

Water-Binding Solid Scintillators: Synthesis, Emission Properties, and Tests in ^3H and ^{14}C Counting

Hans-Joachim Meyer and Thomas Wolff*[a]

Abstract: Spectral and time-resolved fluorescence properties as well as relative fluorescence quantum yields of carbodiimide derivatives of 2,5-diphenyloxazole (PPO) (prepared by H_2S elimination from the corresponding thioureas), of some intermediates in the preparation, and of several other PPO derivatives were investigated in solution and in the solid state to test their

suitability as solid scintillators. The carbodiimides reacted slowly with water under acidic conditions to yield ureas. These systems were compared with solid

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mixtures of other PPO derivatives with sodium sulfate as a drying agent, as chemically water-binding solid scintillators in ^3H and ^{14}C counting. Both the chemically and the absorptive water-binding scintillators proved capable of counting ^3H and ^{14}C decay, and open a way to the counting of aqueous samples by solid scintillators without a drying step.

Introduction

Conversion of the energy of β particles (emitted upon radioactive decay of unstable isotopes) into a corresponding number of fluorescence quanta is known as scintillation. Through collisions the particles promote nearby atoms or molecules to electronically excited states capable of emitting fluorescence. The number of excited states generated depends on the energy of the β particles, that is, on the decaying isotope. Since it was first described, the scintillation phenomenon has been exploited for detection, counting, and identification of radioactive radiation.^[1] Inorganic materials such as thallium-doped sodium iodide,^[2–4] cerium-doped yttrium silicate,^[5, 6, 7] solid and liquid noble gases,^[8] and organic scintillators such as 2,5-bis(2-benzoxazolyl)phenol in polystyrene,^[9] 2,5-diphenyloxazole (PPO), and 1,4-bis(2-methylstyryl)benzene (bis-MSB) in paraffin,^[10, 11] or PPO and 1,4-bis-2-(5-phenyloxazolyl)benzene (POPOP) in organic solvents^[12–14] are commonly used as scintillators. The latter systems usually contain surfactants in order to form microemulsions when water has to be taken up from biological and medical samples containing radioactively labeled substances in aqueous solution.

The liquid scintillation counting method is superior for the detection of weak β radiation from ^3H (tritium) or ^{14}C decay. Liquid scintillation counters and many suitable scintillator

solutions (cocktails) are available commercially. Although this technique has been developed to give an excellent performance, disposal of the weakly radioactive organic liquid waste is problematic.

There is therefore growing interest in solid, disposable scintillators that can be used for measuring aqueous samples stemming from biological, pharmaceutical, and medical research or diagnostics. Suitable scintillating solids can be found,^[5, 15] but before their application to aqueous samples a drying procedure is necessary. Besides being time-consuming, this drying step implies the risk of ^3H emission since there may be some tritium in the solvent water, arising from hydrogen exchange with labeled solutes.

Here we describe attempts to find solid scintillators for use without a drying step in aqueous samples. The scintillators (or mixtures containing the scintillator), therefore, have to bind the water of aqueous samples. This is achieved either by the addition of a drying chemical or by synthesizing scintillators bearing groups capable of binding the water chemically; the carbodiimide group, for example, forms urea with water.

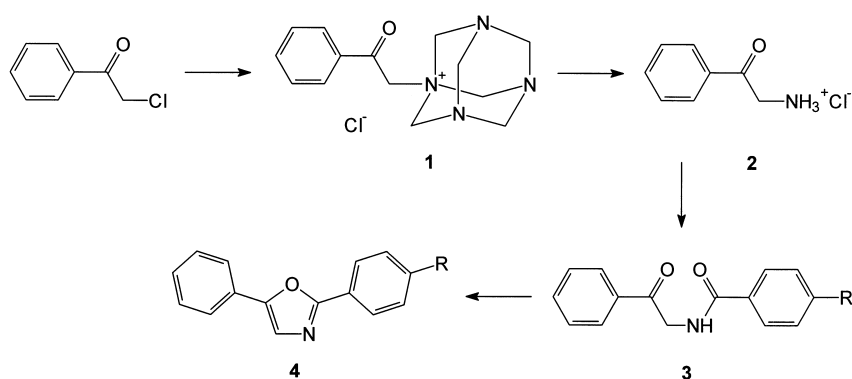
Results

Choice of scintillator chromophore: Some principles of traditional liquid scintillation counting hold for solid scintillators. The fluorescence quantum yield should be as high as possible; reabsorption of fluorescence in the system should be low; the fluorescence maximum of the scintillator should be not too far from 420 nm, to meet the maximum sensitivity of common detectors (photomultipliers). Emission properties

[a] Prof. Dr. T. Wolff, Dr. H.-J. Meyer
Institut für Physikalische Chemie und Elektrochemie der Technischen Universität Dresden
01062 Dresden (Germany)
Fax: + (49) 351-463-3391
E-mail: thomas.wolff@chemie.tu-dresden.de

often differ for the same fluorophore in solution and in the solid state. In most cases the emission spectrum of the solid is red-shifted relative to solutions (in nonpolar solvents) because of interactions of the closely arranged fluorescent molecules.^[16, 17] We therefore tested five fluorescent substances (known to be used in liquid scintillation counting) under our conditions: 2,5-diphenyloxazole (PPO), 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP), *trans*-stilbene, 1,4-bis(2-methylstyryl)benzene (bis-MSB), and 9,10-dimethylantracene. These compounds in ternary mixtures with sodium sulfate and sodium dodecyl sulfate (to adsorb water and to allow homogeneous wetting, respectively; see Experimental Section) were treated with [³H]water and scintillation was counted. The counting efficiencies decreased in the order PPO (7.6%), bis-MSB (5.6%), POPOP (4.2%), *trans*-stilbene (1.1%), 9,10-dimethylantracene (0.24%). This result prompted us to use PPO as the basic chromophore in this study. Another advantage of PPO for our purpose was the comparative simplicity of the synthesis of carbodiimide-substituted derivatives exhibiting the desired fluorescence properties.

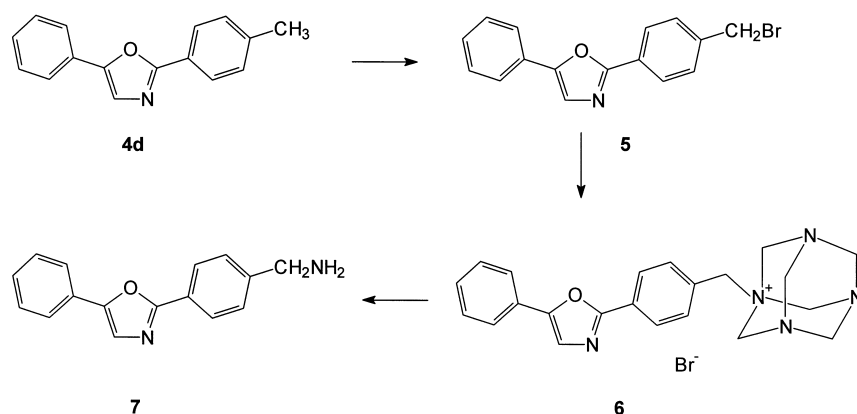
Syntheses: Generally PPO derivatives were synthesized in four steps (Scheme 1) according to Robinson and Lister^[18] and Gabriel.^[19] From phenacyl



Scheme 1. Synthesis of 4'-substituted 2,5-diphenyloxazoles **4**.

chloride, the first two steps yielded ammonium salts **2** via the hexamethylenetetramine adduct **1** (Delépine reaction).^[20] In the presence of a base (pyridine^[21] or aqueous sodium carbonate^[22]) **2** reacted with 4-substituted benzoic acid chlorides to form amides **3**. Dehydration thereafter led to R-substituted PPOs: R = F (**4a**), Cl (**4b**), Br (**4c**), CH₃ (**4d**).

Radical substitution at the methyl group of **4d** with *N*-bromosuccinimide^[23] led to **5**. Compound **6**, obtained in a two-



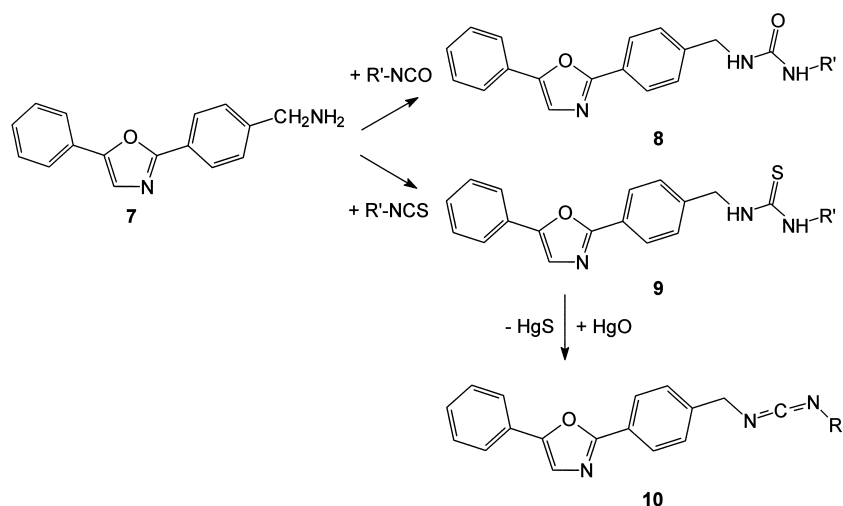
Scheme 2. Synthesis of aminomethyl-PPO **7**.

Abstract in German: Carbodiimid-Derivate des 2,5-Diphenyloxazols (PPO) wurden aus den korrespondierenden Thioharnstoffen durch H₂S-Eliminierung hergestellt. Fluoreszenzspektren und -lebensdauern sowie relative Fluoreszenzquantenausbeuten dieser und einiger verwandter PPO-Verbindungen wurden sowohl im gelösten als auch im festen Zustand untersucht, um die Eignung der Substanzen als Feststoffsintillatoren zu prüfen. Unter sauren Bedingungen reagierten die Carbodiimide mit Wasser allmählich zu Harnstoffen. Diese Systeme wurden als chemisch wasserbindende Szintillatoren für die Zählung von ³H- und ¹⁴C-Zerfällen getestet und verglichen mit festen Mischungen aus PPO-Derivaten und Natriumsulfat als Trockenmittel. Sowohl die chemisch wasserbindenden als auch die adsorptiv wasserbindenden Szintillatoren konnten ³H- und ¹⁴C-Zerfälle zählen und eröffnen eine Möglichkeit, wässrige Proben mit Feststoffsintillatoren zu vermessen, ohne dass ein Trocknungsschritt nötig ist.

step Delépine reaction, formed the primary amine **7** upon acidic alcoholysis (Scheme 2). Yields were moderate in **5** and high in **6** and **7**.

The addition of isocyanates R'-NCO^[24] and isothiocyanates R'-NCS^[25] led to ureas **8** and thioureas **9** (Scheme 3): R' = C₂H₅ (**8a**, **9a**), *i*Pr (**8b**, **9b**), Ph (**8c**, **9c**). Yields were excellent for thioureas **9** and good for ureas **8**. By elimination of H₂S employing HgO^[26] the corresponding carbodiimides **10** were obtained in moderate (**10a**) to fair (**10b**, **10c**) yields. Elimination of H₂O from the ureas **8** by various methods^[24, 27, 28] failed.

The hydration of the carbodiimides **10** in the solid state to yield the ureas **8** was essential to this study, so we followed the progress of urea formation in the scintillation test samples, that is, in powdered carbodiimide (900–1100 mg, sufficient for stoichiometric reaction with water) and sodium dodecyl sulfate (10%, w/w) after the addition of 50 µL of the aqueous solution of the labeled probes (containing 0.05 mol L⁻¹ trifluoroacetic acid). Water consumption after one day was 35% in **10a**, 27% in **10b**, and 19% in **10c**; after seven days it



Scheme 3. Synthesis of PPO substituted by ureas, thioureas, and carbodiimides.

was 51 %, 37 %, and 24 %, respectively. In $[D_6]DMSO$ solution the reaction of the carbodiimides with aqueous trifluoroacetic acid was complete within a few hours.

Fluorescence properties: Table 1 shows emission properties of argon-saturated solutions of the synthesized compounds in cyclohexane or methanol. Fluorescence quantum yields are given relative to an absolute value $\Phi_F=1$ for PPO in cyclohexane.^[29] Natural lifetimes τ_0 were calculated from measured lifetimes and fluorescence quantum yields according to Equation (1), which is valid when fluorescence (rate

$$\tau_0 = \frac{\tau_m}{\Phi_F} \quad (1)$$

Table 1. Emission properties of synthesized compounds.^[a]

Substance	Φ_F	τ [ns]	τ_0 [ns]	$\Delta\nu$ [cm ⁻¹]	$\lambda_{a,max}$ [nm] ^[b]	$\lambda_{e,max}$ [nm]	λ_{CG} [nm]
cyclohexane							
PPO(4,R = H)	1	1.7 ^[c]	1.7	2860 ^[c]	303(4.53)	354	370
4a	0.97	1.8	1.8	3000	302(4.49)	355	371
4b	0.98	2.1	2.2	2760	307(4.52)	360	376
4c	0.33	1.0	3.1	2490	309(4.54)	361	374
4d	0.98	1.5	1.5	2920	304(4.48)	355	372
5	0.06	1.5	24.8	1540	314(4.51)	359	364
7	0.96	1.8	2.0	2730	305(4.50)	358	372
10a	0.92	1.9	2.1	2700	306(4.47)	359	372
10b	0.92	1.9	2.0	2780	306(4.51)	359	372
10c	0.24	1.3	5.4	2590	307(4.49)	357	372
methanol							
PPO	0.79	2.0	2.5	2980	302(4.48)	362	372
6	0.64	1.5	2.3	3060	308(4.47)	372	379
8a	0.64	1.4	2.2	2830	305(4.51)	362	374
8b	0.69	1.3	1.9	2940	304(4.50)	362	375
8c	0.62	1.4	2.3	2840	305(4.50)	363	375
9a	0.17	1.4	8.2	2420	305(4.52)	351	367
9b	0.15	1.2	8.0	2350	306(4.52)	355	364
9c	0.09	1.5	16.7	1730	306(4.55)	350	356

[a] Fluorescence quantum yield Φ_F (relative to PPO in cyclohexane^[29]), lifetime τ , natural lifetime τ_0 , Stokes shift $\Delta\nu$, wavelength of the absorption maximum $\lambda_{a,max}$ ^[b], wavelength of the emission maximum $\lambda_{e,max}$, and wavelength of the center of gravity of the emission spectrum λ_{CG} . All values for degassed solutions at $c = 50 \mu\text{mol dm}^{-3}$ in two solvents at 25 °C. [b] Values in parentheses: $\log(\epsilon [\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}])$. [c] Ref.[29]: $\tau = 1.5 \text{ ns}$; $\nu = 2900 \text{ cm}^{-1}$.

constant k_F), internal conversion (k_{IC}), and intersystem crossing (k_{ISC}) are the only processes deactivating the electronically excited fluorescent state, according to Equation (2).

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC}} \quad (2)$$

Stokes shifts (the energy loss between absorption and emission spectra) were calculated as the difference between the wavenumber of the 0–0 transition (ν_{00}) and that of the center of gravity of the emission spectrum curve (ν_{CG}).^[29] The

intersection of normalized absorption and emission spectra was taken as ν_{00} . Large Stokes shifts were desirable to suppress possible reabsorption of emitted fluorescence quanta.

Table 1 reveals low quantum yields in solution for brominated compounds (4c, 5) and for the thioureas, especially the phenyl derivative 9c, but the carbodiimides and their hydration products, the ureas 10 (except 10c), were highly fluorescent and thus appeared suitable for this study.

In the solid state, however, the quantum yields of carbodiimides and ureas were lower (Table 2). Comparing the spectral features $\lambda_{e,max}$ and λ_{CG} in Tables 1 and 2 the

Table 2. Fluorescence quantum yield (relative to PPO) Φ_F , lifetime τ , wavelength of the emission maximum $\lambda_{e,max}$, and wavelength of the center of gravity of the emission spectrum λ_{CG} . All for powdered solids at 25 °C.

Substance	Φ_F	τ [ns]	$\lambda_{e,max}$ [nm]	λ_{CG} [nm]
PPO(4,R = H)	1	2.5	392	400
4a	0.76	2.3	398	410
4b	0.63	2.3	396	412
4c	0.18	1.3	393	407
4d	0.68	1.7	387	402
5	0.05	2.2	460	395
6	0.35	1.9	398	407
7	0.20	2.2	438	437
8a	0.44	2.2	426	426
8b	0.24	2.3	407	419
8c	0.36	1.7	412	400
9a	0.43	2.1	414	426
9b	0.31	1.5	438	438
9c	0.18	2.2	441	433
10a	0.17	2.5	401	410
10b	0.13	2.2	408	415
10c	0.16	1.8	393	411

expected red shift in solids relative to solutions is evident. The λ_{CG} values were in the high photomultiplier sensitivity range, as desired. Powdered mixtures (as used in the scintillation experiments described below) of the substances investigated, Na_2SO_4 , and sodium dodecyl sulfate showed only slight deviations from the fluorescence properties of

the pure substances (compare Table 3 with Table 2), indicating that these additives did not quench fluorescence significantly.

Table 3. Relative fluorescence quantum yields Φ_F , lifetimes τ , wavelength of the emission maximum $\lambda_{e,max}$, and wavelength of the center of gravity of the emission spectrum λ_{CG} . All for powdered solids mixed with Na_2SO_4 and sodium dodecyl sulfate (weight ratio 8:1:1) at 25 °C.

Substance	Φ_F	τ [ns]	$\lambda_{e,max}$ [nm]	λ_{CG} [nm]
PPO(4,R = H)	0.95	2.4	393	399
4a	0.76	2.8	397	409
4b	0.59	2.3	395	407
4c	0.20	1.4	395	402
4d	0.77	1.8	389	402
5	0.06	1.9	— ^[a]	396
6	0.36	2.0	395	405
7	0.20	2.3	437	436
8a	0.42	2.8	431	425
8b	0.28	2.1	399	413
8c	0.36	1.8	402	410
9a	0.42	2.5	424	429
9b	0.25	1.6	442	429
9c	0.20	2.2	439	433
10a	0.16	2.6	401	413
10b	0.13	2.4	392	411
10c	0.18	1.4	398	412

[a] Signal to noise ratio too low for the determination of λ_{max} .

Scintillation: Samples of ^3H -labeled water and ^{14}C -labeled sodium benzoate (^{14}C in the carboxyl group) in aqueous solution were used to test scintillation in two series: i) in powdered mixtures of the fluorescent substance (scintillator), sodium sulfate, and sodium dodecyl sulfate; and ii) in powdered mixtures of the synthesized carbodiimides (0.9–1 g) and sodium dodecyl sulfate. In i), a weight ratio of 10 % sodium sulfate and 10 % sodium dodecyl sulfate in 400 mg samples was chosen. Scintillator contents exceeding 80 % did not increase the counting efficiency. In ii), the drying agent sodium sulfate was omitted. Sodium dodecyl sulfate, a surfactant, was added in both cases to allow wetting of the organic material. The samples were treated with 50 μL of the aqueous probes.

Intermediate products of the syntheses were included in the investigation, for comparison. From Table 4, counting efficiencies S of compounds with low fluorescence quantum yields were low, as expected. Counting was much more efficient for ^{14}C than for ^3H , reflecting the difference in β -particle energy for tritium decay (β -emission extending to 18.6 keV) and for ^{14}C decay (β -emission extending to 156.5 keV).^[1] The maximum counting efficiency was found in the ureas **8** (in mixtures with sodium sulfate and sodium dodecyl sulfate); these were the products of the reaction of the corresponding carbodiimides **10** with water. Since carbodiimides **10** (in mixtures without sodium sulfate) counted less efficiently, a time dependence of the counting efficiency was to be expected.

Tables 5 and 6 show the temporal development of counting efficiencies. In ^3H counting, small changes with time were generally observed. In ^{14}C counting of **10c**, however, the counting efficiency increased by a factor of 1.7 within one week.

Table 4. Scintillation counting efficiencies S (counts per minute/decays per minute) for various solid powders measured 5 min after treatment of the mixtures with aqueous solutions of labeled samples. The powdered mixtures contain 10 % sodium dodecyl sulfate (by weight), and 10 % sodium sulfate (if applicable).

Substance	$S(^3\text{H})$	$S(^{14}\text{C})$	$S(^3\text{H})$	$S(^{14}\text{C})$
	Mixtures with Na_2SO_4		Mixtures without Na_2SO_4	
PPO(4,R = H)	0.076	0.251		
4a	0.023	0.151		
4b	0.014	0.14		
4c	0.0032	0.02		
4d	0.014	0.04		
5	0.0002	0.005		
6	0.0064	0.15		
7	0.0050	0.24		
8a	0.049	0.63		
8b	0.060	0.66		
8c	0.045	0.44		
9a	0.026	0.52		
9b	0.020	0.49		
9c	0.0007	0.02		
10a			0.015	0.138
10b			0.0013	0.068
10c			0.0049	0.096

Table 5. Scintillation counting efficiencies S (counts per minute/decays per minute) for various solid powders measured at various times after treatment of the mixtures with aqueous solutions of labeled samples. The mixtures contain sodium dodecyl sulfate and sodium sulfate, each at 10 % by weight.

Substance	$S(^3\text{H})$	$S(^3\text{H})$	$S(^3\text{H})$	$S(^3\text{H})$	$S(^3\text{H})$	$S(^3\text{H})$	$S(^3\text{H})$
	at 5 min	at 39 min	at 73 min	at 107 min	at 141 min	at 24 h	at 7 d
PPO(4,R = H)	0.076	0.075	0.073	0.068	0.067		
4a	0.023	0.021	0.019	0.018	0.017		
4b	0.014	0.014	0.014	0.013	0.013		
4c	0.0032	0.0019	0.0017	0.0016	0.0014		
4d	0.014	0.014	0.013	0.012	0.012		
5	0.0002	0.0003	0.0003	0.0003	0.0002		
6	0.0064	0.0061	0.0061	0.0059	0.0059		
7	0.0050	0.0056	0.0057	0.0059	0.0059		
8a	0.049	0.060	0.060	0.061	0.063		
8b	0.060	0.062	0.063	0.066	0.064		
8c	0.045	0.047	0.046	0.046	0.046		
9a	0.026	0.025	0.023	0.021	0.020		
9b	0.020	0.022	0.021	0.020	0.020		
9c	0.0007	0.0008	0.0008	0.0009	0.0009		
10a ^[a]	0.015	0.014	0.013	0.012	0.010	0.012	0.0050
10b ^[a]	0.0013	0.0011	0.0011	0.0011	0.0013	0.0014	0.0012
10c ^[a]	0.0049	0.0055	0.0059	0.0061	0.0059	0.0062	0.0060

[a] Without Na_2SO_4 .

Table 6. Scintillation counting efficiencies S (counts per minute/decays per minute) for various solid powders measured at various times after treatment of the mixtures with aqueous solutions of labeled samples. The mixtures contain 10 % sodium dodecyl sulfate (by weight).

Substance	$S(^{14}\text{C})$	$S(^{14}\text{C})$	$S(^{14}\text{C})$	$S(^{14}\text{C})$	$S(^{14}\text{C})$	$S(^{14}\text{C})$	$S(^{14}\text{C})$
	at 5 min	at 39 min	at 73 min	at 107 min	at 141 min	at 24 h	at 7 d
10a	0.138	0.133	0.128	0.125	0.122	0.112	0.103
10b	0.068	0.066	0.064	0.063	0.062	0.050	0.035
10c	0.096	0.102	0.107	0.110	0.113	0.144	0.169

Discussion

Synthesis: The PPO derivatives **4a–4d** were prepared according to literature procedures^[31, 18, 21] with a few modifications: the intermediate **1** was obtained in better yields when prepared in dichloromethane (85 %) than in chloroform^[31] (60 %). Dichloromethane was also less toxic. In the preparation of **3a–3d** toluene was used as a solvent and aqueous sodium carbonate was used as a base^[22] instead of pyridine.^[21] In the biphasic system the concentration of base was kept low so that the concentration of free amines was also low, leading to fewer by-products and slightly higher yields. Use of POCl₃^[21] rather than sulfuric acid^[22] in the dehydration of **3** to form **4** was found to be advantageous, since the workup was facilitated. The yield of **5** prepared from **4d** has been reported to be 98 %^[23], but we obtained only 55–60 % in several attempts.

Compounds **8a–10c** have not been described previously. The synthesis chosen led to high (sometimes excellent) yields of the ureas **8** and the thioureas **9**. Unfortunately the yields of carbodiimides **10** were only moderate, probably due to the presence of four phases in the reaction mixture (toluene, water, solid **9**, and solid HgO). The possible hydration of **10** during this reaction, however, was less likely to decrease the yields, since it was found to proceed slowly (see above). In contrast, the complete failure to prepare carbodiimides by dehydration of ureas may have been due to fast rehydration of carbodiimides under the reaction conditions.

Fluorescence: The fact that the quantum yields of brominated compounds fall short of those of the other compounds can be attributed mainly to the well-known heavy-atom effect, which accelerates the spin-forbidden intersystem crossing process^[33] (k_{ISC}) to yield the excited triplet state at the expense of fluorescence emission (k_F). Additionally in these cases, the strikingly high natural lifetimes τ_0 calculated for **5** and **9c** (Tables 1 and 2) may indicate that the condition of Equation (2) is not met. There may be two different reasons: i) photochemical reactions may be competing with fluorescence, internal conversion, and intersystem crossing; or ii) because of the comparatively small Stokes shift, considerable reabsorption may be a partial cause of the low quantum yields measured in **5** and **9c**.

Scintillation: The counting efficiencies (Table 4) are generally low compared with common liquid scintillation counting results, largely due to the measuring geometry of the Packard Tricarb 2550 TR/LL counter, in which the detectors (photomultipliers) are positioned beside the sample. Modern technical developments have led to scintillation counters capable of multiple measurements simultaneously. For example, the Top Count Reader (Packard Instrument BV, Groningen, The Netherlands) has an array of photomultipliers placed on top of the samples in microtiter plates. This might provide a more suitable geometry for counting with solid scintillators such as those studied here, since most fluorescence quanta are emitted upwards. Thus, improvements in absolute counting efficiencies rest on optimizing the technical equipment.

The influence of the spectral distributions of the fluorescence emission on the counting efficiency S may be assessed by plotting S/Φ_F , where Φ_F is the corresponding fluorescence quantum yield, as a function of the centers of gravity of the emission spectra, λ_{CG} , as shown in Figure 1 for ³H counting. Compounds with λ_{CG} around 420 nm are superior by far, in accordance with the maximum sensitivity of the photomultipliers used in the scintillation counter, which operates in this wavelength range. Similar features for ¹⁴C counting are shown in Figure 2.

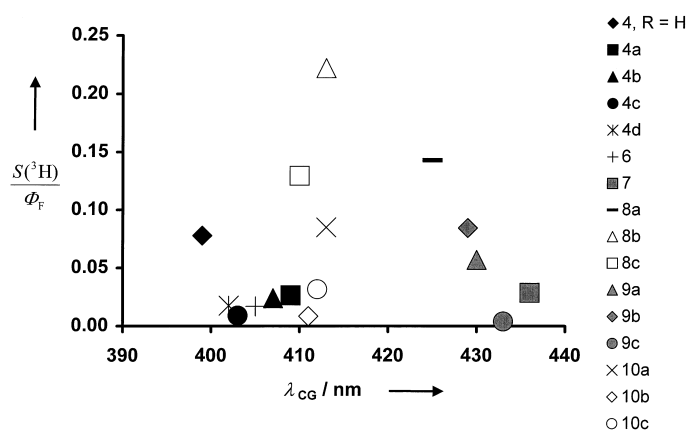


Figure 1. Reduced ³H counting efficiencies as a function of the centers of gravity of the emission spectra (cf. Table 3).

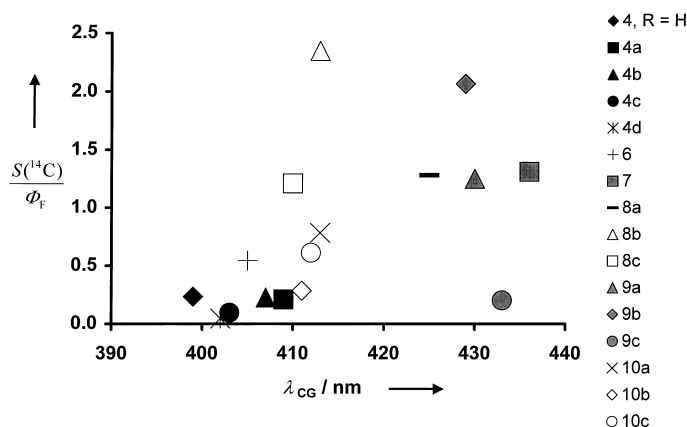


Figure 2. Reduced ¹⁴C counting efficiencies as a function of the centers of gravity of the emission spectra (cf. Table 3).

In the absence of effects specific to the scintillator, $S(^{14}\text{C})/S(^3\text{H})$ ratios as a function of λ_{CG} should reflect the ratio of β -particle energy, $E(^{14}\text{C})/E(^3\text{H})$, according to Equation (3), as

$$\frac{S(^{14}\text{C})}{S(^3\text{H})} = \frac{E(^{14}\text{C})}{E(^3\text{H})} \approx 8.6 \quad (3)$$

was found for **4a–4c**, **8a–8c**, and **10a** (Figure 3). Values above and below 8.6, therefore, indicate a higher sensitivity for ¹⁴C counting (**7**, **9a–9c**, **10b**, **10c**) and for ³H counting (PPO, **4d**), respectively.

These observations can be explained by taking the molecular interactions of the scintillators and [¹⁴C]benzoic acid into account: values exceeding 8.6 indicate attraction, most effective in polar or polarizable compounds (consequently

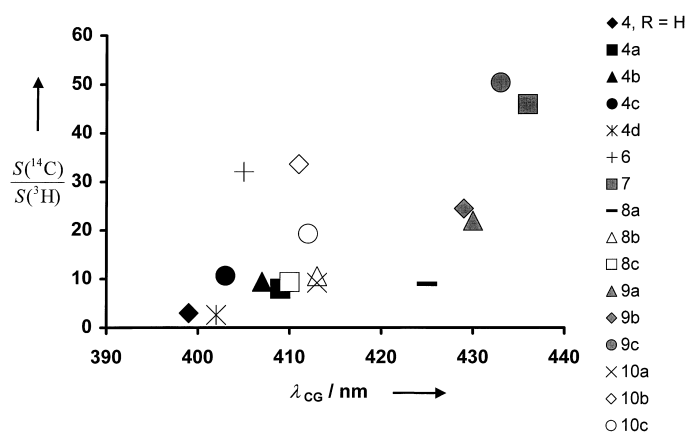


Figure 3. Ratios of ^{14}C and ^3H counting efficiencies as a function of the centers of gravity of the emission spectra (cf. Table 3).

exhibiting λ_{CG} at higher wavelengths), while values below 8.6 may reveal repulsion of scintillator and benzoic acid. Thus the observed specificities of the scintillators are probably not due to distinctions in the electronic excitation by collisions with the β particles.

Temporal changes in counting efficiencies S were expected from two effects: i) the aqueous sample being sucked into the powder of the scintillation mixture; and ii) the reaction of carbodiimides **10** with the water of the aqueous samples yielding ureas **8** which in powdered samples count more efficiently than the carbodiimides (Table 4), in accordance with the differences in quantum yields (Table 3). Effect i) can be expected to decrease S , since fluorescence quanta emitted from the interior of the powder are less likely to be detected, and therefore it may explain the data in Table 5. In contrast, effect ii) should increase S values. This, however, is found in the ^{14}C counting of **10c** only, although the hydration reaction is faster for **10a** and **10b**.

In principle it is disadvantageous that we cannot fully exploit the good scintillation properties of the ureas **8** since the hydration reaction is slow compared with the scintillation experiment. However, a fast reaction with water would raise problems in storing the carbodiimides under ambient humidity. Moreover, in fast hydration reactions warming of the sample may lead to undesired evaporation of water. As the reaction of the carbodiimides with water in $[\text{D}_6]\text{DMSO}$ solution proceeds quantitatively within a couple of hours, we may expect complete consumption of water in the solid samples after sufficient time.

Like the carbodiimides, the hexamethylene tetramine derivative **6** is capable of reacting with water and thus may be employed as a chemically water-binding solid scintillator. We did not pursue this possibility since volatile products are formed upon hydrolysis of hexamethylene tetramine so that the emission of tritium with NH_3 and H_2CO is likely, contrary to the aim of this study.

Conclusion

Scintillation counting of aqueous samples using solid scintillators without a drying step is possible. Counting efficiencies

vary with the fluorescence quantum yields and with the spectral distribution of the emission in relation to the photomultiplier sensitivity of the scintillation counter. Mixtures of PPO derivatives containing a drying chemical (sodium sulfate) count better than chemically water-binding PPO derivatives bearing carbodiimide substituents, which are accessible through elimination of H_2S from the respective thioureas.

Experimental Section

Syntheses: Chemicals were taken from the stocks of the Chemistry Department, Technische Universität Dresden; purchased from Sigma–Aldrich, Acros, Merck, Baker, or Lancaster; or provided by Packard Instrument.

1-(2-Oxo-2-phenylethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane

chloride (1): At room temperature hexamethylene tetramine (226.9 g, 1.618 mol) was dissolved in dichloromethane (3.3 L). Phenacyl chloride (250.0 g, 1.617 mol) was added while the solution was stirred. After stirring for 1 h a white precipitate was formed. The suspension was stirred for another hour. The precipitate was filtered off, washed twice with dichloromethane (200 mL) and dried in vacuo for 6 h. Yield 403.7 g (1.370 mol, 84.7 %); m.p. 145–147 °C (decomp, lit. m.p. 145 °C^[31]).

1-(2-Oxo-2-phenylethyl)ammonium chloride (2): Upon addition of concentrated HCl (37 %, 400 mL) to **1** (403.0 g, 1.367 mol) suspended in ethanol (96 %, 3.3 L), **1** dissolved completely, with a slight warming. The solution was stirred for three days at room temperature. The white precipitate that had formed was filtered and washed twice with ethanol (100 mL). The organic phases were combined and the solvent was evaporated. The residue was crystallized from distilled H_2O (50 mL) and washed four times with acetone. The colorless crystals were dried in vacuo for 4 h. Yield 199.4 g (1.162 mol, 85.0 %); m.p. 194–195 °C (decomp; lit. m.p. 186–187 °C^[31]).

4-Fluoro-N-[1-(2-oxo-2-phenylethyl)]benzamide (3a): 4-Fluorobenzoyl chloride (12.1 mL, 100 mmol) was dissolved in dry pyridine (130 mL). At room temperature **2** (17.2 g, 100 mmol) was added in portions to the stirred solution within 15 min. The suspension was stirred and refluxed for 2 h. The red solution was allowed to cool for 15 min, then distilled H_2O (130 mL) was added. A light yellow precipitate was formed. After the suspension had been kept at 5 °C overnight the precipitate was filtered off. The crude product was washed three times with distilled H_2O (50 mL), recrystallized from ethanol (96 %, 250 mL) and dried in vacuo. Colorless needles; yield 18.8 g (73.1 mmol, 73.1 %); m.p. 135 °C (lit. m.p. 134–135 °C^[21]).

4-Chloro-N-[1-(2-oxo-2-phenylethyl)]benzamide (3b): This was prepared analogously to **3a**, from 4-chlorobenzoyl chloride (97 %, 13.1 mL, 100 mmol) and **2** (17.2 g, 100 mmol). After crystallization from ethanol (96 %, 350 mL) and drying in vacuo, colorless needles were obtained. Yield 21.5 g (78.5 mmol 78.5 %); m.p. 149 °C (lit. m.p. 148–148.5 °C^[21]).

4-Bromo-N-[1-(2-oxo-2-phenylethyl)]benzamide (3c): Preparation of **3c**, from 4-bromobenzoyl chloride (25.0 g, 114 mmol) and **2** (19.7 g, 115 mmol) in dry pyridine (130 mL), was analogous to that of **3a**. The crude product was recrystallized from ethanol (96 %, 600 mL) and dried in vacuo to yield colorless needles. Yield 28.1 g (88.2 mmol; 77.4 %); m.p. 167–168 °C (lit.: m.p. 164–165 °C^[21]).

4-Methyl-N-[1-(2-oxo-2-phenylethyl)]benzamide (3d): To a stirred solution of **2** (85.8 g, 0.500 mol) in distilled H_2O (200 mL) at room temperature, toluene (200 mL) and 1-methyl-4-chlorobenzene (98 %, $\rho = 1.169 \text{ g mL}^{-1}$, 67.5 mL, 0.500 mol) were added. Under further vigorous stirring, aqueous Na_2CO_3 (10 % w/w, 600 mL) was added dropwise within 2 h. A light yellow precipitate formed. After this suspension had been stirred for 2 h the precipitate was separated, washed with distilled H_2O until neutrality and recrystallized from ethanol (96 %, 300 mL). Colorless needles; yield 103.8 g (0.410 mol, 82.0 %); m.p. 125–126 °C (lit. m.p. 125 °C^[18, 32]).

2-(4-Fluorophenyl)-5-phenyloxazole (4a): After **3a** (15.4 g, 59.9 mmol) and POCl_3 (98 %, $\rho = 1.68 \text{ g mL}^{-1}$, 30 mL, 320 mmol) had been stirred and thoroughly refluxed for 3 h, the hot solution was poured onto ice (1 kg).

The suspension formed thereby was vigorously stirred for 30 min. A precipitate formed which was filtered off, dissolved in dichloromethane (500 mL) and washed with aqueous NaHCO_3 until neutrality. The organic phase was dried over Na_2SO_4 and filtered. After evaporation of the solvent the crude product was purified by column chromatography (twice) on Al_2O_3 (neutral, activity I) with CHCl_3 eluent ($R_f = 0.57$ – 0.61) and recrystallization from ethanol (100 mL) (Merck, UVASOL). Yield 11.1 g (46.4 mmol, 77.5%); m.p. 83°C (lit. m.p. 81 – $82^\circ\text{C}^{[21]}$); ^1H NMR (500.13 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 8.09$ (dd, $^3J(\text{H,H}) = 8.8$ Hz, 2H, $^4J(\text{H,F}) = 5.5$ Hz, C9–H, C9'–H), 7.70 (d, $^3J(\text{H,H}) = 7.4$ Hz, 2H, C3–H, C3'–H), 7.44 (t, $^3J(\text{H,H}) = 7.8$ Hz, 2H, C2–H, C2'–H), 7.42 (s, 1H, C6–H), 7.34 (t, $^3J(\text{H,H}) = 7.5$ Hz, 1H, C1–H), 7.16 (t, $^3J(\text{H,H}) = 8.7$ Hz, 2H, C10–H, C10'–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 165.01$ (d, $^1J(\text{C,F}) = 251.5$ Hz, C11), 160.31 (C7), 151.31 (C5), 128.93 (C2, C2'), 128.47 (C1), 128.35 (d, $^3J(\text{C,F}) = 8.6$ Hz, C9, C9'), 127.89 (C4), 124.15 (C3, C3'), 123.82 (d, $^4J(\text{C,F}) = 3.5$ Hz, C8), 123.40 (C6), 116.00 (d, $^2J(\text{C,F}) = 22.6$ Hz, C10, C10'); UV/Vis (cyclohexane): $\lambda_{\text{a,max}}$ (ϵ) = 302 nm ($30\,800\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$).

2-(4-Chlorophenyl)-5-phenyloxazole (4b): This was prepared analogously to **4a**, from **3b** (16.4 g, 59.9 mmol) and POCl_3 (98%, $\rho = 1.68\text{ g mL}^{-1}$, 30 mL, 320 mmol). The crude product was purified by column chromatography (twice) on Al_2O_3 (neutral, activity I) with CHCl_3 eluent ($R_f = 0.52$ – 0.56) and recrystallization from ethanol (130 mL) (Merck, UVASOL). Yield 11.7 g (45.8 mmol, 76.5%); m.p. 116°C (lit. m.p. 115 – $116^\circ\text{C}^{[21]}$); ^1H NMR (500.13 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 8.03$ (d, $^3J(\text{H,H}) = 8.6$ Hz, 2H, C9–H, C9'–H), 7.70 (d, $^3J(\text{H,H}) = 7.4$ Hz, 2H, C3–H, C3'–H), 7.42–7.45 (m, 5H, C10–H, C10'–H, C6–H, C2–H, C2'–H), 7.34 (t, $^3J(\text{H,H}) = 7.5$ Hz, 1H, C1–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 160.17$ (C7), 151.49 (C5), 136.35 (C11), 129.11 (C10, C10'), 128.93 (C2, C2'), 128.57 (C1), 127.78 (C4), 127.48 (C9, C9'), 125.91 (C8), 124.20 (C3, C3'), 123.52 (C6); UV/Vis (cyclohexane): $\lambda_{\text{a,max}}$ (ϵ) = 307 nm ($33\,200\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$).

2-(4-Bromophenyl)-5-phenyloxazole (4c): This was prepared in analogy to **4a**, from **3c** (22.3 g, 70.1 mmol) and POCl_3 (98%, $\rho = 1.68\text{ g mL}^{-1}$, 40 mL, 430 mmol). The crude product was purified by column chromatography (twice) on Al_2O_3 (neutral, activity I) with CHCl_3 eluent ($R_f = 0.42$ – 0.49) and recrystallization from 210 mL ethanol (Merck, UVASOL). Yield 14.1 g (47.0 mmol, 67.0%); m.p. 116 – 117°C (lit. m.p. 115 – $116^\circ\text{C}^{[21]}$); ^1H NMR (500.13 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 7.94$ (d, $^3J(\text{H,H}) = 8.5$ Hz, 2H, C9–H, C9'–H), 7.69 (d, $^3J(\text{H,H}) = 7.3$ Hz, 2H, C3–H, C3'–H), 7.59 (d, $^3J(\text{H,H}) = 8.7$ Hz, 2H, C10–H, C10'–H), 7.43 (t, $^3J(\text{H,H}) = 7.6$ Hz, 2H, C2–H, C2'–H), 7.42 (s, 1H, C6–H), 7.34 (t, $^3J(\text{H,H}) = 7.4$ Hz, 1H, C1–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 160.17$ (C7), 151.48 (C5), 132.01 (C10, C10'), 128.90 (C2, C2'), 128.55 (C1), 127.73 (C4), 127.62 (C9, C9'), 126.29 (C8), 124.69 (C11), 124.17 (C3, C3'), 123.52 (C6); UV/Vis (cyclohexane): $\lambda_{\text{a,max}}$ (ϵ) = 309 nm ($34\,400\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$).

5-Phenyl-2-*p*-tolyloxazole (4d): After **3d** (47.1 g, 200 mmol) and POCl_3 (98%, $\rho = 1.68\text{ g mL}^{-1}$, 90 mL, 970 mmol) had been stirred and refluxed thoroughly for 3 h, the hot solution was poured onto ice (1 kg). The suspension formed thereby was stirred vigorously for 30 min. A precipitate formed which was filtered off, dissolved in dichloromethane (500 mL) and washed with aqueous NaHCO_3 until neutrality. The organic phase was dried over Na_2SO_4 and filtered. After evaporation of the solvent the crude product was purified by column chromatography (twice) on Al_2O_3 (neutral, activity I) with CHCl_3 (Merck, UVASOL) eluent ($R_f = 0.55$ – 0.57). Remnants of the solvent were removed in vacuo and the product was recrystallized from *n*-hexane (200 mL) (UVASOL). Colorless needles; yield 39.3 g (167 mmol, 83.5%); m.p. 75 – 76°C (lit. m.p. $75^\circ\text{C}^{[28]}$ $77^\circ\text{C}^{[18]}$); ^1H NMR (500.13 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 7.99$ (d, $^3J(\text{H,H}) = 8.1$ Hz, 2H, C9–H, C9'–H), 7.71 (d, $^3J(\text{H,H}) = 7.9$ Hz, 2H, C3–H, C3'–H), 7.42–7.45 (m, 3H, C6–H, C2–H, C2'–H), 7.33 (t, $^3J(\text{H,H}) = 7.5$ Hz, 1H, C1–H), 7.28 (d, $^3J(\text{H,H}) = 7.9$ Hz, 2H, C10–H, C10'–H), 2.41 (s, 3H, C12–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 161.41$ (C7), 150.91 (C5), 140.60 (C11), 129.49 (C10, C10'), 128.87 (C2, C2'), 128.26 (C1), 128.09 (C4), 126.21 (C9, C9'), 124.75 (C8), 124.09 (C3, C3'), 123.32 (C6), 21.51 (C12); UV/Vis (cyclohexane): $\lambda_{\text{a,max}}$ (ϵ) = 304 nm ($29\,900\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$).

4-(5-Phenyloxazol-2-yl)benzyl bromide (5): *N*-Bromosuccinimide (18.2 g, 100 mmol) and azobisisobutyronitrile (0.5 g) were added to **4d** (23.5 g, 100 mmol) dissolved in dry CCl_4 (100 mL) in a flask (500 mL) fitted with a reflux condenser. The suspension was stirred for 6 h under vigorous reflux, the hot suspension was filtered, the residue was extracted three times with hot CCl_4 (10 mL), the CCl_4 phases were combined, and the solvent was evaporated. The crude product was recrystallized from ethanol (130 mL,

96%). Long light yellow needles; yield 18.4 g (58.6 mmol, 58.6%); m.p. 129 – 130°C (lit. m.p. $130^\circ\text{C}^{[23]}$); ^1H NMR (500.13 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 8.07$ (d, $^3J(\text{H,H}) = 8.4$ Hz, 2H, C9–H, C9'–H), 7.71 (d, $^3J(\text{H,H}) = 7.1$ Hz, 2H, C3–H, C3'–H), 7.50 (2H, d, $^3J(\text{H,H}) = 8.3$ Hz, C10–H, C10'–H), 7.42–7.45 (m, 3H, C6–H, C2–H, C2'–H), 7.34 (t, $^3J(\text{H,H}) = 7.5$ Hz, 1H, C1–H), 4.52 (s, 2H, C12–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 160.52$ (C7), 151.44 (C5), 139.85 (C11), 129.52 (C10, C10'), 128.93 (C2, C2'), 128.55 (C1), 127.81 (C4), 126.64 (C9, C9'), 127.31 (C8), 124.21 (C3, C3'), 123.49 (C6), 32.72 (C12); UV/Vis (cyclohexane): $\lambda_{\text{a,max}}$ (ϵ) = 314 nm ($32\,400\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$); $\text{C}_{16}\text{H}_{12}\text{ONBr}$ (314.2): calcd: C 61.17, H 3.85, N 4.46, Br 25.43; found: C 61.34, H 3.86, N 4.58, Br 25.51.

1-[4-(5-Phenyloxazol-2-yl)benzyl]-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]-decane bromide (6): Hexamethylene tetramine (30.0 g, 214 mmol), **5** (62.8 g, 200 mmol), and dichloromethane (1 L) were mixed in a flask (2 L) fitted with a reflux condenser. The suspension was stirred for 6 h at room temperature and filtered. The solid residue was washed three times with dichloromethane (100 mL) and dried for 6 h in vacuo to yield a colorless powder. This salt was purified by extraction with dichloromethane (Merck, UVASOL) in a Soxhlet extractor for 12 h. Yield 83.2 g (183 mmol, 91.5%); m.p. 185 – 187°C (decomp); ^1H NMR (500.13 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 8.21$ (d, $^3J(\text{H,H}) = 8.1$ Hz, 2H, C9–H, C9'–H), 7.92 (s, 1H, C6–H), 7.87 (d, $^3J(\text{H,H}) = 7.7$ Hz, 2H, C3–H, C3'–H), 7.71 (d, $^3J(\text{H,H}) = 8.1$ Hz, 2H, C10–H, C10'–H), 7.52 (t, $^3J(\text{H,H}) = 7.7$ Hz, 2H, C2–H, C2'–H), 7.41 (t, $^3J(\text{H,H}) = 7.4$ Hz, 1H, C1–H), 5.19 (s, 6H, C13–H, C13'–H, C13''–H), 4.60 (d, $^2J(\text{H,H}) = 12.5$ Hz, 3H, C14–H_a, C14'–H_a, C14''–H_a), 4.46 (d, $^2J(\text{H,H}) = 12.5$ Hz, 3H, C14–H_b, C14'–H_b, C14''–H_b), 4.25 (s, 2H, C12–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 159.57$ (C7), 151.19 (C5), 133.23 (C10, C10'), 129.11 (C2, C2'), 128.77 (C1), 128.13 (C11), 127.93 (C4), 127.19 (C8), 126.41 (C9, C9'), 124.46 (C6), 124.09 (C3, C3'), 77.67 (C13, C13', C13''), 69.76 (C14, C14', C14''), 58.52 (C12); UV/Vis (methanol): $\lambda_{\text{a,max}}$ (ϵ) = 308 nm ($29\,800\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$); $\text{C}_{22}\text{H}_{24}\text{N}_5\text{OBr}$ (454.4): calcd: C 58.16, H 5.32, N 15.41, Br 17.59; found: C 57.93, H 5.41, N 15.22, Br 17.55.

4-(5-Phenyloxazol-2-yl)benzylamine (7): To a mixture of **6** (22.7 g, 50.0 mmol) and ethanol (96%, 350 mL) in a flask (500 mL) fitted with a reflux condenser, conc. H_2SO_4 (10 mL) was added with stirring. The mixture was refluxed thoroughly for 4 h. Ethanol was evaporated and the residue was suspended in distilled H_2O (100 mL). The suspension was stirred for 1 h at room temperature, filtered, and the liquid phase was mixed with toluene (600 mL) and aqueous NaOH (10% w/w, 200 mL). The aqueous phase was separated, extracted twice with toluene (200 mL), and the combined organic phases were dried over KOH (30 g). The solvent was evaporated from the dried solution and the light yellow residue was recrystallized from cyclohexane (200 mL). Yield 11.0 g (43.9 mmol, 87.9%); m.p. 109 – 110°C ; ^1H NMR (500.13 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 8.05$ (d, $^3J(\text{H,H}) = 8.3$ Hz, 2H, C9–H, C9'–H), 7.70 (d, $^3J(\text{H,H}) = 7.3$ Hz, 2H, C3–H, C3'–H), 7.40–7.43 (m, 5H, C6–H, C2–H, C2'–H, C10–H, C10'–H), 7.32 (t, $^3J(\text{H,H}) = 7.3$ Hz, 1H, C1–H), 3.92 (s, 2H, C12–H), 1.47 (s, 2H, C12–NH); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{CHCl}_3$): $\delta = 161.07$ (C7), 151.05 (C5), 145.63 (C11), 128.85 (C2, C2'), 128.32 (C1), 127.98 (C4), 127.39 (C10, C10'), 126.43 (C9, C9'), 125.95 (C8), 124.10 (C3, C3'), 123.35 (C6), 46.18 (C12); UV/Vis (cyclohexane): $\lambda_{\text{a,max}}$ (ϵ) = 305 nm ($31\,400\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$); $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ (250.3): calcd C 76.78, H 5.64, N 11.19; found C 76.55, H 5.64, N 11.20.

***N*-Ethyl-1-[4-(5-phenyloxazol-2-yl)benzyl]urea (8a):** Ethyl isocyanate (98%, $\rho = 0.91\text{ g mL}^{-1}$, 2.0 mL, 25 mmol) was added dropwise to a stirred solution of **7** (5.0 g, 20 mmol) in THF (dried, 100 mL) in a flask (250 mL). When stirring was continued at room temperature for 16 h, a suspension was formed. The solvent was evaporated and the colorless crude product was recrystallized from 1,4-dioxane (320 mL). Yield 5.6 g (17 mmol, 87%); m.p. 223 – 224°C ; ^1H NMR (500.13 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 8.04$ (d, $^3J(\text{H,H}) = 8.2$ Hz, 2H, C9–H, C9'–H), 7.84 (d, $^3J(\text{H,H}) = 7.3$ Hz, 2H, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.51 (t, $^3J(\text{H,H}) = 7.8$ Hz, 2H, C2–H, C2'–H), 7.41 (m, 2H, C10–H, C10'–H), 7.39 (m, 1H, C1–H), 6.41 (t, $^3J(\text{H,H}) = 6.0$ Hz, 1H, C12–NH), 5.96 (t, $^3J(\text{H,H}) = 5.6$ Hz, 1H, C14–NH), 4.28 (d, $^3J(\text{H,H}) = 6.0$ Hz, 2H, C12–H), 3.04 (m, 2H, C14–H), 1.01 (t, $^3J(\text{H,H}) = 7.2$ Hz, 3H, C15–H); ^{13}C NMR (125.77 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 160.31$ (C7), 157.99 (C13), 150.56 (C5), 143.99 (C11), 129.12 (C2, C2'), 128.56 (C1), 127.61 (C10, C10'), 127.45 (C4), 125.93 (C9, C9'), 125.12 (C8), 124.15 (C6), 124.00 (C3, C3'), 42.59 (C12), 34.21 (C14), 15.70 (C15); UV/Vis (methanol): $\lambda_{\text{a,max}}$ (ϵ) =

305 nm (32 600 mol⁻¹ dm³ cm⁻¹); C₁₉H₁₉N₃O₂ (321.4): calcd: 71.01, H 5.6, N 13.08; found: C 71.19, H 6.12, N 13.20.

N-Isopropyl-[4-(5-phenyloxazol-2-yl)benzyl]urea (8b): In a flask (500 mL) fitted with a dropping funnel, **7** (9.0 g, 36 mmol) was dissolved in THF (dried, 250 mL). Isopropyl isocyanate (98%, $\rho = 0.866$ g mL⁻¹, 3.7 mL, 37 mmol) in THF (dried, 50 mL) was added dropwise. After 15 min a colorless precipitate was observed. This suspension was stirred for 16 h at room temperature. The solvent was evaporated and the crude product was crystallized from 1,4-dioxane (270 mL). The colorless needles obtained were washed twice with methanol (UV quality, 30 mL) and dried in vacuo. Yield 9.9 g (30 mmol, 82%); m.p. 228–229 °C; ¹H NMR (500.13 MHz, [D₆]DMSO): $\delta = 8.04$ (d, ³J(H,H) = 8.3 Hz, 2H, C9–H, C9'–H), 7.84 (d, ³J(H,H) = 7.3 Hz, 2H, C3–H, C3'–H), 7.82 (s, 1H, C6–H), 7.51 (t, ³J(H,H) = 7.8 Hz, 2H, C2–H, C2'–H), 7.41 (m, 2H, C10–H, C10'–H), 7.39 (m, 1H, C1–H), 6.28 (t, ³J(H,H) = 6.0 Hz, 1H, C12–NH), 5.83 (d, ³J(H,H) = 7.7 Hz, 1H, C14–NH), 4.28 (d, ³J(H,H) = 6.0 Hz, 2H, C12–H), 3.70 (m, 1H, C14–H), 1.05 (d, ³J(H,H) = 6.4 Hz, 6H, C15–H, C15'–H); ¹³C NMR (125.77 MHz, [D₆]DMSO): $\delta = 160.28$ (C7), 157.41 (C13), 150.54 (C5), 144.05 (C11), 129.08 (C2, C2'), 128.52 (C1), 127.64 (C10, C10'), 127.43 (C4), 125.91 (C9, C9'), 125.12 (C8), 124.11 (C6), 123.97 (C3, C3'), 42.67 (C12), 41.01 (C14), 23.21 (C15, C15'); UV/Vis (methanol): $\lambda_{a,max}$ (ϵ) = 304 nm (31 400 mol⁻¹ dm³ cm⁻¹); C₂₀H₂₁N₃O₂ (335.4): calcd: C 71.62, H 6.31, N 12.53; found: C 71.45, H 6.26, N 12.42.

N-Phenyl-[4-(5-phenyloxazol-2-yl)benzyl]urea (8c): Phenyl isocyanate (98%, $\rho = 1.096$ g mL⁻¹, 5.7 mL, 51 mmol) in THF (dried, 200 mL) was added dropwise with stirring to **7** (12.5 g, 49.9 mmol) dissolved in THF (dried, 200 mL) in a two-necked flask (1 L) fitted with a dropping funnel. A colorless precipitate was observed. This suspension was stirred for 16 h at room temperature. The solvent was evaporated and the colorless product crystallized from 1,4-dioxane (1500 mL). Yield 14.8 g (40.2 mmol, 80.3%); m.p. 235–40 °C; ¹H NMR (125.77 MHz, [D₆]DMSO): $\delta = 8.63$ (s, 1H, C14–NH), 8.06 (d, ³J(H,H) = 8.2 Hz, 2H, C9–H, C9'–H), 7.84 (d, ³J(H,H) = 7.5 Hz, 2H, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.51 (m, 2H, C2–H, C2'–H), 7.48 (m, 2H, C10–H, C10'–H), 7.42 (d, ³J(H,H) = 7.8 Hz, 2H, C15–H, C15'–H), 7.39 (t, ³J(H,H) = 7.4 Hz, 1H, C1–H), 7.23 (t, ³J(H,H) = 7.9 Hz, 2H, C16–H, C16'–H), 6.90 (t, ³J(H,H) = 7.3 Hz, 1H, C17–H), 6.71 (1H, t, ³J(H,H) = 6.0 Hz, C12–NH), 4.39 (d, ³J(H,H) = 6.0 Hz, 2H, C12–H); ¹³C NMR (125.77 MHz, [D₆]DMSO): $\delta = 160.23$ (C7), 155.24 (C13), 150.56 (C5), 143.29 (C11), 140.37 (C14), 129.07 (C2, C2'), 128.61 (C16, C16'), 128.53 (C1), 127.72 (C10, C10'), 127.41 (C4), 125.98 (C9, C9'), 125.27 (C8), 124.13 (C6), 123.96 (C3, C3'), 121.11 (C17), 117.72 (C15, C15'), 42.52 (C12); UV/Vis (methanol): $\lambda_{a,max}$ (ϵ) = 305 nm (31 700 mol⁻¹ dm³ cm⁻¹); C₂₃H₁₉N₃O₂ (369.4): calcd: C 74.78, H 5.18, N 11.37; found: C 74.86, H 5.19, N 11.33.

N-Ethyl-[4-(5-phenyloxazol-2-yl)benzyl]thiourea (9a): Ethyl isothiocyanate (97%, $\rho = 0.997$ g mL⁻¹, 10.8 mL, 120 mmol) was added dropwise, within 15 min, to a stirred solution of **7** (27.5 g, 110 mmol) and toluene (370 mL) in a two-necked flask (1 L) fitted with a dropping funnel. A light yellow precipitate formed. The suspension was stirred for 16 h at room temperature; then the solid was filtered off, washed twice with toluene (50 mL), and the crude product was recrystallized from ethanol (96%, 350 mL). Light yellow crystals; yield 35.4 g (105 mmol, 95.4%); m.p. 165–166 °C; ¹H NMR (500.13 MHz, [D₆]DMSO): $\delta = 8.05$ (d, ³J(H,H) = 8.2 Hz, 2H, C9–H, C9'–H), 7.91 (b, 1H, C12–NH), 7.84 (d, ³J(H,H) = 8.3 Hz, 2H, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.58 (b, 1H, C14–NH), 7.50 (t, ³J(H,H) = 7.7 Hz, 2H, C2–H, C2'–H), 7.46 (d, ³J(H,H) = 8.2 Hz, 2H, C10–H, C10'–H), 7.39 (t, ³J(H,H) = 7.5 Hz, 1H, C1–H), 4.75 (b, 2H, C12–H), 3.40 (b, 2H, C14–H), 1.09 (t, ³J(H,H) = 7.2 Hz, 3H, C15–H); ¹³C NMR (125.77 MHz, [D₆]DMSO): $\delta = 182.23$ (C13), 160.25 (C7), 150.59 (C5), 142.46 (C11), 129.09 (C2, C2'), 128.54 (C1), 127.84 (C10, C10'), 127.43 (C4), 125.91 (C9, C9'), 125.32 (C8), 124.14 (C6), 123.98 (C3, C3'), 46.55 (C12), 38.43 (C14), 13.43 (C15); UV/Vis (methanol): $\lambda_{a,max}$ (ϵ) = 305 nm (32 900 mol⁻¹ dm³ cm⁻¹); C₁₉H₁₉N₃OS (337.4): calcd: C 67.63, H 5.68, N 12.45, S 9.50; found: C 67.85, H 5.75, N 12.51, S 9.44.

N-Isopropyl-[4-(5-phenyloxazol-2-yl)benzyl]thiourea (9b): To a well-stirred solution of **7** (25.0 g, 100 mmol) in toluene (350 mL) in a two-necked flask (1 L) fitted with a dropping funnel, isopropyl isothiocyanate (97%, 11.5 g, 110 mmol) was added dropwise within 15 min. Upon further stirring a light yellow precipitate formed after 30 min. After an additional 16 h of stirring the solid was filtered off and washed twice with toluene (50 mL). The product was recrystallized from ethanol (96%, 650 mL) to yield tiny

light yellow needles. Yield 33.2 g (94.4 mmol, 94.4%); m.p. 188–189 °C; ¹H NMR (500.13 MHz, [D₆]DMSO): $\delta = 8.05$ (d, ³J(H,H) = 8.3 Hz, 2H, C9–H, C9'–H), 7.84 (d, ³J(H,H) = 7.4 Hz, 2H, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.75 (b, 1H, C12–NH), 7.51 (t, ³J(H,H) = 7.8 Hz, 2H, C2–H, C2'–H), 7.45 (d, ³J(H,H) = 8.2 Hz, 2H, C10–H, C10'–H), 7.44 (b, 1H, C14–NH), 7.39 (t, ³J(H,H) = 7.5 Hz, 1H, C1–H), 4.75 (b, 2H, C12–H), 4.27 (b, 1H, C14–H), 1.13 (d, ³J(H,H) = 6.5 Hz, 6H, C15–H, C15'–H); ¹³C NMR (125.77 MHz, [D₆]DMSO): $\delta = 181.56$ (C13), 160.24 (C7), 150.60 (C5), 142.45 (C11), 129.11 (C2, C2'), 128.57 (C1), 127.88 (C10, C10'), 127.42 (C4), 125.94 (C9, C9'), 125.33 (C8), 124.16 (C6), 124.00 (C3, C3'), 46.49 (C12), 45.09 (C14), 22.30 (C15, C15'); UV/Vis (methanol): $\lambda_{a,max}$ (ϵ) = 306 nm (32 800 mol⁻¹ dm³ cm⁻¹); C₂₀H₂₁N₃OS (351.7): calcd: C 68.35, H 6.02, N 11.96, S 9.12; found: C 68.60, H 6.04, N 12.02, S 8.99.

N-Phenyl-[4-(5-phenyloxazol-2-yl)benzyl]thiourea (9c): Phenyl isothiocyanate (95%, $\rho = 1.13$ g mL⁻¹, 15.1 mL, 120 mmol) was added dropwise, with stirring, to a solution of **7** (27.5 g, 110 mmol) in toluene (370 mL) in a two-necked flask (1 L) fitted with a dropping funnel. After 40 min a light yellow precipitate formed. The suspension was stirred at room temperature. The solid was filtered off, washed twice with toluene (50 mL), and purified by Soxhlet extraction with methanol (UVASOL). Yield 38.3 g (99.4 mmol, 90.3%); m.p. 202 °C (dec.); ¹H NMR (500.13 MHz, [D₆]DMSO): $\delta = 9.74$ (b, 1H, C12–NH), 8.29 (b, 1H, C14–NH), 8.07 (d, ³J(H,H) = 8.2 Hz, 2H, C9–H, C9'–H), 7.85 (2H, d, ³J(H,H) = 7.5 Hz, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.52 (m, 2H, C10–H, C10'–H), 7.48 (m, 2H, C2–H, C2'–H), 7.45 (d, ³J(H,H) = 7.8 Hz, 2H, C15–H, C15'–H), 7.39 (t, ³J(H,H) = 7.3 Hz, 1H, C1–H), 7.34 (t, ³J(H,H) = 7.8 Hz, 2H, C16–H, C16'–H), 7.13 (t, ³J(H,H) = 7.3 Hz, 1H, C17–H), 4.85 (d, ³J(H,H) = 5.2 Hz, 2H, C12–H); ¹³C NMR (125.78 MHz, [D₆]DMSO): $\delta = 180.94$ (C13), 160.23 (C7), 150.59 (C5), 142.00 (C11), 139.05 (C14), 129.09 (C2, C2'), 128.68 (C16, C16'), 128.56 (C1), 128.01 (C10, C10'), 127.42 (C4), 125.93 (C9, C9'), 125.36 (C8), 124.40 (C17), 124.17 (C6), 123.98 (C3, C3'), 123.44 (C15, C15'), 46.93 (C12); UV/Vis (methanol): $\lambda_{a,max}$ (ϵ) = 306 nm (35 500 mol⁻¹ dm³ cm⁻¹); C₂₃H₁₉N₃OS (385.5): calcd: C 71.66, H 4.97, N 10.90, S 8.32; found: C 71.65, H 5.14, N 10.80, S 8.36.

N-Ethyl-[4-(5-phenyloxazol-2-yl)benzyl]carbodiimide (10a): An aqueous suspension of HgO (freshly prepared, 8.66 g, 40.0 mmol in 20 mL H₂O^[26]) was added to **9a** (13.5 g, 40.0 mmol) and toluene (400 mL) in a flask (1 L). After thorough shaking for 20 min the suspension became dark green. The solid was separated and washed twice with toluene (200 mL). The organic phases were combined and dried over Na₂SO₄. After filtration the solvent was distilled off. The residue formed very small light yellow crystals from methylcyclohexane (UV quality, 100 mL) at –40 °C. Yield 7.1 g (23 mmol, 58%); m.p. 41 °C; ¹H NMR (500.13 MHz, [D₆]DMSO): $\delta = 8.08$ (d, ³J(H,H) = 8.2 Hz, 2H, C9–H, C9'–H), 7.84 (d, ³J(H,H) = 8.1 Hz, 2H, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.51 (d, ³J(H,H) = 7.9 Hz, 2H, C10–H, C10'–H), 7.50 (t, ³J(H,H) = 7.7 Hz, 2H, C2–H, C2'–H), 7.39 (t, ³J(H,H) = 7.3 Hz, 1H, C1–H), 4.45 (s, 2H, C12–H), 3.16 (q, ³J(H,H) = 7.2 Hz, 2H, C14–H), 1.07 (t, ³J(H,H) = 7.1 Hz, 3H, C15–H); ¹³C NMR (125.78 MHz, [D₆]DMSO): $\delta = 160.05$ (C7), 150.69 (C5), 141.35 (C11), 140.33 (C13), 129.05 (C2, C2'), 128.55 (C1), 128.19 (C10, C10'), 127.37 (C4), 126.09 (C9, C9'), 125.78 (C8), 124.17 (C6), 123.99 (C3, C3'), 49.08 (C12), 40.59 (C14), 16.50 (C15); UV/Vis (cyclohexane): $\lambda_{a,max}$ (ϵ) = 306 nm (29 300 mol⁻¹ dm³ cm⁻¹); C₁₉H₁₇N₃O (303.4): calcd: C 75.23, H 5.56, N 13.85; found: C 75.47, H 5.70, N 13.81.

N-Isopropyl-[4-(5-phenyloxazol-2-yl)benzyl]carbodiimide (10b): The preparation, from **9b** (14.1 g, 40.1 mmol), was analogous to that of **10a**. Compound **10b** was obtained as light yellow crystals from methylcyclohexane (UV quality, 150 mL) at –40 °C. Yield 8.9 g (28 mmol, 70%); m.p. 59 °C; ¹H NMR (500.13 MHz, [D₆]DMSO): $\delta = 8.08$ (d, ³J(H,H) = 8.2 Hz, 2H, C9–H, C9'–H), 7.83 (d, ³J(H,H) = 8.2 Hz, 2H, C3–H, C3'–H), 7.83 (s, 1H, C6–H), 7.50 (d, ³J(H,H) = 8.2 Hz, 2H, C10–H, C10'–H), 7.49 (t, ³J(H,H) = 8.2 Hz, 2H, C2–H, C2'–H), 7.38 (t, ³J(H,H) = 7.4 Hz, 1H, C1–H), 4.43 (s, 2H, C12–H), 3.48 (sp, ³J(H,H) = 6.4 Hz, 1H, C14–H), 1.05 (d, ³J(H,H) = 6.4 Hz, 6H, C15–H); ¹³C NMR (125.78 MHz, [D₆]DMSO): $\delta = 160.03$ (C7), 150.69 (C5), 141.31 (C11), 140.15 (C13), 129.04 (C2, C2'), 128.73 (C1), 128.36 (C10, C10'), 127.37 (C4), 126.12 (C9, C9'), 125.82 (C8), 124.08 (C6), 123.99 (C3, C3'), 49.22 (C12), 48.31 (C14), 24.30 (C15, C15'); UV/Vis (cyclohexane): $\lambda_{a,max}$ (ϵ) = 306 nm (32 000 mol⁻¹ dm³ cm⁻¹); C₂₀H₁₉N₃O (317.4): calcd: C 75.69, H 6.03, N 13.24; found: C 75.75, H 6.03, N 13.09.

N-Phenyl-[4-(5-phenyloxazol-2-yl)benzyl]carbodiimide (10c): The preparation, from **9c** (15.4 g, 40 mmol), was analogous to that of **10a**. Compound **10c** was obtained as light yellow crystals from methylcyclohexane (UV quality, 150 mL) at 5 °C. Yield 7.5 g (21 mmol, 53 %); m.p. 77.5–78 °C; ¹H NMR (500.13 MHz, [D₆]DMSO): δ = 8.11 (d, ³J(H,H) = 8.0 Hz, 2H, C9–H, C9'–H), 7.85 (d, ³J(H,H) = 5.3 Hz, 2H, C3–H, C3'–H), 7.84 (s, 1H, C6–H), 7.60 (d, ³J(H,H) = 8.0 Hz, 2H, C10–H, C10'–H), 7.50 (t, ³J(H,H) = 7.6 Hz, 2H, C2–H, C2'–H), 7.39 (t, ³J(H,H) = 7.3 Hz, 1H, C1–H), 7.32 (t, ³J(H,H) = 7.7 Hz, 2H, C16–H, C16'–H), 7.13 (t, ³J(H,H) = 7.3 Hz, 1H, C17–H), 7.06 (d, ³J(H,H) = 7.7 Hz, 2H, C15–H, C15'–H), 4.77 (s, 2H, C12–H); ¹³C NMR (125.78 MHz, [D₆]DMSO): δ = 159.96 (C7), 150.76 (C5), 140.57 (C11), 139.58 (C14), 136.56 (C13), 129.59 (C16, C16'), 129.09 (C2, C2'), 128.61 (C1), 128.26 (C10, C10'), 127.36 (C4), 126.28 (C9, C9'), 126.06 (C8), 125.02 (C17), 124.22 (C6), 124.03 (C3, C3'), 123.41 (C15, C15'), 49.10 (C12); UV/Vis (cyclohexane): λ_{a,max} (ε) = 307 nm (31 100 mol^{−1} dm³ cm^{−1}); C₂₃H₁₇N₃O (351.4): calcd: C 78.61, H 4.88, N 11.96; found: C 78.41, H 4.85, N 11.91.

Hydration of solid carbodiimides: In a polyethylene scintillation vial (5 mL), a mortared solid mixture of a water-binding scintillator (**10a–10c**) (2.8 mmol) and sodium dodecyl sulfate (10 % w/w) was treated with 50 μL of water containing trifluoroacetic acid (2 mol L^{−1}). After either one or seven days, each mixture was homogenized by thorough mortaring. ¹H NMR spectra were recorded for solutions of the mixtures (10 mg) in [D₆]DMSO. The amounts of ureas formed were determined by comparing the integrals of the signals for C9 or C12 in **10a–10c** and **8a–10c**. For comparison, the hydration was followed in solutions of **10a–10c** in [D₆]DMSO for two days.

Fluorescence: Spectra were recorded at room temperature on a Shimadzu (model RF-5000) spectral fluorimeter or on homemade apparatus described previously.^[34] Spectra from solid samples were taken from the surface at 30° to the exciting light. Integrated fluorescence spectra obtained under identical absorption conditions were taken as measures for relative quantum yields, using PPO (scintillation grade; Packard Instrument) in cyclohexane or solid powdered PPO, respectively, as the reference. Measured values were reproducible within 3 % in solutions and 5 % in solids.

Lifetimes were measured at room temperature in apparatus described elsewhere,^[35, 36] modified in that i) a nitrogen laser from ILEE (model NN-100, pulse width 0.5 ns) was used as excitation source, ii) a photodiode from Soliton (Model UPD-500UP, rise time < 500 ps) was employed as the detector, and iii) signals were recorded on a Hewlett-Packard digital oscilloscope (model 54615B). Measured lifetimes were reproducible with deviations of ±0.2 ns in solutions and ±0.4 ns in solids.

Solutions for fluorescence experiments were deaerated by bubbling with argon. Solid samples were prepared under argon.

Analyses: NMR spectra were recorded on a Bruker model DRX500 spectrometer at 500.13 MHz for ¹H and at 124.77 MHz for ¹³C resonance. 2D NMR was employed to exclude equivocal assignments. Elemental analyses were performed by the Institute of Organic Chemistry of the Technical University of Dresden. Melting points are uncorrected.

Scintillation counting: A scintillation counter (model Tricarb 2550TR/LL) and various scintillation cocktails were provided by Packard Instrument. Counting efficiencies *S* (counts min^{−1}/decays min^{−1}) were determined with reference to ³H₂O and to aqueous sodium [¹⁴C]benzoate solution containing trifluoroacetic acid (2 mol L^{−1}) in Ultima Gold cocktails (Packard Instrument).

Compounds used as solid scintillators (PPO, **4a–4d**, **5**, **7**, **8a–8c**, **9a–9c**) were mixed with sodium dodecyl sulfate (a surfactant mediating wetting of the organic solids) and sodium sulfate (a drying agent) in a ratio of 8:1:1. Portions (400 mg) of these mixtures were mortared thoroughly and transferred to a glass scintillation vial. The aqueous solution containing the labeled probe (³H₂O or sodium [¹⁴C]benzoate) (50 g L^{−1}) was dropped onto the powder. Scintillation counting was started 5 min later.

Each of the compounds **10a–10c** (0.9–1 g; the stoichiometric amount for 50 μL of water) used as chemically reactive scintillators was mixed with sodium dodecyl sulfate (as a surfactant mediating wetting of the organic solids; the drying agent was omitted) and treated as described above. Counting efficiencies were reproducible within 5 %.

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