CHAPTER 5

New Organic Scintillators

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ABSTRACT

Several new organic scintillators have been synthesized based on quaterphenyl and sexiphenyl structures. Physical properties of the new fluors are given. The fluors were compared with commercial scintillators in a variety of applications. The sexiphenyl structure was the most efficient fluor as well as the most resistant to chemical quenching from nitromethane. Both the sexiphenyl and quaterphenyl structures were much more efficient than either PPO or b-PBD based systems for scintillation solutions capable of emulsifying aqueous samples.

INTRODUCTION

Since the development of liquid scintillation counting, those involved in improvements of the technique have sought better and more efficient scintillators. In a paper presented by Birks[1] the focus was minimizing quench rather than compensating for quench. In the same spirit we would like to report on new primary scintillators that lead to improved scintillation efficiency.

In Birks' report, he ranked a variety of scintillator systems with respect to two counting conditions: minimal quench and strong quench due to carbon tetrachloride. He found that while some systems performed well in minimal quench circumstance (the quaterphenyl BBQ or BIBUQ was 2% more efficient than PBD systems), these same systems performed quite poorly in the presence of strong quenchers (BBQ was 49% less efficient than PBD systems with added carbon tetrachloride).

It is obvious from these results that sample conditions causing quench affect the ranking of scintillator systems. Since most liquid scintillation cocktail is used in bioresearch, primarily with aqueous samples, we will rank scintillator systems for aqueous quench as well as minimum quench and strong chemical quench.

Table 1. Fluor Systems Investigated

System[a] Number	1^0 Fluor[b]	2^0 Fluor[c]
1	PPO	—
2	PPO	Bis-MSB
3	b-PBD	—
4	b-PBD	Bis-MSB
5	PPF	—
6	PPF	Bis-MSB
7	d-CH_3O-PPF	—
8	d-amyl-PPF	—
9	$(PF)_2$	—

[a] Solvent—pseudocumene.
[b] Primary fluor at 2.26×10^{-2} M.
[c] Secondary fluor at 1.6×10^{-3} M.

EXPERIMENTAL

Synthesis

The new primary fluors based on quaterphenyl and sexiphenyl ring structures are pictured in Figure 1. Detailed synthetic procedures will be submitted for publication at a later date. Synthetic details for PPF and d-CH_3O-PPF are also found in the Ph.D. thesis of Alem Ghiorghis.[2]

New Fluors: Physical Properties

- PPF 2,7-diphenyl-9,9-dipropylfluorene
  m.p. 195.5–197.5
  NMR: 7.8–7.2 (m, 16H, aromatic), 2.0 (m, 4H, $CH_2CH_2CH_3$)
  0.7 (m, 10H, $CH_2CH_2CH_3$).
  UV: 330 (4.76)
  Emission: 357 and 375 (excitation 326)

- *d-amyl*-PPF
  2,7-bis(4-t-amylphenyl)-9,9-dipropylfluorene
  m.p. 202–204.5
  NMR: 7.8–7.4 (m, 14H, aromatic), 2.05 (m, 4H, $CH_2CH_2CH_3$)
  1.7 (q, 4H, $C(CH_3)_2CH_2CH_3$), 1.35 (s, 12H, $C(CH_3)_2CH_2CH_3$)
  0.75 (m, 16H, $C(CH_3)_2CH_2$-CH_3 and CH_2-CH_2-$CH_{3)}$)
  UV: 212 (4.785), 328 (4.716)
  Emission: 365, 383, 401 (excitation 344)

- *d*-CH_3O-PPF
  2,7-bis(4-methoxyphenyl)-9,9-dipropylfluorene
  m.p. 197.5–201.5
  NMR: 7.8-6.9 (m, 14H, aromatic), 3.9 (s, 6H, OCH_3), 2.0 (m, 4H, CH_2-CH_2CH_3), 0.65 (m, 10H, $CH_2CH_2CH_3$)
  UV: 335 (4.748)
  Emission: 371, 390 (excitation 337)

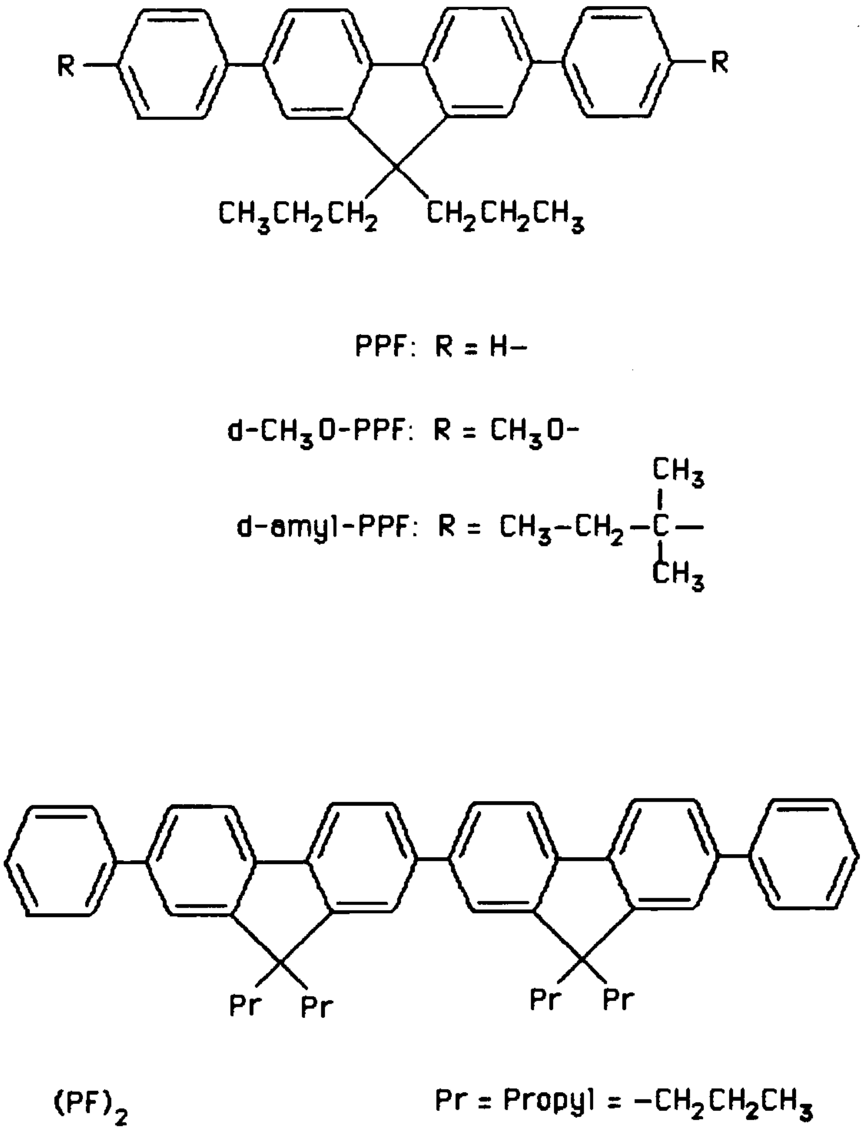

Figure 1. Structures of new oligophenylene fluors.

- *(PF)$_2$* 7,7′-diphenyl-9,9,9′,9′-tetrapropyl-2,2′-bifluorene
  m.p. 241.5–242.5
  NMR: 7.9–7.3 (m, 20 H, aromatic), 2.15 (m, 8H, $\mathit{CH_2}$-$\mathrm{CH_2CH_3}$, 0.8 (bs, 20 H, $\mathrm{CH_2}\mathit{CH_2CH_3}$)
  UV: 204 (4.98) 347 (4.93)
  Emission: 386, 408, 430 (excitation 347)

- Other Material

  pseudocumene, PPO, b-PBD and bis-MSB purchased from Beckman Instruments, used as received.

  nonylphenolpolyethoxylate purchased from Dorsett and Jackson, Long Beach, CA.

  scintillation measurements made with Model 3801 liquid scintillation counter from Beckman Instruments.

Procedure

1. Primary fluor, 2.26×10^{-4} mol, and 5 mg of secondary fluor (when required) were placed in a maxi glass scintillation vial. Pseudocumene, 10 ml, was added to the vial, capped, and shaken, and an average of 5 H-numbers was determined. This was repeated for each sample. Then each vial was opened and 30 μL of nitromethane were added. The vials were again capped and shaken, and an average of 5 H-numbers was determined for each vial.
2. Primary fluor, 2.26×10^{-4} mol, and 5 mg of secondary fluor (if required) were added to a maxi-glass scintillation vial. Pseudocumene, 6 g, was added to each vial. The vial was capped and shaken until the fluors dissolved. Then 4 g of nonylphenolpolyethoxylate emulsifier and 1 g of water were added to each vial and then capped and shaken. The average of 5 H-numbers was determined for each vial.

CALCULATIONS

Horrocks[3] established a relationship between pulse height (PH) and energy (E) on a Beckman Model 9800 liquid scintillation counter that has been maintained through subsequent models. That relationship is

$$PH = 76 + 280 \log E_i. \tag{1}$$

The pulse height for the Compton edge inflection point for ^{137}Cs, energy 478 KeV, is by definition 826. The amount of quench of a sample is the difference between the inflection point of the Compton edge of that sample compared with the inflection point of the Compton edge of the unquenched standard. This difference is quantified as the H-number and defined as

$$H\# = PH_0 - PH_i \tag{2}$$

where PH_0 = the pulse height of the unquenched standard at the Compton edge inflection point

PH_i = pulse height of the sample in question at the Compton edge inflection point.

By combining Equations 1 and 2 the relationship of Equation 3 may be established

$$H\# = PH_0 - PH_i = (76 + 280 \log 478) - (76 + 280 \log E_i) \tag{3}$$

Table 2. Relative Light Output Air-Quenched Cocktail System

System[a]	H-Number	Relative Light Output
$(PF)_2$	1.5	100
PPF	4.5	98
PPF/bis	7.0	95
d-CH_3O-PPF	8.0	95
d-amyl-PPF	8.0	95
b-PBD/bis	9.5	94
b-PBD	11.5	92
PPO/bis	18.8	86
PPO	30.0	78

[a] 10 mL of cocktail—air quenched only.

Solving for log E_i we arrive at Equation 4

$$\log E_i = 2.6794 - H\#/280 \tag{4}$$

E_i is the apparent energy of the quenched sample, i. However, since the decay energy of the ^{137}Cs has not changed, it must be the amount of light from the scintillator per unit of energy input that has changed.

Horrocks[3] has also established a relationship between energy (E_i) and number of photoelectrons generated at the photocathode of the PMT, (Equation 5), where $\#e_i$ is the number of photoelectrons

$$E_i = 20 + (0.666)\ \#e_i \tag{5}$$

The number of photoelectrons generated at the photocathode is directly proportional to the scintillator light impinging on the PMT face. Therefore, the ratio of photoelectrons between two scintillators expresses the relative light output of the two scintillators (Equation 6). Using this relationship we may compare and rank the new scintillators with standard commercial scintillators.

$$\begin{aligned} &\text{Relative light output} = \text{RLO} \\ &\text{RLO} = (e_i \div e_s) \times 100 = [(E_i - 20) \div (E_j - 20)] \times 100 \end{aligned} \tag{6}$$

RESULTS

The traditional fluor systems of PPO or b-PBD, with or without secondary fluor, performed in our tests as would be predicted from Birks' work for minimal quench and heavy chemical quench (Tables 2 and 3). It is suprising to see in Table 4 the equivalence of the two systems in formulations for aqueous samples (one of the most common applications of scintillation cocktails). Therefore, the more expensive fluor, b-PBD, offers no advantage in scintillation performance over the less expensive fluor, PPO, for the measurement of aqueous samples.

Three of the new fluors based on fluorene are structurally related to

Table 3. Relative Light Output Nitromethane Quenched Cocktail System

System[a]	H-Number	Relative Light Output
$(PF)_2$	124	100
b-PBD/bis	150	77.8
b-PBD	152	76.6
d-CH_3O-PPF	176	60.5
PPF/bis	188	53.7
PPO/bis	199	47.8
PPF	208	43.6
d-amyl PPF	212	41.8
PPO	220	38.2

[a] 10 mL of cocktail system—quenched with 30 μL of nitromethane.

quaterphenyls. Quaterphenyls are known to be effective fluors. One example, BBQ, is reported by Birks[1]. BBQ was the result of an exhaustive study by Wirth[4] of substitution on oligophenylenes to improve solubility and maximize scintillation pulse height. The latter was achieved only at much higher concentrations than were required with PPO.

Barnett et al.[5] showed that the *o,o'*-methylene-bridged quaterphenyls, 2,2'-bifluorene, and 2,7-diphenylfluorene (PPF without propyl groups) gave superior pulse heights to quaterphenyl in liquid scintillation counting, a process related to lasing, at least in that the S_1-S_0 transition of the fluor or dye occurs mainly by fluorescence.

Pavlopoulos and Hammond[6] suggested that methylene bridged quaterphenyls such as 2,2'-bifluorene and 2,7-diphenylfluorene might prove to be superior laser dyes. All of these quaterphenyls have very low solubility, which severely limits their utility.

Both 2,2' bifluorene and 2,7-diphenylfluorene have recently been reported by Rinke[7] as effective eximer-pumped laser dyes. Both the solubility and photochemical stability of these laser dyes were dramatically improved when non-aromatic hydrogens were replaced by propy groups as reported by Kauffman.[8] PPF and d-CH_3O-PPF were among the quaterphenyls studied as laser dyes.

Recently PPF as well as other fluorenes were examined by Kauffman[9] as

Table 4. Relative Light Output Aqueous Cocktail Systems

System[a]	H-Number	Relative Light Output
$(PF)_2$	75.0	100
PPF	80.0	95.6
d-CH_3O-PPF	81.5	94.3
PPF/bis	82.2	93.7
d-amyl-PPF	82.5	93.4
PPO/bis	100.5	79.4
b-PBD/bis	100.8	79.2
b-PBD	116.8	68.4
PPO	118.5	67.3

[a] 6 g of solvent fluor system, 4 g of nonylphenolpolyethoxylate emulsifier and 1 g of D.I. water constitute the aqueous cocktail system.

scintillation fluors in a polysiloxane matrix for detection of gamma rays, mainly in quest of radiation hardness. Despite the low concentrations of fluor obtainable in the polymer, the light output of PPF was surprisingly high, which encouraged us to examine PPF as a fluor for liquid scintillation solutions.

In the current study all three quatraphenyls structures, PPF, di-t-amyl PPF and di-methoxy PPF, have similar scintillation properties. All three have similar performance to b-PBD systems and are much better than PPO based systems for experiments with only air quenching present (see Table 2). All three have poorer performance than b-PBD systems, but better than PPO systems when a strong organic chemical quencher, such as nitromethane, is present (see Table 3). The dimethoxy derivative was more quench resistant to nitromethane than either the parent or di-t-amyl quaterphenyl. Finally, all three diphenyl fluorene systems perform much better than either b-PBD or PPO systems when aqueous samples are a cause of the quench (see Table 4).

The final new fluor, $(PF)_2$, which is named here as a dimer of phenylfluorene, is structurally a sexiphenyl. Its scintillation properties are outstanding compared to any of the other new or traditional fluors. It is the most efficient fluor for all three test systems; air quench, strong chemical quench, and aqueous quench.

The sexiphenyl structure would appear to be a promising direction for research into more efficient and more quench resistant scintillation solutions.

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