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## Transparent Plastic Scintillators for Neutron Detection Based on Lithium Salicylate

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**Abstract:** Transparent plastic scintillators with pulse shape discrimination containing lithium-6 salicylate have been synthesized by bulk polymerization with a maximum lithium-6 loading of 0.40 wt%. Photoluminescence and scintillation responses to gamma-rays and neutrons are reported herein. Plastics containing lithium-6 salicylate exhibit higher light yields and permit a higher loading of lithium-6 as compared to previously reported plastics based on lithium 3-phenylsalicylate. However, pulse shape discrimination performance is reduced in lithium salicylate plastics due to the requirement of adding more nonaromatic monomers to the polymer matrix as compared to those based on lithium 3-phenylsalicylate. Reduction in light yield and pulse shape discrimination performance in lithium-loaded plastics as compared to pulse shape discrimination plastics without lithium is interpreted in terms of energy transfer interference by the aromatic lithium salts.

**Keywords** – Neutron detector, plastic scintillator, lithium salicylate, pulse shape discrimination

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1    1. Introduction

2  
3    Neutron detection is relevant to the fields of nuclear physics, nuclear power generation, homeland  
4    security, oil well logging, and medical imaging [1, 2]. Gas tubes filled with helium-3 are widely used to  
5    detect neutrons in the presence of gamma-ray background but due to the shortage of this material,  
6    many efforts have been made to develop replacement technologies for neutron detection. Among these  
7    technologies, plastic scintillators are relevant candidates due to their low cost, fast decay times, wide  
8    range of environmental stability, low toxicity, ease of handling, and ease of scaling to large volumes. Fast  
9    neutrons produce signals in plastic scintillators by elastic scattering from hydrogen atoms which  
10   generate recoil protons with kinetic energy sufficient to ionize and excite the surrounding matrix. These  
11   ionizations and excitations produce a flash of light which is detectable by a photomultiplier tube (PMT).  
12   Unambiguous detection of the presence of neutrons is often complicated by gamma-ray background  
13   which produces Compton-scattered electrons in the scintillator. These Compton-scattered electrons  
14   generate signals inside the scintillator which overlap with signals generated by neutrons.

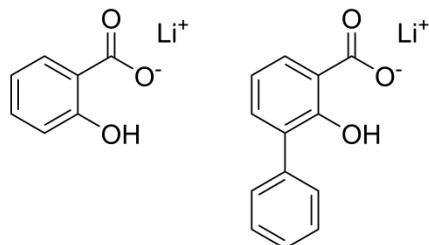
15  
16   One method by which scintillators can be used to discriminate between neutrons and gamma-rays  
17   exploits the difference in the time required for light to be emitted in response to energy deposition by  
18   the different radiation quanta. Compton-scattered electrons deposit energy over a large area, usually on  
19   the order of millimeters, whereas heavy ions such as recoil protons generated by fast neutrons deposit  
20   energy over a very short distance, usually on the order of micrometers. The higher concentration of  
21   ionizations and excitations leads to an enhanced probability of triplet-triplet annihilation which results in  
22   delayed fluorescence. Thus, heavy ions produce signals over a longer timescale than gamma-rays. This  
23   time difference in signal generation can be exploited to determine if the energy was deposited by a  
24   heavy ion or a gamma-ray and is known as pulse shape discrimination (PSD). The first PSD plastic was  
25   reported by Brooks et. al. in 1960 which comprised *p*-terphenyl and isopropylbiphenyl in a  
26   polyvinyltoluene matrix [3]. This plastic formulation, which comprises *p*-terphenyl and isopropylbiphenyl  
27   in a polyvinyltoluene matrix, is unstable after a short period of time and results in an unusable opaque  
28   material [4]. Recently, plastic scintillators with PSD and improved stability have been developed using  
29   different strategies [5-7]. Since the development of these materials, improvements, variations, and  
30   characterizations by multiple groups have been made [4, 8-12]. These materials are summarized well in  
31   a recent review article [13].

32  
33   Moderation around neutron-emitting materials can partially thermalize the resulting neutron energy  
34   spectrum. These thermalized neutrons can be detected by capture reactions that result in the emission  
35   of ionizing radiation that has sufficient kinetic energy to induce signals inside a detector. Common  
36   nuclides used for this purpose include  $^6\text{Li}$ ,  $^{10}\text{B}$ , and  $^{157}\text{Gd}$ . Addition of these nuclides adds new  
37   functionality to PSD plastics in that they become capable of generating usable signals from both fast and  
38   thermal neutrons [14, 15]. After neutron capture,  $^{157}\text{Gd}$  emits gamma-rays over a range of energies so it  
39   is not an ideal neutron capture element for PSD plastics. As was known before PSD plastics were  
40   developed, carborane can be loaded into plastics to produce transparent scintillators capable of  
41   detecting thermal neutrons via the  $^{10}\text{B}$  capture reaction [16]. Pawełczak et. al. demonstrated that this  
42   can be applied to PSD plastics to produce optically transparent scintillators which are capable detecting  
43   thermal neutrons by the  $^{10}\text{B}$  capture reaction as well as fast neutrons [14]. Zaitseva et. al. demonstrated  
44   that lithium 3-phenylsalicylate (LiPSA) can be loaded into PSD plastics to produce transparent  
45   scintillators which are capable of detecting thermal neutrons via the  $^6\text{Li}$  capture reaction as well as fast  
46   neutrons [15]. Lithium-loading in PSD plastics was also accomplished utilizing lithium pivalate by  
47   Cherepy et. al. [17]. Even though the thermal neutron capture cross section of  $^6\text{Li}$  is lower than that of  
48    $^{10}\text{B}$  (942 vs 3840 barns, respectively [2]),  $^6\text{Li}$  may have advantages as compared to  $^{10}\text{B}$  in PSD plastics.

49 Thermal neutron capture by  ${}^6\text{Li}$  produces an alpha particle and a triton with a reaction energy of 4.78  
50 MeV. Thermal neutron capture by  ${}^{10}\text{B}$  results in two possible reactions: release of an alpha particle and a  
51  ${}^7\text{Li}$  nucleus with a reaction energy of 2.79 MeV (6%) and release of an alpha particle and  ${}^7\text{Li}$  nucleus with  
52 2.31 MeV as well as a 0.48 MeV gamma-ray (94%). The gamma-ray is undesirable in PSD plastics because  
53 it results in a faster average scintillation time corresponding to the neutron capture reaction.

54  
55 The incorporation of  ${}^6\text{Li}$  by dissolution in pure aromatic plastics has proven to be difficult and currently  
56 only a few compositions exist. Martinez et. al. recently demonstrated that copolymerizing aromatic and  
57 nonaromatic monomers such as styrene and methyl methacrylate produces PSD-capable plastics with  
58 improved mechanical properties. Although incorporation of nonaromatic monomers reduces the  
59 scintillation performance as compared to pure aromatic matrices [9], it opens up the realm of  
60 possibilities of incorporating  ${}^6\text{Li}$ -bearing compounds which are soluble in nonaromatic matrices such as  
61 poly(methyl methacrylate) (PMMA) but insoluble in aromatic matrices such as polystyrene (PS) into PSD-  
62 capable plastics. The present work seeks to expand the development of PSD plastics which can detect  
63 thermal neutrons. In particular, we found that suitable processing procedures permit the incorporation  
64 of lithium-6 salicylate ( ${}^6\text{LiSal}$ ), which is cheaper and easier to purify than  ${}^6\text{LiPSA}$ , into PSD plastics. An  
65 image comparing the molecular structures of LiSal and LiPSA is shown in Fig. 1. While the  
66 implementation of  ${}^6\text{LiSal}$  as component of a scintillation detector is not a new concept [18-21], the work  
67 presented herein represents the first report of which the authors are aware of  ${}^6\text{LiSal}$  existing as a  
68 dissolved component inside a transparent plastic scintillation detector.

69



70  
71 Fig. 1. Molecular structures of LiSal and LiPSA.

72  
73 2. Materials and Methods  
74  
75 All chemicals were obtained from Sigma-Aldrich unless otherwise stated. Toluene, acetone, diethyl  
76 ether, methanol, tetrahydrofuran (THF), dimethoxyethane (DME) salicylic acid (Fluka), scintillation grade  
77 2,5-diphenyloxazole (PPO), and scintillation grade 1,4-bis(2-methylstyryl)benzene (bis-MSB) were used  
78 as received. Styrene, methyl methacrylate (MMA), divinylbenzene (DVB), and ethylene glycol  
79 dimethacrylate (EGDMA) were passed through a column containing basic alumina on top of silica to  
80 remove inhibitors and impurities, then were sparged for 45 minutes with a steady stream of dry  
81 nitrogen and stored in an inert atmospherer at -20°C until needed. Free radical initiator 1,1-di(*t*-  
82 butylperoxy)-3,3,5-trimethylcyclohexane (L-231, obtained from Luperox<sup>®</sup>) was sparged for 45 minutes  
83 with a steady stream of dry nitrogen and kept at -20°C until needed.  ${}^6\text{Li}$  metal (95%  ${}^6\text{Li}$ ) suspended in  
84 mineral oil was washed with toluene and acetone before use. Water was passed through Milli-Q water  
85 purification system before use. PSA (TCI America) was recrystallized six times from a 10:1  
86 toluene:acetone solution and collected by vacuum filtration.

87  
88 Anhydrous  ${}^6\text{LiOH}$  was synthesized by reacting small pieces of washed  ${}^6\text{Li}$  metal in a 1:1 solution of  
89 methanol and water, then evaporating the solvents. The material was suspended in diethyl ether,  
90 filtered, and washed with diethyl ether and acetone to remove any residual mineral oil. The resulting

91  $^6\text{LiOH} \cdot \text{H}_2\text{O}$  was dissolved in methanol which was then evaporated under vacuum at 150°C for four  
92 hours to give anhydrous  $^6\text{LiOH}$ .  $^6\text{LiSal}$  was synthesized by titrating salicylic acid with  $^6\text{LiOH}$  in methanol to  
93 pH = 6. The solvent was evaporated and the resulting crude material was washed with anhydrous diethyl  
94 ether to remove excess salicylic acid. The resulting purified material was dried on a Schlenk line at 90°C  
95 under nitrogen for four hours to remove residual solvents.  $^6\text{LiPSA}$  was synthesized by titrating purified  
96 PSA with  $^6\text{LiOH}$  in methanol, evaporating the solvent, washing with diethyl ether, and drying on a  
97 Schlenk line at 90°C under nitrogen for four hours to remove residual solvents. Vials used for  
98 polymerization were cleaned with acetone and dried in an oven at 110°C, then further dried with a torch  
99 immediately before use.

100  
101 Plastic scintillators based on  $^6\text{LiPSA}$  were fabricated according to previously reported procedures [15].  
102 Plastic scintillators based on  $^6\text{LiSal}$  were made by dissolving  $^6\text{LiSal}$  in THF in a flame-dried scintillation  
103 vial, then evaporating the solvent under a stream of dry nitrogen until a constant mass was obtained.  
104 PPO and bis-MSB were added to the vial which was then capped, degassed, then placed into a glovebox.  
105 The vial was charged with appropriate masses of styrene, MMA, crosslinker, and L-231 in the glovebox,  
106 sealed with vinyl tape, and removed from the glovebox. For plastics in which more than half the matrix  
107 was styrene, 5% DVB was added and for plastics in which more than half the matrix was methyl  
108 methacrylate, 1% EGDMA was added. Small plastics were fabricated with a total mass of 10 g and large  
109 plastics were fabricated with a mass of 89 g before machining. Polymerization was conducted by placing  
110 the charged vial in a nitrogen-purged oven. For  $\varnothing 24$  mm plastics, the polymerization program was 60°C  
111 for 1 day, 65°C for 1 day, then 70°C for 4 days. For larger diameter plastics, the temperature program  
112 was 59°C for 3 days, 65°C for 1 day, and 70°C for 6 days. After polymerization, the vials were removed  
113 from the oven, cooled to room temperature, and the plastic cylinders were retrieved by breaking the  
114 vials. The faces of the plastic cylinders were machined and polished before characterization

115  
116 Fluorescence measurements were conducted using a Horiba Jobin Yvon Fluoromax-4 spectrometer  
117 equipped with a 450 W Xe lamp in reflectance mode in which the front face of the scintillator was  
118 irradiated by the incident photons and the emission from that same face was recorded. Fluorescence  
119 spectra were corrected for the wavelength-dependent intensity of the lamp and spectral sensitivity of  
120 the detector PMT. Scintillation responses were characterized by wrapping the polished plastics with  
121 Teflon tape leaving an exposed face which was coupled with optical grease to a Hamamatsu R6231-100-  
122 SEL PMT. Signals collected from the PMT were recorded using a 14-bit high resolution CompuScope  
123 14200 waveform digitizer at a sampling rate of 200 MS/s. Light yields were evaluated from the  $^{137}\text{Cs}$   
124 gamma-ray response for which the 500 keVee location was defined by the 50% position of the Compton  
125 edge. The plastics were exposed to a  $^{252}\text{Cf}$  source moderated by 5.1 cm of lead and high density  
126 polyethylene. Three inches of polyethylene was used for  $\varnothing 24$  mm plastics and four inches was used for  
127 larger plastics. Resulting waveforms were integrated over two time integrals,  $t_{total}$  and  $t_{tail}$ , corresponding  
128 to the total charge ( $Q_{total}$ ) and the delayed component of the signal ( $Q_{tail}$ ), respectively. The ratio  $R =$   
129  $Q_{tail}/Q_{total}$  indicated whether an event was likely produced by a neutron (large  $R$ ) or a gamma-ray (small  
130  $R$ ). Quantification of the PSD was accomplished by calculating standard figures of merit (FoM) as defined  
131 in Eq. 1

132

$$133 \quad F_{\text{OM}} = \frac{\langle n \rangle - \langle \gamma \rangle}{FWHM_n + FWHM_{\gamma}} \quad (1)$$

134  
135 where  $\langle n \rangle$  is the centroid of the thermal or fast neutron distribution,  $\langle \gamma \rangle$  is the centroid of the gamma-  
136 ray distribution, and  $FWHM_n$  and  $FWHM_{\gamma}$  are the full widths at half maximum of the fast or thermal  
137 neutron and gamma-ray distributions, respectively. The time gates were optimized to maximize the FoM

138 as previously described [15]. As an example, for a lithium-loaded plastic the optimization resulted in  
139 classifying the first 45 ns after the peak as the prompt component and out to 1125 ns as the delayed  
140 component. FoM were calculated separately for thermal neutron/gamma-ray discrimination and fast  
141 neutron/gamma-ray discrimination. Thermal neutron/gamma-ray FoM was calculated by fitting the  
142 thermal neutron distribution to a Gaussian function and running the calculation over the energy region  
143  $\pm 2.5\sigma$  around the centroid of the thermal neutron distribution. Fast neutron/gamma-ray discrimination  
144 was calculated over the energy range 450 – 510 keVee unless otherwise noted. The error in the figure of  
145 merit calculations is expected to be around 3%. It was difficult to calculate a reliable and reproducible  
146 FoM for thermal neutron/fast neutron discrimination due to the high degree of overlap between these  
147 two sets of signals so discrimination between fast and thermal neutrons will not be discussed in this  
148 work.

149

### 150 3. Results and Discussion

151

#### 152 3.1. Optical Transparency

153

154 Compositions in terms of percentage of the total mass of the fabricated plastics are shown in Table 1.  
155 The remainder of the mass comprises the matrix, crosslinker at concentrations described in section 2,  
156 and any chelating solvent. The weight percentages of lithium are calculated based on the amounts of  
157 corresponding salts added to the initial mixture. It was previously reported that plastics containing 0.2%  
158  $^{6}\text{Li}$  at appropriate thicknesses can have thermal neutron detection efficiencies as high as 50% [15], so  
159 plastics in this work were fabricated around this concentration. Light yields given as relative values to  
160 pure polystyrene (PS) plastics containing PS containing 30% PPO and 0.2% bis-MSB. Plastics containing  
161 2.8, 5, and 9.5 wt%  $^{6}\text{LiSal}$  with varying ratios of PS and PMMA were fabricated to investigate the effect  
162 of changing the aromatic fraction of the matrix and increasing the concentration of the salt on the  
163 scintillation performance. Plastics containing 5%  $^{6}\text{LiSal}$  were transparent at a matrix containing up to  
164 30% PS and plastics containing 9.5%  $^{6}\text{LiSal}$  were only transparent up to 5% PS. Plastics containing  $^{6}\text{LiPSA}$   
165 at up to 7.6% were transparent in a matrix containing 85% PS. Matrix compositions were prepared with  
166 varying ratios of PS to PMMA to compare the effects of increasing the salt concentration and matrix  
167 composition on scintillation performance. Plastics containing more than 0.40%  $^{6}\text{Li}$  as  $^{6}\text{LiSal}$  and more  
168 than 0.21%  $^{6}\text{Li}$  as  $^{6}\text{LiPSA}$  were not transparent. Samples containing  $^{6}\text{LiSal}$  and  $^{6}\text{LiPSA}$  at 0.12%  $^{6}\text{Li}$  with  
169 optimized matrix compositions for each were fabricated at  $\varnothing 51 \times 24.5$  mm to illustrate the potential for  
170 scaling these plastics to larger sizes. An image of the  $\varnothing 51$  mm plastics is shown in Fig. 2.

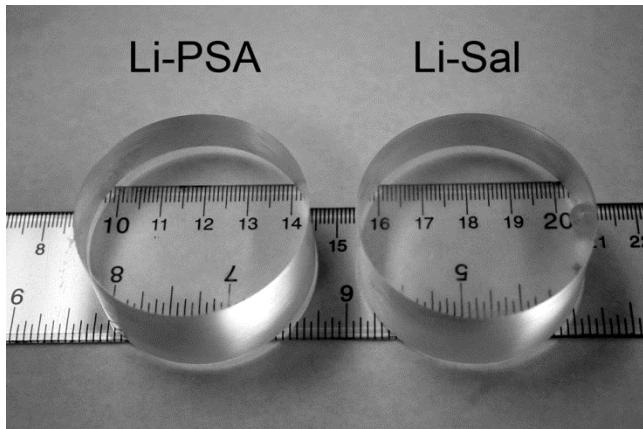
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**Table 1. Compositions by Mass of Fabricated Plastics**

Sample	Matrix	PPO	bis-MSB	Li	wt% $^{6}\text{Li}$	Dimensions
1	PS	30%	0.2%	None	0%	$\varnothing 24 \times 16.5$ mm
2	PMMA	30%	0.2%	None	0%	$\varnothing 24 \times 16.5$ mm
3	85PS:15PMMA	30%	0.2%	None	0%	$\varnothing 24 \times 16.5$ mm
4	PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm
5	5PS:95PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm
6	10PS:90PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm
7	15PS:85PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm
8	20PS:80PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm
9	25PS:75PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm
10	30PS:70PMMA	30%	0.2%	5% $^{6}\text{LiSal}$	0.21%	$\varnothing 24 \times 16.5$ mm

11	30PS:70PMMA	30%	0.2%	7.6% $^6\text{LiPSA}$	0.21%	$\varnothing 24 \times 16.5$ mm
12	PMMA	30%	0.2%	9.3% $^6\text{LiSal}$	0.39%	$\varnothing 24 \times 16.5$ mm
13	5PS:95PMMA	30%	0.2%	9.5% $^6\text{LiSal}$	0.40%	$\varnothing 24 \times 16.5$ mm
14	30PS:70PMMA	30%	0.2%	2.8% $^6\text{LiSal}$	0.12%	$\varnothing 24 \times 16.5$ mm
15	85PS:15PMMA	30%	0.2%	4.3% $^6\text{LiPSA}$	0.12%	$\varnothing 24 \times 16.5$ mm
16	30PS:70PMMA	30%	0.2%	2.8% $^6\text{LiSal}$	0.12%	$\varnothing 51 \times 24.5$ mm
17	85PS:15PMMA	30%	0.2%	4.3% $^6\text{LiPSA}$	0.12%	$\varnothing 51 \times 24.5$ mm

172



173

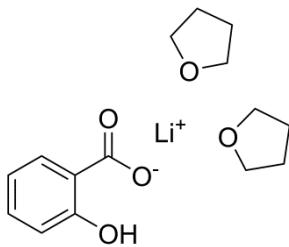
174 Fig. 2. Image demonstrating the optical clarity of  $^6\text{LiSal}$  and  $^6\text{LiPSA}$  plastics with dimensions  $\varnothing 51 \times 24.5$  mm.

175

176

177 Pure  $^6\text{LiSal}$  is insoluble in both styrene and methyl methacrylate monomers which precludes the  
 178 possibility of synthesizing a transparent styrene- or methyl methacrylate-based plastic containing  $^6\text{LiSal}$   
 179 by bulk polymerization using only those components. However, the initial dissolution of  $^6\text{LiSal}$  in THF  
 180 permits subsequent dissolution in liquid monomers and increases the solubility of the salt in plastics up  
 181 to 9.5 wt%. After evaporating the THF from  $^6\text{LiSal}$ , a 1:2 mole ratio of  $^6\text{LiSal:THF}$  remained which was  
 182 soluble in methyl methacrylate and did not become turbid on addition of styrene monomer. A possible  
 183 explanation which accounts for this phenomenon is that the  $^6\text{LiSal}$  forms an adduct with two THF  
 184 molecules as shown in Fig. 3 in which the hard donor oxygen atoms on the THF molecules donate  
 185 electron density to the lithium ion. This result is in agreement with accepted complexation chemistry in  
 186 that lithium ions commonly form complexes with anions and donor ligands as 4-coordinate complexes  
 187 which are the most favorable conformation from an electrostatic point of view [22]. This  
 188 tetracoordinated geometry reduces the effective charge on the lithium ion and shields the ionic charge  
 189 from surrounding weakly polar monomers, thereby facilitating solubility in the resulting polymerized  
 190 matrix. This explanation is further supported by the observation that the masses of the machined  
 191 plastics have remained stable for six months, indicating that the THF is likely stable inside the plastics.  
 192 Likewise,  $^6\text{LiPSA}$  is also insoluble in liquid styrene and methyl methacrylate monomers. By first dissolving  
 193 it in liquid PPO at an elevated temperature or DME, solubility of  $^6\text{LiPSA}$  in liquid monomers and resulting  
 194 polymerized matrices is improved. It is suspected that  $^6\text{LiPSA}$  forms an adduct with the nitrogen or  
 195 oxygen atoms of the PPO molecule or the oxygen atoms of DME which, like  $^6\text{LiSal}$  complexed with THF,  
 196 results in enhanced solubility in plastics due in part to shielding the charge on the ions from the  
 197 surrounding matrix. This framework partially explains the current observations but unfortunately still  
 198 does not provide a method by which transparent lithium-loaded plastic formulations can be predicted.

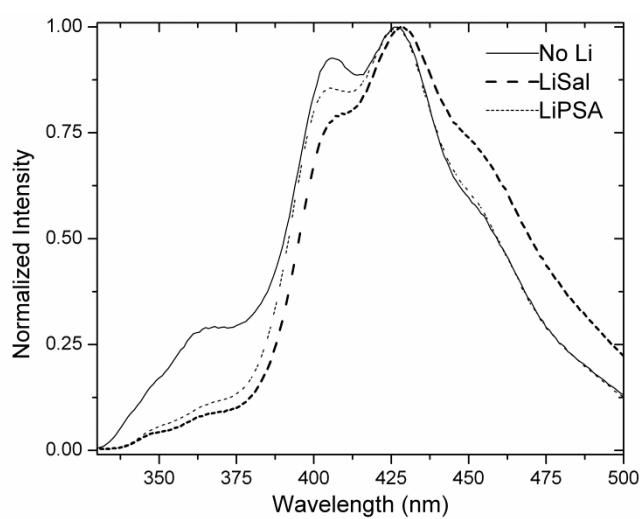
199



200  
201 Fig. 3. Suggested structure of the  $^6\text{LiSal:2THF}$  adduct.  
202  
203

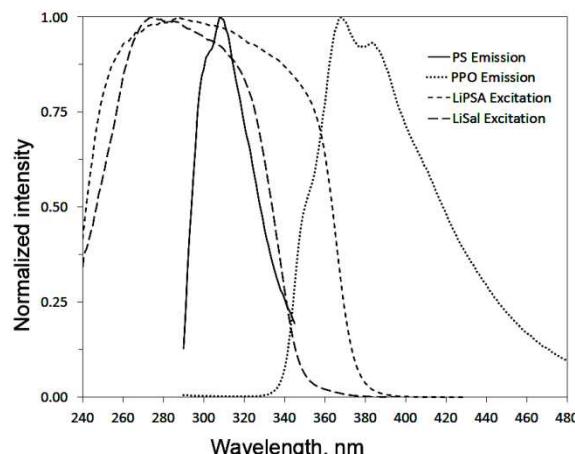
204 3.2. Fluorescence Spectra  
205

206 Emission spectra from plastics containing no lithium,  $^6\text{LiSal}$ , and  $^6\text{LiPSA}$  are shown in Fig. 4. The results  
207 indicate that the primary emission shape is that of the secondary dye (bis-MSB), but the spectra of the  
208 plastics containing lithium are slightly distorted. Most noticeably, the recorded emission from PPO in the  
209 region around 368 nm is markedly reduced in the plastics containing lithium as compared to the plastic  
210 without lithium. This suggests that some of the excitons on PPO are transferred to the lithium salts.  
211 Because the lithium compounds are aromatic, it is expected that they participate in the photon cascade  
212 in which some of the excitons are transferred from the matrix and from PPO to the lithium salts rather  
213 than to bis-MSB, thereby resulting in a noticeable difference in the overall emission spectra.  
214



215  
216 Fig. 4. Emission spectra of plastics containing no lithium,  $^6\text{LiSal}$ , and  $^6\text{LiPSA}$ . Spectra were obtained in  
217 reflectance mode by exciting the styrene subunits at 275 nm and recording the resulting emission.  
218

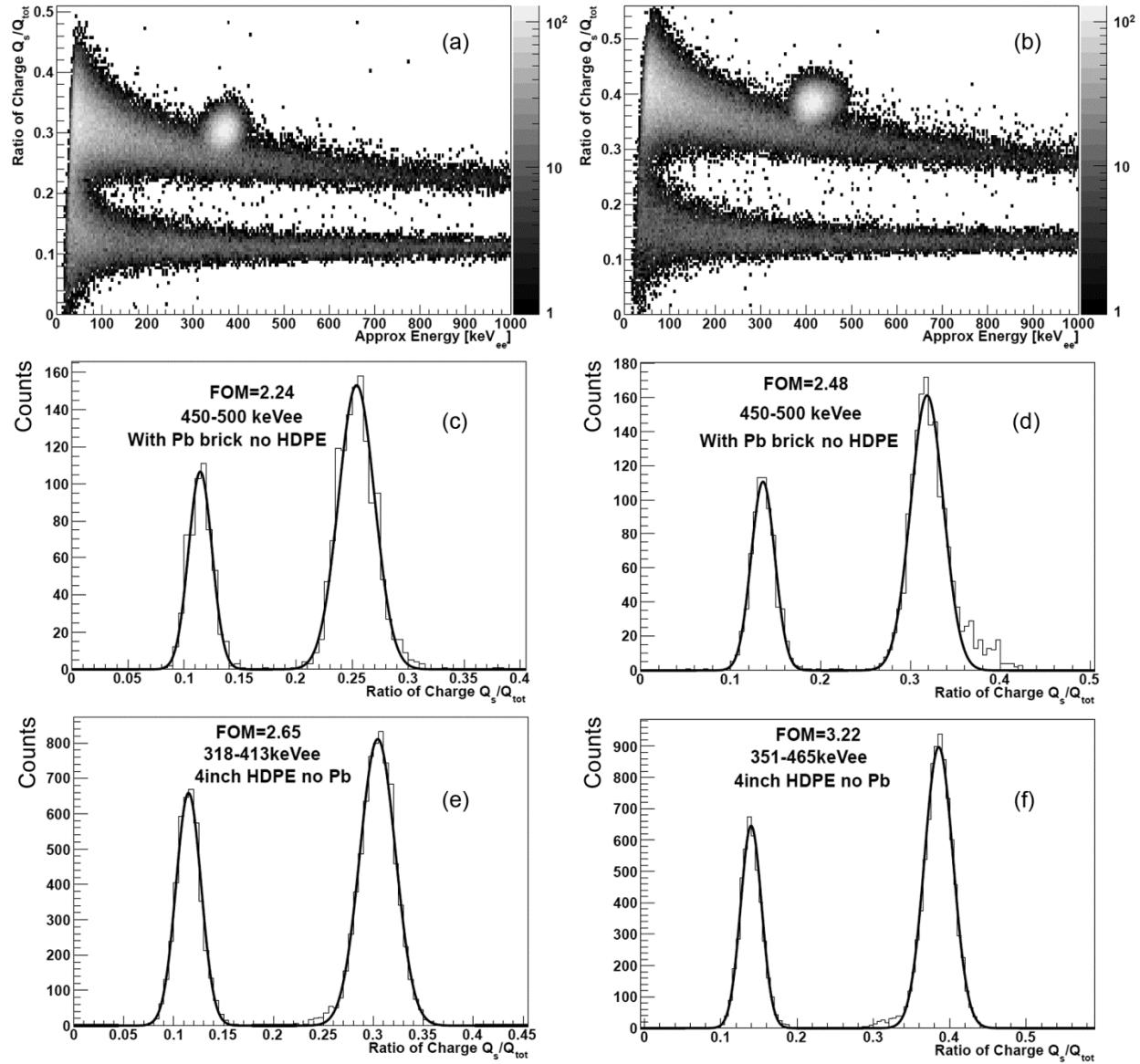
219 The data in Fig. 5 illustrate normalized PS emission, PPO emission, LiSal excitation, and LiPSA excitation  
220 spectra. The excitation spectra of LiSal and LiPSA were measured using PMMA plastics containing 0.12%  
221  $^6\text{Li}$  to in order to obtain molecular excitation in the solid state while avoiding any matrix effects due to  
222 PS absorption. The overlap of LiPSA excitation with PPO emission is greater than that for LiSal, indicating  
223 that the energy transfer from PPO to LiPSA is more efficient than from PPO to LiSal. Due to the lower  
224 scintillation efficiencies of pure LiSal and LiPSA as compared to the more efficient secondary dyes used  
225 for the preparation of PSD plastics, a greater degree of energy transfer to the lithium salts rather than to  
226 bis-MSB should result in a decrease in scintillation efficiency for the plastics described herein.  
227



230 Fig. 5. PS emission, PPO emission, LiSal excitation, and LiPSA excitation. Spectra are normalized to the  
231 maximum intensity value of each response.

### 234 3.3. Effects on Scintillation Performance

236 Plots demonstrating PSD in  $\varnothing 51 \times 24.5$  mm plastics containing  ${}^6\text{LiSal}$  and  ${}^6\text{LiPSA}$  at 0.12%  ${}^6\text{Li}$  exposed to  
237  ${}^{252}\text{Cf}$  are shown in Fig. 6. The left column illustrates the responses from the  ${}^6\text{LiSal}$  plastic and the right  
238 column illustrates those from the  ${}^6\text{LiPSA}$  plastic. The top row contains plots illustrating PSD between fast  
239 neutrons and gamma-rays in the energy region around the  ${}^{137}\text{Cs}$ . FoM calculations were made using Eq.  
240 1. The center row illustrates the total response from  ${}^{252}\text{Cf}$  plotted as  $Q_{\text{tail}}/Q_{\text{total}}$  versus energy in keV<sub>ee</sub>.  
241 The bottom row illustrates the PSD between thermal neutrons and gamma-rays in the region around the  
242 thermal neutron capture spot. As shown in Fig. 6, both plastics exhibit separation between fast neutrons  
243 and gamma-rays above about 80 keV<sub>ee</sub> as well as the presence of a spot corresponding to the thermal  
244 neutron capture reaction by  ${}^6\text{Li}$ . Similar evaluations were made for all fabricated plastics and the results  
245 are shown in Table 2 for which FoM ( $n_{\text{th},\gamma}$ ) is the figure of merit for thermal neutrons and gamma-rays  
246 and FoM ( $n_{\text{f},\gamma}$ ) is the figure of merit for fast neutrons and gamma-rays. All plastics shown are  $\varnothing 24 \times 16.5$   
247 mm except plastics 16 and 17 which are  $\varnothing 51 \times 24.5$  mm. The light yields are normalized to that of the  
248 plastic comprising PS, 30% PPO, and 0.2% bis-MSB. The presence of PMMA in the plastics decreases the  
249 light yield and PSD performance with the deleterious effects being proportional to concentration of  
250 PMMA. This is most clearly seen by comparing plastics 1 and 3 which do not contain  ${}^6\text{Li}$  for which both  
251 the light yields and the FOMs drops significantly on going from a pure PS matrix to a pure PMMA matrix.  
252 This effect is also evident among the plastics containing 5%  ${}^6\text{LiSal}$  for which the light yields decrease  
253 consistently with increasing fraction of PMMA in the matrix. This result is reasonable by considering that  
254 the energy deposited on a methyl methacrylate unit is not transferred to a fluorescent entity whereas if  
255 the energy is deposited on a styrene unit, a fraction of the energy is transferred to the fluors. Thus,  
256 decreasing the fraction of styrene units in the matrix relative to methyl methacrylate units decreases the  
257 number of excitons available to be transferred to the fluors, thereby resulting in fewer emitted optical  
258 photons per scintillation event.



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261 Fig. 6. Plots illustrating PSD in  $\varnothing 51 \times 24.5$  mm plastics containing  ${}^6\text{LiSal}$  (left column) and  ${}^6\text{LiPSA}$  (right column). (a) and (b): Scatter plots illustrating the total responses from  ${}^{252}\text{Cf}$ ; (c) and (d): PSD between fast neutrons and gamma-rays in the energy region around the Compton edge; (e) and (f): PSD between thermal neutrons and gamma-rays in the energy region around the thermal neutron capture spot.

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**Table 2. Scintillation Responses of Fabricated Plastics**

Sample	Matrix	Li	Light Yield (A.U.)	FoM ( $n_{th,\gamma}$ )	FoM ( $n_{f,\gamma}$ )
1	PS	None	$1.00 \pm 0.05$	N/A	3.03
2	PMMA	None	$0.74 \pm 0.04$	N/A	2.58
3	85PS:15PMMA	None	$0.98 \pm 0.05$	N/A	3.06
4	PMMA	5% ${}^6\text{LiSal}$	$0.57 \pm 0.03$	2.43	2.15
5	5PS:95PMMA	5% ${}^6\text{LiSal}$	$0.59 \pm 0.03$	2.59	2.36
6	10PS:90PMMA	5% ${}^6\text{LiSal}$	$0.59 \pm 0.03$	2.64	2.14

7	15PS:85PMMA	5% $^6\text{Li}$ Sal	$0.59 \pm 0.03$	2.65	2.30
8	20PS:80PMMA	5% $^6\text{Li}$ Sal	$0.59 \pm 0.03$	2.70	2.51
9	25PS:75PMMA	5% $^6\text{Li}$ Sal	$0.65 \pm 0.03$	2.97	2.33
10	30PS:70PMMA	5% $^6\text{Li}$ Sal	$0.70 \pm 0.04$	2.99	2.49
11	30PS:70PMMA	7.6% $^6\text{Li}$ PSA	$0.57 \pm 0.03$	2.86	2.44
12	PMMA	9.3% $^6\text{Li}$ Sal	$0.55 \pm 0.03$	2.33	2.00
13	5PS:95PMMA	9.5% $^6\text{Li}$ Sal	$0.62 \pm 0.03$	2.67	2.32
14	30PS:70PMMA	2.8% $^6\text{Li}$ Sal	$0.63 \pm 0.03$	2.72	2.21
15	85PS:15PMMA	4.3% $^6\text{Li}$ PSA	$0.56 \pm 0.03$	3.30	2.33
16	30PS:70PMMA	2.8% $^6\text{Li}$ Sal ( $\varnothing 51 \times 24.5$ mm)	$0.58 \pm 0.03$	2.65	2.24
17	85PS:15PMMA	4.3% $^6\text{Li}$ PSA ( $\varnothing 51 \times 24.5$ mm)	$0.52 \pm 0.03$	3.22	2.48

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267 As shown in the results, the presence of aromatic  $^6\text{Li}$  salts in the plastics decreases the light yield and  
 268 PSD performance relative to the plastics without  $^6\text{Li}$  salts. This implies that the lithium salts are acting as  
 269 exciton traps which only weakly scintillate. This means that a large fraction of the excitons that are  
 270 transferred to or absorbed by the salts rather than to the fluors are lost vibrationally rather than  
 271 resulting in emission of an optical photons. Thus, the presence of the aromatic lithium salts is expected  
 272 to decrease the observed light yield. It is also observed that the FoM between fast neutrons and gamma  
 273 rays is reduced on addition of the aromatic lithium salts. This is likely due to triplet harvesting by the  
 274 lithium salts. Triplet traps such as the aromatic lithium salts decrease the average lifetime of the triplet  
 275 states in the scintillator, thereby decreasing the concentration and therefore the rate of delayed  
 276 emission and resulting in a faster average delayed component of the resulting waveforms from fast  
 277 neutrons. This implies that the use of lithium salts which have absorption bands below that of styrene  
 278 and PPO would not interfere with the energy transfer processes in plastics, thereby preventing  
 279 decreases in light yield and PSD due to exciton trapping.

280

281 Comparing plastics 10 and 11 which contain  $^6\text{Li}$ Sal and  $^6\text{Li}$ PSA, respectively, at 0.21%  $^6\text{Li}$  indicates that  
 282 the light yield of the  $^6\text{Li}$ PSA plastic is lower than that of the  $^6\text{Li}$ Sal plastic. Due to the similarity in the  
 283 atom types in  $^6\text{Li}$ Sal and  $^6\text{Li}$ PSA, it cannot be concluded that the initial number or density of ionizations  
 284 and excitations is very different between the  $^6\text{Li}$ Sal and  $^6\text{Li}$ PSA plastics. The data in Fig. 5 show that the  
 285 transfer of singlet excitation energy is more efficient from PS and PPO to  $^6\text{Li}$ PSA as compared to  $^6\text{Li}$ Sal.  
 286 This makes it reasonable to conclude that after the energy is deposited in the scintillator,  $^6\text{Li}$ PSA collects  
 287 more of the energy from PPO than  $^6\text{Li}$ Sal does; thus, more of the energy is lost to vibrational de-  
 288 excitation rather than being converted into light detectable by the PMT. The difference in PSD between  
 289 plastics 9 and 10 is likely not outside the error of the measurement. This is an interesting result because  
 290 pure LiPSA crystals show significantly better PSD than pure LiSal crystals [15, 21]. This suggests that at  
 291 the concentrations explored in this work, the PSD properties of the  $^6\text{Li}$ -bearing salt do not influence the  
 292 PSD properties of the overall plastic. However, by comparing plastics 14 with 15 as well as plastics 16  
 293 with 17, it can be seen that better PSD can be achieved with  $^6\text{Li}$ PSA plastics as compared to  $^6\text{Li}$ Sal plastics  
 294 due to higher solubility of  $^6\text{Li}$ PSA in matrices with a greater aromatic fraction.

295

296 4. Conclusions

297

298 This work has demonstrated that  ${}^6\text{LiSal}$  can be incorporated into PSD plastics to produce transparent  
299 scintillation detectors at up to 0.40 wt%  ${}^6\text{Li}$ . Though the current scintillation performance of lithium-  
300 loaded plastic scintillators is still inferior to that of unloaded plastic scintillators, improvements have  
301 been made in the neutron detection efficiency, light yield, cost, and ease of production of lithium-  
302 loaded PSD plastics with  ${}^6\text{LiSal}$  as compared to with  ${}^6\text{LiPSA}$ . This work also extended the possibility of  
303 using low-cost and easy to purify materials to produce lithium-loaded PSD plastics easily and showed  
304 that the complexation strategy implemented for  ${}^6\text{LiPSA}$  to produce transparent lithium-loaded plastic  
305 scintillators is not an isolated case. Both  ${}^6\text{LiSal}$  and  ${}^6\text{LiPSA}$  interfere with the photon cascade with a  
306 concomitant decrease in light yield and PSD performance relative to the unloaded plastics. Both  ${}^6\text{Li}$  salts  
307 collect excitation energy from PS and PPO but the effect is more pronounced with  ${}^6\text{LiPSA}$ , thereby  
308 resulting in lower light yields as compared to  ${}^6\text{LiSal}$  for similar matrices. However, for comparable  
309 matrices there was no significant difference in PSD performance between the two salts.

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311

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313

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## 319 References

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- 321 [1] J.B. Birks, The theory and practice of scintillation counting, Pergamon Press, New York, 1964.
- 322 [2] G.F. Knoll, Radiation detection and measurement, 4th ed., John Wiley & Sons, Inc., New York, 2010.
- 323 [3] F.D. Brooks, R.W. Pringle, B.L. Funt, Pulse shape discrimination in a plastic scintillator, IRE Trans. Nucl.  
324 Sci., 7 (1960) 35-38.
- 325 [4] P. Blanc, M. Hamel, C. Dehé-Pittance, L. Rocha, R.B. Pansu, S. Normand, Neutron/gamma pulse shape  
326 discrimination in plastic scintillators: Preparation and characterization of various compositions, Nucl.  
327 Instrum. Meth. A, 750 (2014) 1-11.
- 328 [5] N. Zaitseva, B.L. Rupert, I. Pawełczak, A. Glenn, H.P. Martinez, L. Carman, M. Faust, N. Cherepy, S.  
329 Payne, Plastic scintillators with efficient neutron/gamma pulse shape discrimination, Nucl. Instrum.  
330 Meth. A, 266 (2012) 88-93.
- 331 [6] E.V.v. Loef, Plastic scintillators with neutron-gamma pulse shape discrimination, IEEE Trans. Nucl.  
332 Sci., 61 (2014) 467-471.
- 333 [7] P.N. Zhmurin, V.N. Lebedev, A.F. Adadurov, V.N. Pereymak, Y.A. Gurkalenko, Pulse shape neutrons  
334 and gamma quanta discrimination by means of plastic scintillator of the new generation, Funct. Mater.,  
335 20 (2013) 500-503.
- 336 [8] N.P. Hawkes, G.C. Taylor, Analysis of the pulse shape mechanism in a plastic scintillator with efficient  
337 neutron/gamma pulse shape discrimination, Nucl. Instrum. Meth. A, 729 (2013) 522-526.
- 338 [9] H.P. Martinez, I. Pawełczak, A.M. Glenn, M.L. Carman, N. Zaitseva, S. Payne, Pulse shape  
339 discrimination in nonaromatic plastics, Nucl. Instrum. Meth. A, 771 (2015) 28-31.
- 340 [10] S.A. Pozzi, M.M. Bourne, S.D. Clarke, Pulse shape discrimination in the plastic scintillator EJ-299-33,  
341 Nucl. Instrum. Meth. A, 723 (2013) 19-23.
- 342 [11] D. Cester, G. Nebbia, L. Stevanato, F. Pino, G. Viesti, Experimental tests of the new plastic scintillator  
343 with pulse shape discrimination capabilities EJ-299-33, Nucl. Instrum. Meth. A, 735 (2014) 202-206.

344 [12] P.N. Zhmurin, V.N. Lebedev, V.D. Titskaya, A.F. Adadurov, D.A. Elyseev, V.N. Pereymak, Polystyrene-  
345 based scintillator with pulse-shape discrimination capability, *Nucl. Instrum. Meth. A*, 761 (2014) 92-98.

346 [13] G.H.V. Bertrand, M. Hamel, S. Normand, Pulse shape discrimination between (fast or thermal)  
347 neutrons and gamma-rays with plastic scintillators: State of the art, *Nucl. Instrum. Meth. A*, In Press  
348 (2014).

349 [14] I.A. Pawełczak, A.M. Glenn, H.P. Martinez, M.L. Carman, N.P. Zaitseva, S.A. Payne, Boron-loaded  
350 plastic scintillator with neutron- $\gamma$  pulse shape discrimination capability, *Nucl. Instrum. Meth. A*, 751  
351 (2014) 62-69.

352 [15] N. Zaitseva, A. Glenn, H.P. Martinez, L. Carman, I. Pawełczak, M. Faust, S. Payne, Pulse shape  
353 discrimination with lithium-containing organic scintillators, *Nucl. Instrum. Meth. A*, 729 (2013) 747-754.

354 [16] I.G. Britvich, V.G. Vasil'chenko, V.N. Kirichenko, S.I. Kuptsov, V.G. Lapshin, A.P. Soldatov, A.S.  
355 Solov'ev, V.I. Rykalin, S.K. Chernichenko, I.V. Shein, New polystyrene-based scintillators, *Instrum. Exp.*  
356 *Tech. +*, Translated from *Prib. Tekh. Eksp.*, 45 (2002) 644-654.

357 [17] N.J. Cherepy, R.D. Sanner, P.R. Beck, E.L. Swanson, T.M. Tillotson, S.A. Payne, C.R. Hurlbut,  
358 Bismuth- and lithium-loaded plastic scintillators for gamma and neutron detection, *Nucl. Instrum. Meth.*  
359 *A*, 778 (2015) 126-132.

360 [18] L.R. Greenwood, N.R. Chellew, G.A. Zarwell,  $^{6}\text{Li}$ -loaded liquid scintillators with pulse-shape  
361 discrimination, *Rev. Sci. Instrum.*, 50 (1979) 472-477.

362 [19] H.H. Ross, R.E. Yerick, A new liquid scintillator for thermal neutron detection, *Nucl. Sci. Eng.*, 20  
363 (1964) 23-27.

364 [20] I. Sen, D. Penumadu, M. Williamson, L.F. Miller, A.D. Green, A.N. Mabe, Thermal neutron  
365 scintillation detectors based on poly(2-vinylnaphthalene) composite films, *IEEE Trans. Nucl. Sci.*, 58  
366 (2011) 1386-1393.

367 [21] N. Zaitseva, J. Newby, G. Hall, C. Saw, L. Carman, N. Cherepy, S. Payne, Growth and properties of  
368 lithium salicylate single crystals, *Cryst. Growth Des.*, 9 (2009) 3799-3802.

369 [22] U. Olsher, Coordination chemistry of lithium ion: A crystal and molecular structure review, *Chem.*  
370 *Rev.*, 91 (1991) 137-164.

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