
relative light yields for high concentrations (table 2). This behaviour may be caused by
differences in the energy transfer ability between toluene and the individual PMP derivatives
if excited at 240 nm (table 2), or between the absorption and emission bands of the PMP
derivatives if excited at their absorption bands (table 1). Therefore, it might be in particular
different for scintillator activations of plastics like PS or PVT.

Knowing the extinction coefficients and the "surface emission" spectra (fig. 2, 3 and
4) of the scintillator solutions, we calculated the intensities of transmitted light as a function
of absorption paths l and scintillator concentrations c:

\[ Y(l, c) = \frac{\int_{PM\ 420}^{PM\ P} \int I_0(v) e^{-6(v)c} dv}{\int PM\ P I_0(v) dv} \]

where \( I_0(v) \) is the fluorescence intensity at wave number \( v \), and the integrals span the whole
emission bands in question. Normalization to the PMP 420 is achieved by division by its
emission integral.

The curves drawn in fig. 7 represent these calculations and agree satisfactorily with
the measured values plotted in the same figure. Based on this conformity within the critical
region of the first 50 mm of self–absorption, we extended our calculations to longer
absorption paths. The results for the various scintillator solutions have been entered in
fig. 8. The initial light yields at zero absorption path are normalized to that of PMP 420
according to table 2. The behaviour of the measured extinction coefficients (fig. 4) and
absorption lengths (fig. 5) corresponds to the shape of the calculated absorption curves. In
fact, it is not possible to measure the absorptions through such long paths directly because
of distortions caused by light leakage and reflections at the lateral surfaces of long samples.

The lowest self–absorptions were obtained with PMP 450 and 3–HF. Unfortunately,
their light yields amount to only 70% (PMP 450) and 20% (3–HF) compared to that of
PMP 420. In spite of their lower self–absorption, they cannot compensate for this
disadvantage not even after 2 m of absorption path, where their transmitted light intensities
are 40% (PMP 450) and 12% (3–HF) as compared to 51% for PMP (fig. 8). By far the
highest self–absorption was measured for POPOP, which does not directly serve as a
scintillator like all the other listed compounds, but as a wavelength shifter for p–terphenyl
emission. Its decadic extinction coefficient at its emission peak exceeds by a factor 125 that
of PMP 420 at its corresponding peak (fig. 4). Therefore, its concentration must be kept by
at least one order of magnitude lower than that of the other compounds. This comparatively
low concentration leads to rather long absorption lengths (≥ 0.2 mm) for the radiative
(electric–dipole) [18] exchange between the p–terphenyl emission and POPOP absorption at
around 340 nm wavelength. Consequently, its light emission is by far not as local as with
the PMP compounds, where the non–radiative [19] energy transfer between solvent and the
scintillator takes place within a few nanometers. This might become important in certain applications, in particular in light emission in scintillating fibres with diameters ≤ 0.2 mm.

The highest light yield was measured for p-terphenyl. Since it emits at 340 nm, the absorption is considerable, and therefore a wavelength shifter like POPOP is necessary. For the mono scintillator systems like the PMP compounds and 3–HF, the highest light yield was measured for PMP 420. The lowest light yield with about 20% of PMP was measured for both, the pure 3–HF and the p-terphenyl plus 3–HF solutions.

In conclusion, our measured absorption and emission values show for the scintillators in question that PMP 420 looks most promising for future applications in plastic matrices. This is true above all if we consider scintillating polystyrene fibres of small diameters for particle tracking. In view of that, we intend to measure the decadic extinction coefficients, absorption lengths and light yields, in particular for the most critical overlap regions, of the corresponding scintillators in polystyrene bulk samples.

Acknowledgements

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REFERENCES


REFERENCES (Cont'd)


TABLE 1
Photophysical properties of organic scintillators in toluene at room
temperature in dilute solutions (&lt; 3.10^-3 mole l^-1)

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>PMP 420</td>
<td>264</td>
<td>295</td>
<td>425</td>
<td>10 370</td>
<td>0.75(0.88)a)</td>
<td>2.64(3.01)a)</td>
</tr>
<tr>
<td>PMP 430</td>
<td>278</td>
<td>298</td>
<td>437</td>
<td>10 674</td>
<td>0.79</td>
<td>2.73</td>
</tr>
<tr>
<td>PMP 440</td>
<td>296</td>
<td>304</td>
<td>443</td>
<td>10 321</td>
<td>0.80</td>
<td>2.65</td>
</tr>
<tr>
<td>PMP 450</td>
<td>294</td>
<td>301</td>
<td>451</td>
<td>11 050</td>
<td>0.74</td>
<td>3.57</td>
</tr>
<tr>
<td>PMP 460</td>
<td>312</td>
<td>308</td>
<td>461</td>
<td>10 776</td>
<td>0.78</td>
<td>3.02</td>
</tr>
<tr>
<td>p-Terphenylb)</td>
<td>230</td>
<td>287.5</td>
<td>360</td>
<td>7 010</td>
<td>0.85</td>
<td>1.2</td>
</tr>
<tr>
<td>POPOPb)</td>
<td>364</td>
<td>365</td>
<td>415</td>
<td>3 300</td>
<td>0.85</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a) Value in brackets measured in degassed solution.
b) Ref. 12.

TABLE 2
Spectroscopic properties of the investigated scintillators in toluene at 0.025 molar solutions

<table>
<thead>
<tr>
<th>Scintillator</th>
<th>Absorption maximum [nm]</th>
<th>Emission maximum [nm]</th>
<th>Stokes shift [cm^-1]</th>
<th>Light^a) yield</th>
<th>Range of absorption^b) length [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMP 420</td>
<td>295</td>
<td>422</td>
<td>10 200</td>
<td>1</td>
<td>0.02 → 9.0</td>
</tr>
<tr>
<td>PMP 430</td>
<td>295</td>
<td>432</td>
<td>10 750</td>
<td>0.90</td>
<td>0.03 → 3.0</td>
</tr>
<tr>
<td>PMP 440</td>
<td>305</td>
<td>440</td>
<td>10 060</td>
<td>0.85</td>
<td>0.008 → 3.0</td>
</tr>
<tr>
<td>PMP 450</td>
<td>300</td>
<td>448</td>
<td>11 012</td>
<td>0.70</td>
<td>0.08 → 10.0</td>
</tr>
<tr>
<td>PMP 460</td>
<td>309</td>
<td>458</td>
<td>10 528</td>
<td>0.60c)</td>
<td>0.1 → 2.0c)</td>
</tr>
<tr>
<td>3 HF</td>
<td>338</td>
<td>528</td>
<td>10 650</td>
<td>0.20</td>
<td>2.0 → 3.0</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>275</td>
<td>344</td>
<td>7 295</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>POPOPd)</td>
<td>352</td>
<td>418</td>
<td>4 485</td>
<td>0.0001</td>
<td>2.0 → 2.0</td>
</tr>
</tbody>
</table>

a) Excited at 240 nm (surface excitation) and normalized to PMP 420.
b) Across full width at half maximum of the emission band.
c) 0.01 molar solution.
d) 0.0025 molar solution.
FIGURE CAPTIONS

Fig. 1 Arrangement of quartz cuvettes filled with scintillator solutions for surface excitation and self-absorption measurements (figs 6 and 7) in the sample compartment of the spectrofluorimeter.

Fig. 2 Measured absorption and emission bands of p-terphenyl, the wavelength shifter POPOP, 3–HF, and the solvent toluene. The emission peaks are normalized to PMP 420 (unity). Note the different scales.

Fig. 3 Measured absorption and emission bands of five PMP scintillators with large Stokes' shifts, in toluene at > 10^{-2} mole l^{-1}. The emission peaks are normalized to PMP 420 (unity).

Fig. 4 Decadic molar extinction coefficients within the overlap regions of absorption and emission bands. The maxima of the emission wavelengths are indicated for each scintillator by vertical lines. 1 nm spacing between measuring points.

Fig. 5 Absorption lengths $\Lambda$ for 0.025 molar scintillator solutions in toluene. $\Lambda$ means the optical path, which reduces the initial light intensity to 1/e.

Fig. 6 Distortions of the short wavelength flank of a 0.025 molar PMP 420 solution in toluene caused by different absorption paths of the same solution compared with a 0.0025 molar POPOP solution. The POPOP concentration had to be 10 times lower, because of its strong self-absorption in the overlap region.

Fig. 7 Light yield reduction due to self-absorption, measured with the arrangement shown in fig. 1. The solid lines are calculated from measured extinction coefficients and surface emission spectra according to eq. 6.

(a) Comparison between PMP 420, 3–HF and POPOP dissolved in toluene and normalized to unity for zero absorption path. Note the 10 times lower POPOP concentration and the little light yield of 3–HF (table 2).

(b) Comparison between PMP compounds normalized to the light yields as listed in table 2.

Fig. 8 Light intensities for different scintillator solutions calculated from eq. 6 versus the absorption path. The initial light yields at zero absorption path are normalized to that of PMP 420 according to table 2.
Fig. 1
Fig. 2
Fig. 3
Fig. 8