

Die Solvens-induzierte Aggregation optisch aktiver Polyphenylenethynylene (PPEs) kann je nach deren Fähigkeit, die chirale Makrostruktur zu stabilisieren, auf verschiedenen Wegen erfolgen. Bei einem neuen Ansatz, bei dem zum ersten Mal Chiralität in Kombination mit „kissenartigen“ Strukturelementen verwendet wird, werden systematisch starke elektronische Kopplungen unter Aufrechterhaltung hoher Quantenausbeuten erzeugt. Mehr dazu in der folgenden Veröffentlichung von Swager et al.

Three-Dimensional Electronic Delocalization in Chiral Conjugated Polymers**

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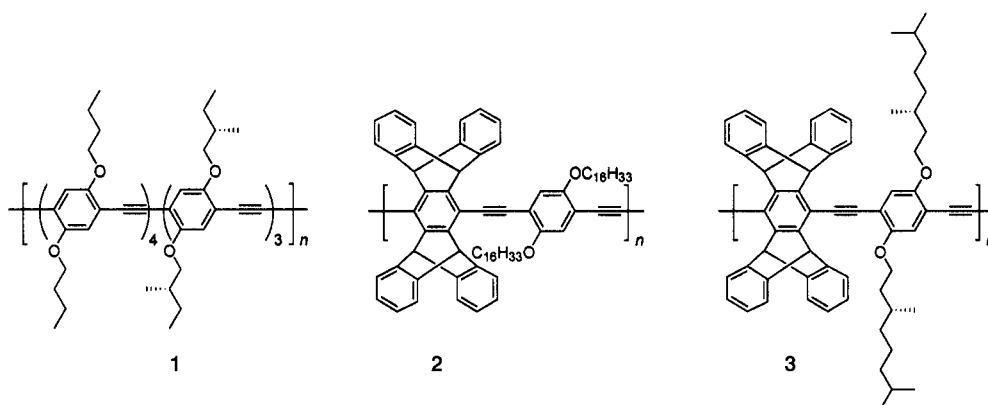
Transport properties are the central performance determinant of electronic materials in most applications. Strong, extended electronic interactions have long been understood to be critical to obtaining molecules and polymers with high charge-carrier mobility. It has been further revealed recently that strong electronic coupling is the dominant contributor to intramolecular exciton transport in solutions of some conjugated polymers.^[1] As a result, the production of extended electronic interactions both within and between electronic polymers is critical to the optimization of their transport of charge and excitons, which underpins future applications in transistors,^[2] electroluminescent devices,^[3] sensors,^[4] and photovoltaic devices.^[5] However, in devices requiring luminescence and/or exciton transport, researchers have generally avoided the strong interpolymer electronic coupling that will enhance transport because of the strong self-quenching that nearly exclusively accompanies these interactions. Self-quenching lowers the light output of luminescent devices and also lowers the diffusion length of excitons, which reduces sensory responses. As a result, most researchers seeking to create highly emissive films of electronic polymers use large structures such as dendrimers^[6] or smaller rigid scaffolds^[7] to prevent interchain interactions. It can therefore be stated that present design principles for maintaining high emission quantum yields in conjugated polymers have been diametrically opposed to those for the optimization of charge and exciton transport. To

address this limitation we present herein a general design for producing strongly interacting polymer chains with 3D electronic interactions while maintaining high luminescence efficiency. This ability to optimize charge and exciton transport simultaneously in conjugated polymers has broad implications for optoelectronic devices. Herein we describe experimental results that demonstrate that 3D electronic interactions enhance exciton transport.

With few exceptions, strong electronic interactions between chains of conjugated polymers (often accompanying aggregation) dramatically lower their quantum efficiency. Previous studies on carefully designed Langmuir films have revealed

that interchain interactions in poly(phenylene ethynylene) species (PPEs) give new low energy bands in the UV/Vis absorption spectra.^[8] Recently, a theoretical account by Brédas, et al.^[9] and an unexpected result reported by us^[10] have suggested that an oblique orientation between neighboring transition dipole moments of conjugated polymers might prevent fluorescence quenching upon aggregation. Indeed, based upon the exciton-coupling model,^[11] a parallel orientation of polymer chains is expected to result in cancellation of transition dipoles to give a forbidden S_0 – S_1 transition, whereas coupled chromophores with oblique organizations should exhibit an allowed S_0 – S_1 transition. Considering that polymer-backbones twist, which is promoted by introducing chirality, may introduce such an oblique arrangement we embarked on a program to produce chiral PPEs that would self-assemble into stable aggregates with high quantum yields.

These studies build on a detailed understanding of the electronic spectra of PPEs deduced through studying ordering and phase transitions in Langmuir films, which allowed for a deconvolution of the effects of backbone planarization (conjugation length) and interpolymer interactions (aggregation).^[12] To promote high degrees of aggregation, we initially investigated simple structures, such as **1**, which contains chiral

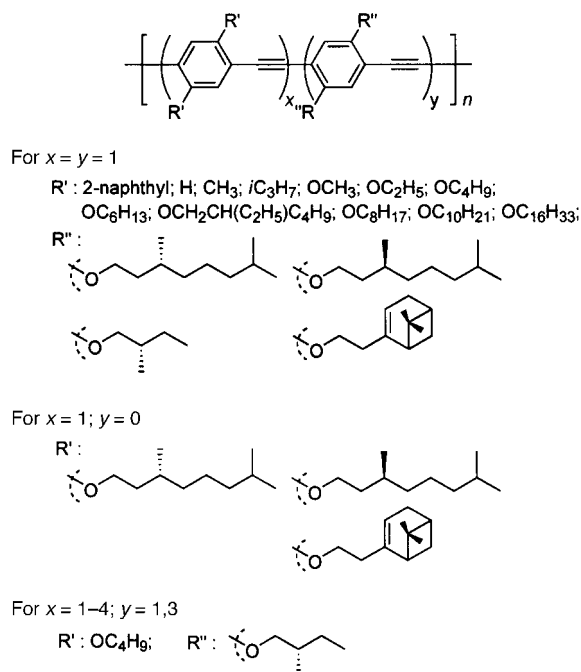


alkyloxy groups. Poly(2,5-bis[2-(*S*)-methylbutoxy]-1,4-phenylene ethynylene) was previously investigated.^[13] However, our results contrasted significantly from the earlier studies,^[14] which prompted a detailed investigation. The addition of poor solvents to a solution of the conjugated polymer generates stable solutions of very small nonscattering particles^[15] that allow quantitative studies of the optical properties by avoiding the scattering, reflection, and waveguiding of the emitted light that complicate thin-film studies. To develop a comprehensive understanding of polymers containing chiral alkyloxy side chains, we undertook the systematic investigation of the 58 different compositions shown in Scheme 1. While a detailed description of all of these materials is beyond the scope of this present contribution, we have established that molecular weight is a critical variable and that lower molecular-weight materials ($M_n < 12000$) gave different results from higher molecular-weight compounds.

We chose to study the well-defined polymer **1**, because it yielded consistent results that are representative of the entire family of polymers. The addition of methanol ($\geq 40\%$) to

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Scheme 1. Structures of the polymers under investigation.

chloroform solutions of **1** introduces an band at 492 nm in the UV/Vis absorption spectrum (Figure 1) caused by an aggregate. Consistent with our previous studies, the fluorescence is strongly quenched by the aggregate. Commensurate with the appearance of the band arising from the aggregate at low methanol concentrations, we see circular dichroism (CD) bands indicative of a chiral structure.^[16] The large peak in the CD spectrum at low methanol concentrations is coincident with the band caused by aggregation and confirms that the new aggregate chromophore is chiral.^[17] The other features in the CD spectrum indicate the presence of a second chromophore at higher energy, which has the same sign in the CD. The inflection point at 454 nm is the same as the absorption maxima of unaggregated and less-conjugated segments of the polymer, which indicates the presence of exciton-coupled CD (ECCD).^[18] The small negative CD peak at 467 nm in the composite spectrum at low methanol concentrations is the result of cancellation of the strong positive second Cotton Effect (CE) from the aggregate chromophore and the negative first CE from the exciton-coupled polymers.

The most striking feature of the behavior of **1**, and indeed related structures in Scheme 1, is that above methanol concentrations of 50% the CD drops off dramatically, while the aggregate peak continues to grow (UV/Vis). This effect can be understood as shown schematically in Figure 2a–c. Initially a chiral aggregate forms with a small angle between polymer chains to give an organization reminiscent of a cholesteric liquid crystal. However, the polymer ultimately favors a stronger aggregate structure with coincident alignment of polymer chains and the helical structure is lost. We note that in previous studies this behavior was not observed.^[13] The resultant organization gives a low or non-existent dihedral angle between polymer chains and, as expected, the fluorescence quantum yield drops to only <5% ($\Phi = 0.04$) of its original value.

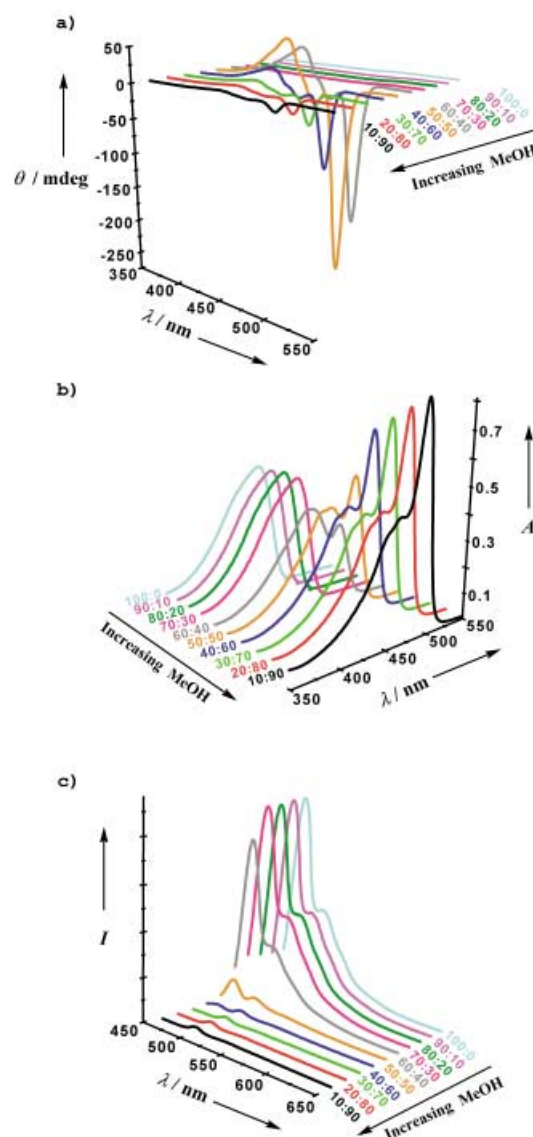


Figure 1. Circular dichroism (a), absorption (b), and fluorescence (c) spectra of (*S*)-**1** recorded in good solvent/poor solvent mixtures at 25 °C (100:0 denotes 100 v/v % of chloroform and 0 v/v % of methanol, 20:80 indicates a solvent mixture consisting of 20 v/v % chloroform and 80 v/v % methanol).

To stabilize a strongly aggregated chiral and emissive organization of polymers, we have investigated specific architectures that prevent aggregated chains from achieving a collinear structure. We had previously developed the polymers **2** containing the pentyptylene group and found that this group was excellent in preventing chain aggregation in spin-cast films.^[19] We have found, however, that addition of methanol (30%) to solutions of **2** gives aggregates with significantly quenched emission ($\Phi = 0.21$). This aggregate is much slower to assemble than **1** and we hypothesized that the polymer chains assemble into an interlocking structure, in which the polymer chains are constrained in the clefts between pentyptylene groups.

We considered that an interlocking structure, such as that of **2**, would stabilize chiral aggregates by preventing a coincidence of strongly interacting polymer chains. Studies of the chiral analogue **3** confirm the restricted nature of the aggre-

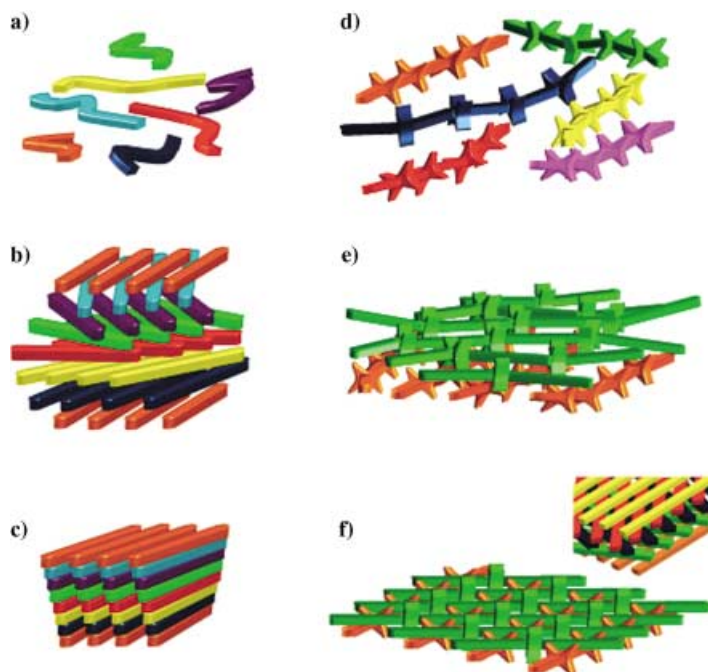


Figure 2. Illustration of three stages of aggregation of **1** (a)–(c) and **3** (d)–(f). Top: **1** (a) and **3** (d) dissolved in neat chloroform. Both polymers are highly solvated and there are no interactions between polymer chains. Middle: Aggregation of **1** occurred and the rigid-rod PPEs form a lamella structure within each plane (b). The chiral side chains guide the polymers into a chiral macrostructure as depicted. The formation of the optically active macrostructure is guided by the influence of the chiral side chains. Polymer **3** aggregates analogously to **1**, but because of the presence of the pentiptycene groups, a slightly irregular interlocked structure results (e). Macrostructure **3** is shown in a two-layer graphic for simplification and clarity. Bottom: The initial chiral macrostructure of **1** has been “untwisted” (c), which is favorable as it maximizes π – π stacking in the edge-on conformation. The dihedral angle assumes a very small value, affording a very weak dichroic signal and low fluorescence quantum yield. Polymer **3** self-assembles into a tighter structure (f) by incorporating the polymer into the clefts of the pentiptycene groups. Because the “untwisting” motion observed in **1** is hindered, polymer **3** is able to maintain its optically active structure and its high fluorescence quantum yield. The inset illustrates the anticipated chiral gridlike structure.

gated state; the structure of the CD and absorption spectra evolve slowly over approximately five minutes. Although the absorption spectra are similar to those of **1**, with more fine structure, the CD spectra are very different (Figure 3). Like that of **1** in the aggregated state ($\geq 30\%$ methanol), the spectrum of **3** displays two dominant contributions that are associated with the “aggregate” band at $\lambda_{\text{max}} = 460$ nm and the band arising from unaggregated species at 430 nm. However, there are key differences between **1** and **3**. Most striking is the change in shape and even sign of the CD bands upon forming the tightest aggregate structure in high methanol concentrations ($\geq 50\%$). We believe this complication is the result of the polymer chains being constrained in interlocked irregular structures as shown in Figure 2e. The position of the CD band and the near coincidence of the inflection point with the λ_{max} of the aggregate indicates an ECCD effect that only originates from the interpolymer interaction of the planar chromophores. Hence it appears that only well-structured (planar) polymer chains are incorporated into the grid. Portions of the material that probably have a less ordered and therefore a less

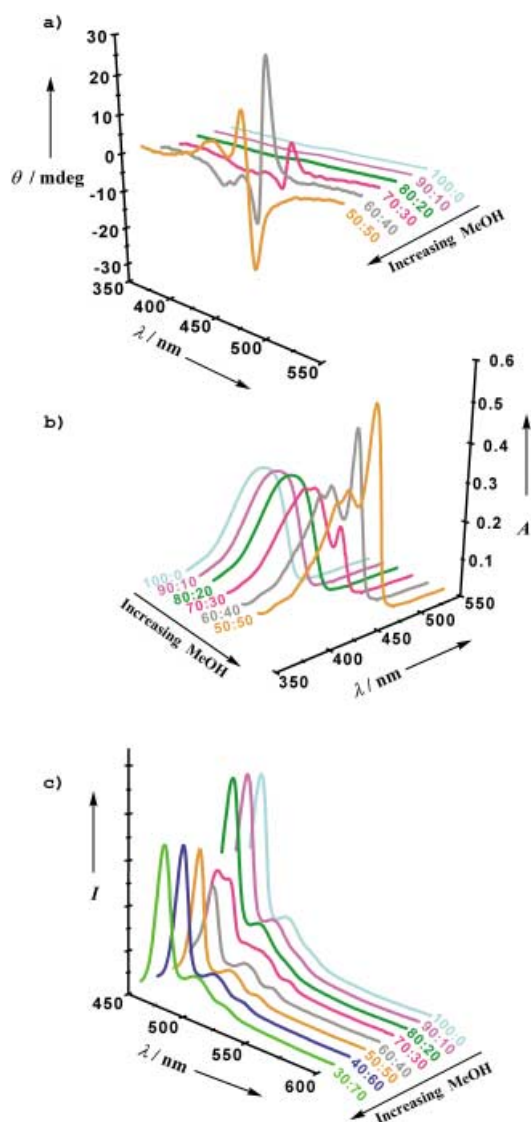


Figure 3. Circular dichroism (a), absorption (b), and fluorescence (c) spectra of (*R*)-**3** recorded in good solvent/poor solvent mixtures at 25°C (100:0 denotes 100 v/v % of chloroform and 0 v/v % of methanol, 30:70 indicates a solvent mixture consisting of 30 v/v % chloroform and 70 v/v % methanol).^[24]

conjugated electronic structure are not incorporated into the gridlike structure because of their higher steric demands that make them unsuitable to fit in the cleft of the polymer. These “solutionlike” portions of the material communicate poorly with each other electronically and therefore give rise to a broad CD band at 430 nm, which is difficult to analyze.

The CD signal and the aggregate band in the absorption spectrum are both consistent with interpolymer electronic interactions. However, as shown in Figure 3, in contrast to other polymers, **3** maintains the majority of its fluorescence intensity with aggregation ($\Phi = 0.61$).^[25] The CD does not diminish at high methanol concentration and, interestingly, upon initial aggregation the intensity is slightly lower than the more highly aggregated form. Control experiments utilizing the opposing enantiomer to **3** yielded UV/Vis and fluorescence spectra of identical shape and intensity, and a CD spectrum that differs only in the signs of the Cotton effects.

Furthermore, a solution containing 50 % (*S*)-**3** and 50 % (*R*)-**3** gave absorption spectra similar to pure solutions of (*S*)-**3** or (*R*)-**3**, but no CD signals, as expected. Consistent with chirality being a critical element to maintain a high quantum yield, this aggregate maintained a Φ of only 0.3. Achiral aggregates present in the 50:50 mixture of enantiomeric polymers are probably responsible because the long-range dipole–dipole interactions responsible for the excitonic coupling are extended beyond nearest neighbors.

To illustrate the advantages of a 3D structure for the design of optoelectronic devices, the performance of **3** as a self-amplifying sensory polymer was investigated under solution and solid-state conditions by means of Stern–Volmer quenching experiments (Figure 4). In solution, fully aggregated **3** displayed a 15-fold steeper quenching slope toward the

conducting studies as a function of film thickness. Because of limited exciton transfer between polymer chains, which limits exciton diffusion, **2** displayed a dramatic 45 % decrease in sensitivity in thicker films (OD = 0.3) relative to thinner films (OD = 0.04).^[23] In contrast, **3** displays only a 10 % decrease in quenching sensitivity in thick films (OD = 0.2) relative to thin films (OD = 0.02).

To summarize, the high quantum yield of **3** in its aggregated state results from the formation of a helical grid structure and an oblique orientation of the transition dipole moments of the neighboring polymer chains. We have discovered that rigid scaffolds prevent collinear aggregation of polymer chains. Chirality has been used for the first time to create strong electronic coupling systematically while maintaining high fluorescence efficiency. These chiral, 3D interactions produce sensitive sensory materials with excellent quantum yields. Similar approaches will probably enhance the performance of electronic polymers for many other optoelectronic-device applications.

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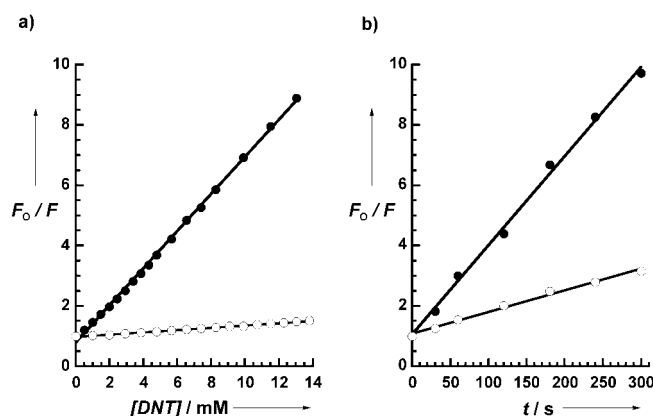


Figure 4. Stern–Volmer plots of **3** in a nonaggregated form (○) and an aggregated form (●) in solutions at OD = 0.09 (a). Stern–Volmer plot of **2** (○) and **3** (●) in films of OD = 0.03 upon exposure to TNT vapors (b).

explosives dinitrotoluene (DNT) and trinitrotoluene (TNT) than nonaggregated **3**. In solid-state experiments, **3** was compared to **2**, a material with a self-amplified sensory response arising from efficient exciton transport that is the basis of new landmine detection technology with femtogram detection limits.^[7] Polymer **2** exhibits its best performance when spin-coated from nonaggregated solutions to give films of non-interacting chains. These films of **2** were compared with films that were spin-coated from aggregated solutions of **3** (55:45 chloroform:methanol). Both films were uniform and of identical optical density. Upon exposure to a static 10 ppb vapor of TNT,^[20] **3** displayed a Stern–Volmer plot that is four times steeper than that of **2**. It should be noted that thin films of **3** (optical density (OD) = 0.04) exhibit a quenching response of $\approx 75\%$ in 10 seconds that is significantly more sensitive than previously published materials.^[7,21–23] We attribute this observation to the improved diffusion length of excitons in 3D-coupled chiral grids of **2**. Our recent work^[1] suggested that strong electronic coupling provides the best exciton transport and hence the excitonic coupling enhances the interchain transport. Further, the highly organized aggregate probably extends the conjugation length of the polymer, which may also enhance exciton transport. We have ruled out the possibility that the sensitivity enhancement is caused by a higher partitioning of TNT to **3** than to **2** by

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- [20] The saturation vapor pressure of TNT at 22 °C is 8.02×10^{-6} mmHg or about 10 ppb. *Handbook of Physical Properties of Organic Chemicals* (Eds.: P. H. Howard, W. M. Meylan), CRC, Boca Raton, FL, **1997**.
- [21] For comparison, other electronic polymers reportedly decreased their fluorescence intensity by 8.2% after exposure to similar vapor concentrations with turbulent flow for 10 min (H. Sohn, R. M. Calhoun, M. J. Sailor, W. C. Trogler, *Angew. Chem. Int. Ed.* **2001**, *113*, 2162; *Angew. Chem. Int. Ed.* **2001**, *40*, 2104). Hence **3**, which was studied under static conditions, is at least 560 times more sensitive.
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- [24] The CD and absorption spectra end at 50:50 chloroform:methanol as the rigid, gridlike aggregates precipitate readily at higher methanol content. The fluorescence spectra could be recorded up to 30:70 chloroform:methanol as the concentration of the polymer was only 1/10 of that of the absorption studies and therefore precipitation occurred at higher methanol concentrations.
- [25] Similarly, **3** had a photoluminescence efficiency which was four times higher than that of **2** in films of identical optical density.

High-Throughput Multilevel Performance Screening of Advanced Materials

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High-throughput screening and combinatorial chemistry have been successfully extended from pharmaceutical applications into other scientific disciplines.^[1] Performance of rapidly fabricated compounds is typically evaluated by relating results of high-throughput analysis to the intrinsic properties of starting materials or final products.^[2] We report a general scheme for screening of complex materials developed by using high-throughput and combinatorial methods, where simple screening for intrinsic properties of starting materials or final compounds does not provide information about long-term material performance.

Our general approach employs fabrication of materials arrays followed by their testing against single or several performance parameters at *multiple* levels. This testing process imitates the end-use application and alters materials properties in a detectable manner that is impossible to quantitatively predict using existing knowledge.^[3] Our scheme of high-throughput evaluation of advanced materials fabricated by using high-throughput and combinatorial methods is

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very general and includes diverse testing methodologies such as solar radiation, mechanical stress, aggressive fluids, heat, and others. Tested arrays are further analyzed by using high-throughput screening (HTS) tools.

We demonstrated our strategy for high-throughput performance screening of polymeric materials. Weathering is a critical consideration in the development of new engineering thermoplastics for outdoor applications.^[4] A determining factor in the outdoor weathering lifetime of these materials is the received UV radiation dose. It leads to material photodegradation that initially causes the loss of appearance such as surface discoloration and gloss loss.^[5,6] Other environmental (humidity, temperature, frequency of light/dark cycles) and material (catalyst residues, crystallinity, molecular weight, end groups) factors do not appreciably affect the appearance of engineering thermoplastics upon weathering.^[4,7] These factors, however, do have a pronounced effect on other types of polymers.^[4,6] Additives and pigments (typical loadings of 0.01–5 wt %) greatly affect the stability of engineering and other types of polymers.^[8] Thus, studies of polymer–additive and polymer–pigment combinations are of great importance.

Resistance toward weathering presents a particular challenge for HTS since exposure times for adequate outdoor weatherability testing are thousands of hours.^[4] In principle, acceleration of this process can be achieved either by increasing the level of environmental stress or by very early detection of material degradation. In laboratory weathering methods, a dose equivalent to one year of exposure to conditions in Florida can be reduced to about 1100 h.^[9] However, a further acceleration of materials weathering to the HTS level becomes problematic because of loss of correlation with traditional test methods.^[4,8,10]

We use fluorescence imaging and spectroscopy to quantify photodegradation in arrays of materials at short exposure times that open up HTS capabilities in weathering studies. Our libraries combine the variables of polymer composition, pigment type, and exposure time, but are easily extendable to incorporation of stabilizers and other additives at different loadings that may affect the rate of degradation.

Unlike traditional measurements of weatherability-related appearance based on color changes and gloss loss,^[4,8b,11] fluorescence analysis^[12] advances the studies of polymeric materials libraries produced by using high-throughput methods to a previously unavailable level of capabilities. Fluorescence detects trace amounts of weathering degradation products and thus requires a considerably shorter testing time. Measurements are performed on both lightly and highly colored samples with a comparable level of sensitivity. Because fluorescence light is isotropic, the whole combinatorial library is imaged without the need for an integrating sphere or a goniophotometer. Different fluorescence excitation–emission conditions can be selected to analyze different fluorescent species.

To demonstrate the applicability of our screening strategy, three types of aromatic polymers (polycarbonate, PC; poly(butylene terephthalate), PBT; and their 45/55 wt % blend, PC/PBT) were made in combination with two types of pigments (rutile TiO₂ and carbon black, CB) and tested under