Single-Compound Libraries of Organic Materials: Parallel Synthesis and Screening of Fluorescent Dyes**

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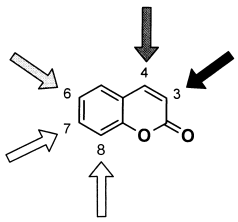
The potential of combinatorial chemistry in the pharmaceutical industry has been demonstrated for lead-structure identification and optimization with numerous examples published.[1] Similar change of paradigm has been seen in the areas of materials and catalyst research.[2] To date the principles of combinatorial chemistry have been applied in the areas of inorganic solid-state materials (e.g. luminescence[3]), homogenous and heterogeneous catalysts, and polymeric materials. The combinatorial concept facilitates the efficient generation of a large number of substances and their screening for desirable properties. These properties are dependent on numerous interdependent parameters.

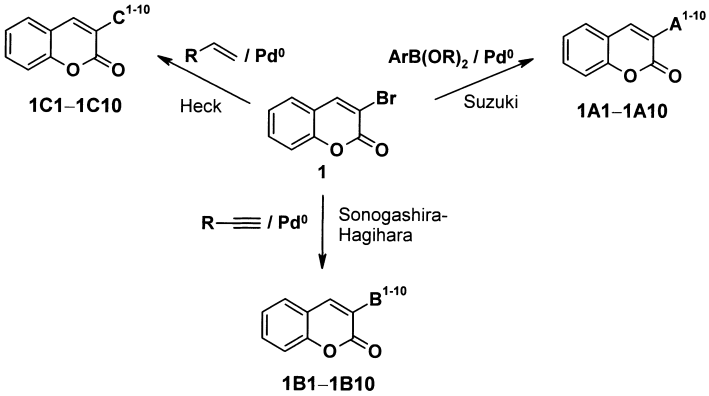
A further field of research in materials science, where structure–property relationships are often not predictable and an empirical identification process is required for the elicitation of lead structures and their further development, is that of organic materials. Consequently, we asked whether the concepts of combinatorial chemistry are applicable to the development of novel organic materials? We report here and in the following correspondence[4] the efficient generation and screening of single-compound libraries containing fluorescent dyes[5] and π-conjugated oligomers; with these studies we show that the concepts of combinatorial chemistry can be successfully applied to organic materials using rapid parallel and mix-and-split synthesis in solution and also on solid supports. For a successful screening and subsequent data analysis highly pure compounds are of the utmost importance. The analysis of the data sets encompassed the structure–property relationships[4] which should make a rational design of novel organic materials with desirable properties possible.

In this study we concentrate on fluorescent dyes of the coumarin type which are of interest not only because of their pharmacological activity[6] but also because of their applications as laser dyes,[7] fluorescent labels[8] (e.g. in biological applications), emission layers in organic light-emitting diodes (OLED),[9] and as optical brighteners.[10] The correlation between optical properties (especially the fluorescence quantum yield) and the molecular structure can currently be described only empirically, since no detailed theoretical predictions are possible. A large number of compounds in a combinatorial library should correlate to a better understanding of the inherent structure–property relationships from which specifically tailored materials can be produced. Consequently, our goal was the development of a fast, parallel synthesis of highly pure coumarins and screening them for optical properties. Through substituent manipulation of the coumarin scaffold at positions 3, 4, 6–8 (Scheme 1) increased diversity is introduced which crucially alters the electronic structure and the associated dye properties.[11]



Scheme 1. Substituent variation on the coumarin scaffold.

Starting from 3-bromocoumarin **1**[12] we introduced substituents at the 3-position of the scaffold which extended the π system of the parent chromophore; this was achieved by Pd-catalyzed cross-coupling reactions. These types of reactions involving coumarin have not been widely published.[13] The efficiency of a combinatorial synthetic approach greatly depends on the compatibility of the coupling components and their suitability with the reaction conditions. Therefore, the initial step requires the optimization of the synthetic method for each individual reaction type. Scheme 2 shows the coupling reactions of compound **1**. Utilizing C–C bond formation reactions of Suzuki, Sonogashira–Hagihara, and Heck type with the coupling components **A1**–**A10**, **B1**–**B10**, and **C1**–**C10** (Scheme 3) facilitated the introduction of arene, ethynylene, and ethenylene moieties.



Scheme 2. Cross-coupling reactions with 3-bromocoumarin **1**. The product numbering is derived from the corresponding starting materials (e.g. **1A1** is from **1** and **A1**). For the definitions of **A1**–**C10** see Scheme 3.

First, bromocoumarin **1** was coupled in a parallel synthesizer[14] with the (hetero)aromatic boronic esters **A1**–**A10**, with $[Pd(PPh_3)_4]$ as catalyst and CsF as base. The generation of the boronic esters was accomplished using reported procedures.[15] The coupling products between these boronic esters and compound **1** were pre-purified by parallel filtration with SPE-columns[16] followed by further purification and analysis by sequential automated high-pressure liquid chromatography-mass spectrometry (HPLC-MS).[17] From these parallel reactions we obtained 3-(hetero)aryl substituted coumarins **1A1**–**1A10** in yields of 67–97% with greater than 99% purity. The Sonogashira–Hagihara coupling reactions of coumarin **1** and terminal acetylenes **B1**–**B10** utilizing

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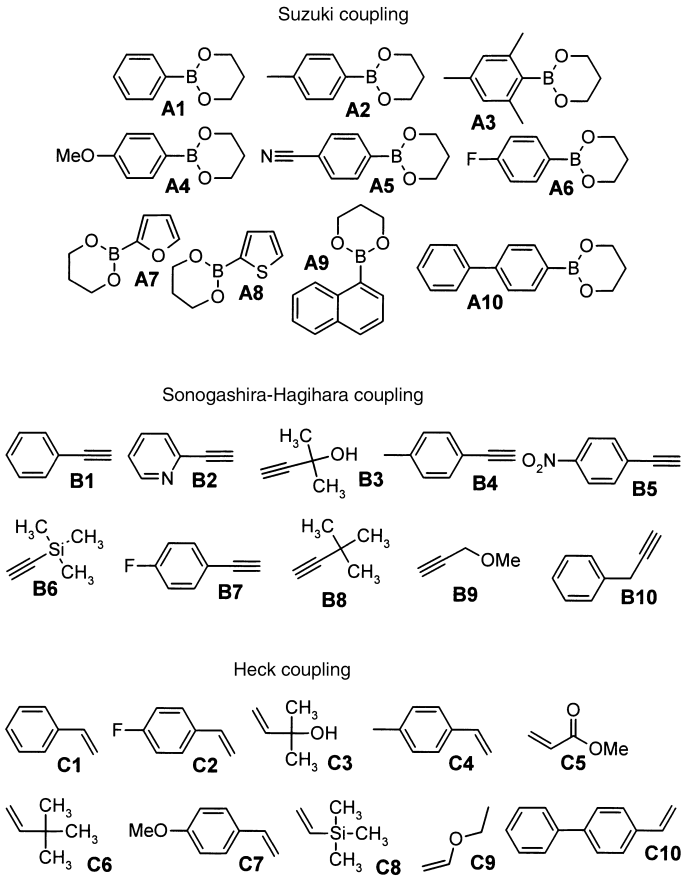
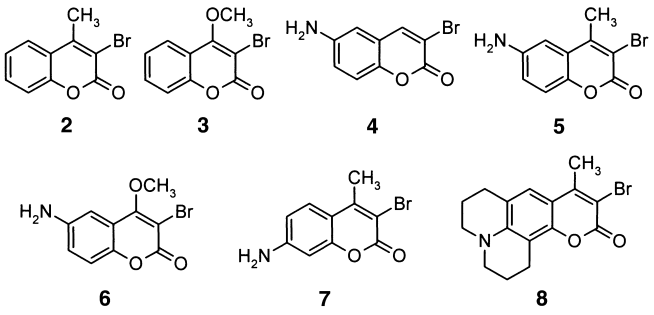


Scheme 3. Coupling components for the Pd-catalyzed parallel syntheses of 3-bromocoumarins **1**–**8**.

the catalytic system of $[Pd(PPh_3)_2Cl_2]$/CuI furnished the 3-ethynylcoumarins **1B1**–**1B10** in yields of 74–95%. Similarly, the Heck coupling with alkenes **C1**–**C10** utilizing the catalytic system $[Pd_2(dba)_3]$/AgOAc (dba = dibenzylideneacetone, OAc = acetate) gave isomerically pure 3-(*E*)-ethenylcoumarins **1C1**–**1C10** in yields of 30–94%. The efficiency of the synthetic methods is shown in that all 30 products were isolated with high purity and in yields sufficient for further screening.

Additionally, seven 3-bromocoumarins **2**–**8** which incorporated functional groups at the 4-, 6-, 7-, and 8-positions were synthesized for the parallel generation of further coumarin



libraries.[18] The aforementioned reaction conditions of the three cross-coupling reactions were optimized for selected combinations of coumarins **2**–**8** and the coupling components **A1**–**A10**, **B1**–**B10**, and **C1**–**C10** and the resulting synthetic method employed for the generation of all possible combinations.[19] From a possible 240 coumarin derivatives 151 (63%) were isolated in >99% purity[20] and of these 127 (84%) were previously unpublished compounds. The remaining compounds could not be isolated in sufficient purity for screening because of low conversions or separation difficulties.

The purified library members were screened for the desired optical properties. The use of a microplate reader allowed the accelerated recording of fluorescence and excitation spectra of the coumarins in ethanol. The determined absorption maxima ($\lambda_{max} = 314-430$ nm) and the emission maxima ($\lambda_{max} = 400-569$ nm) covered a wide range of values. The quantity of the acquired data was sufficient for a detailed correlation between the geometrical and electronic structures of the dyes to be deduced. These results should allow the rational design of dyes which contain specifically desired properties and results pertaining to this will be published in due course.

While the structure–property relationships can be deduced for absorption and fluorescence, the correlation between these factors with respect to the fluorescence quantum yield is still not totally understood. To estimate the quantum yield of the individual compounds, ethanolic solutions of the coumarins were irradiated in microplates with a UV lamp (Figure 1). From the coumarin library 34 derivatives with the most intensive fluorescence (in different emission ranges) were

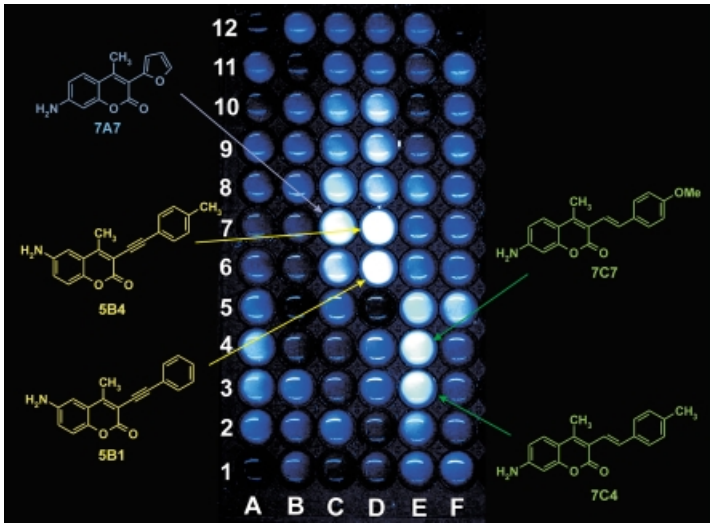


Figure 1. Screening of a coumarin library in a microtiter plate. In the row A–F the coumarins are sorted with respect to their absorption properties.

selected and the fluorescence quantum yield of each was determined by standard procedures (Table 1).[21] The following "hits" were identified (Figure 2): **5A9** ($\phi_f = 0.18$, $\lambda_{abs} =$ 373 nm, $\lambda_{em} = 535$ nm), **8A2** ($\phi_f = 0.90$, $\lambda_{abs} = 395$ nm, $\lambda_{em} =$ 478 nm), **7C4** ($\phi_f = 0.62$, $\lambda_{abs} = 393$ nm, $\lambda_{em} = 480$ nm), and **7B1** ($\phi_f = 0.98$, $\lambda_{abs} = 397$ nm, $\lambda_{em} = 455$ nm). Among these "hits" the 3-phenylethynyl substituted coumarin **7B1** exhibited a higher fluorescence quantum yield than the comparable

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Table 1. Absorptions and emission properties of selected coumarins based on the fluorescence quantum yields.

Coumarin	λ_{abs}[a] [nm]	λ_{em}[b] [nm]	ϕ_f[c]	Coumarin	λ_{abs}[a] [nm]	λ_{em}[b] [nm]	ϕ_f[c]
1A4	337	439	0.94	**4A7**	385	553	0.02
1A8	355	442	0.91	**4A8**	394	564	0.02
1A10	334	438	0.72	**4B4**	394	578	0.03
1C1	355	447	0.67	**5A9**	373	535	**0.18**
1C2	354	446	0.66	**5B1**	389	549	0.10
1C4	360	452	0.72	**5B4**	387	548	0.09
1C10	371	463	0.73	**6A5**	382	565	0.12
2A7	341	439	0.25	**6A6**	364	532	0.16
2C2	346	435	0.32	**6A10**	361	530	0.10
2C4	352	441	0.38	**7C4**	393	480	**0.62**
2C7	360	466	0.57	**7C7**	396	485	0.58
7A2	360	449	0.35	**8A2**	395	478	**0.90**
7A5	370	469	0.26	**8A6**	395	479	0.77
7A7	378	481	0.40	**8A7**	411	495	0.73
7A9	363	442	0.70	**8A8**	405	506	0.55
7B1	397	455	**0.98**	**8A9**	394	474	0.84
7C6	369	455	0.38	**8C7**	427	496	0.58

[a] Absorption maxima in ethanol (longest wavelength transition). [b] Maxima of the corrected emission spectra in ethanol. [c] External standard: 9,10-diphenylanthracene ($\phi_f = 0.95$, in cyclohexane).[20]

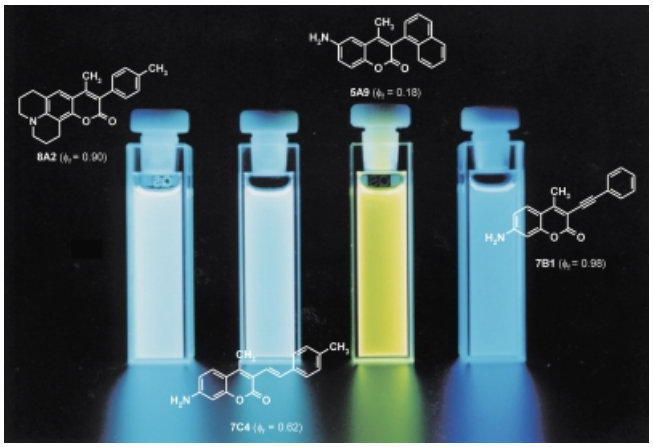

Figure 2. "Hits" identified by the qualitative and subsequent quantitative screening of the fluorescence quantum yield: **8A2**, **7C4**, **5A9**, and **7B1**.

and commercially available coumarin 120 ($\phi_f = 0.88$, $\lambda_{abs} = 354$ nm, $\lambda_{em} = 435$ nm in ethanol).[22] In view of possible applications of these compounds (e.g. as fluorescent labels in biological systems) the NH_2 substituted derivatives **7B1**, **7C4**, and **5A9** are of interest since these dyes can be linked to a biomolecule through their amino groups. Also, the following step of the combinatorial development process, namely the application of these novel chromophores as active layers in organic light-emitting diodes and their optimization should be possible. The application of combinatorial strategies for the screening and optimization of organic charge-transporting materials in a spatially addressable library of organic light-emitting diodes was recently reported by Schmidt et al.[23]

This work clearly demonstrates that the concepts of combinatorial chemistry can be successfully applied to development and improvement of novel materials. The efficient synthetic method for the parallel execution of Pd-catalyzed cross-coupling reactions yielded a large number of unpublished fluorescent coumarin dyes. Following the automated purification the screening for optical properties identified several "hits" with high fluorescence quantum yields. The development of structure–property relationships based on the collective data sets should allow the rational design of coumarin dyes. This study demonstrates the successful application of a combinatorial approach strategy encompassing the design of the lead structure, development of synthetic routes, efficient library synthesis and purification techniques, screening, and data analysis.

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[17] Purification and mass detection were performed on an HPLC-MS (Waters) fitted with a LC/MS detector (Micromass ZMD; electrospray ionization (ESI) mode). Chromatography performed on Xterra RP-18 (analytic: 3.5 μm, 4.6 × 100 mm; semi-preparative: 7.0 μm, 19 × 150 mm) columns (Waters) with an acetonitrile – water gradient.
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[19] Representative example for a parallel Suzuki cross-coupling: synthesis of 7-amino-4-methyl-3-*p*-tolyl-chromen-2-one (**7 A 2**): Coumarin **7** (25.4 mg, 0.1 mmol), boronic ester **A 2** (35.2 mg, 0.2 mmol), CsF (121 mg, 0.8 mmol), and $[Pd(PPh_3)_4]$ (5.78 mg, 5 mol %) were heated at 90 °C under argon in dry dioxane for 16 h. The solvent was evaporated and the residue was dissolved in acetonitrile/water. This solution was then filtered through a SPE (RP-18) column and purified by automated HPLC-MS affording the pure product (21.2 mg, 80 %). M.p. 260 – 262 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 7.44 (d, J = 8.7 Hz, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.60 (dd, J = 8.7, 1.9 Hz, 1H), 6.45 (d, J = 1.9 Hz, 1H), 6.07 (broad s, 2H), 2.33 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 160.8, 154.6, 152.8, 148.6, 136.6, 132.5, 130.5 (2C), 128.7 (2C), 126.8, 119.8, 111.6, 109.4, 98.5, 21.0, 16.3; UV/Vis (ethanol): λ_{max} (ε [L mol^{-1} cm^{-1}]) = 360 nm (22 500); EI-MS (70 eV): m/z (%) : 265 (88) [M^+], 237 (100) [M^+ – CO].
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Single-Compound Libraries of Organic Materials: From the Combinatorial Synthesis of Conjugated Oligomers to Structure – Property Relationships**

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The development process of novel materials is often encumbered by the time-consuming "one-at-a-time" process of material synthesis and evaluation. This situation is particularly true for π-conjugated oligomers which serve as model compounds for conducting polymers and are recognized as materials in their own right.[1] Accordingly, there is a need for novel methods that provide for both rapid compound generation and subsequent evaluation. Combinatorial methodologies that were developed for the high-speed synthesis and high-throughput screening of pharmaceuticals could help to overcome these bottlenecks in the materials development process.[2] Moreover, the rapid generation of data sets provided by combinatorial methods and their subsequent translation into structure – property relationships may enable the rational design of new materials.

While most of the combinatorial approaches in materials science concentrate on the development of inorganic solid-state materials, polymeric materials, and catalytic systems,[3] we report here and in the preceding correspondence[4] the development of combinatorial strategies for the generation of organic materials. The focus of this study is the combinatorial synthesis and subsequent screening of oligothiophenes which are one of the most examined classes of π-conjugated oligomers.[5] The strategy covers all stages of the combinatorial discovery process: design of the lead structure, elaboration of the synthetic route, generation of the library and purification, screening, and data analysis. We focused on a regioregular head-to-tail coupled quater(3-arylthiophene) as the lead structure (Scheme 1). Because of their defined structure these aryl substituted oligomers, together with the already intensively investigated oligo(3-alkylthiophene)s, are outstanding model compounds for the parent (polydisperse) poly(3-arylthiophene)s and poly(3-alkylthiophene)s.[6] The

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