Highlight Review

From Industrial Colorants to Single Photon Sources and Biolabels: The Fascination and Function of Rylene Dyes

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Abstract

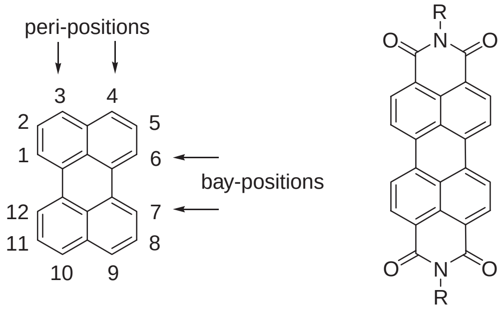
Perylene dyes are key chromophores in dyestuff chemistry. The solubility, absorption, and emission behavior of this class of materials can be efficiently controlled by functionalization using a variety of different synthetic procedures. Moreover, these chemical modifications have allowed their widespread application as functional dyes. New NIR-absorbers have been synthesized by introducing additional naphthalene units to the perylene scaffold to form the higher homologues of the series of rylenediimides. Such dyes can be used for laser welding and laser marking of polymers. Highly fluorescent nanoparticles containing multiple chromophores have been prepared by decorating polyphenylene dendrimers with rylenes on the surface. Depending on the chromophoric interactions, these types of materials can serve as single photon sources. When in addition to the surface, the interior and the dendritic scaffold are equipped with donor and acceptor dyes, synthetic light-harvesting complexes are obtained, which collect light from the whole visible spectrum. Due to the outstanding chemical and photochemical stabilities as well as their high fluorescence quantum yields, the perylene- and terrylenediimides have been established as key chromophores for single molecule spectroscopy allowing photophysical processes, e.g. energy and electron transfer to be studied on the single molecule level over extended periods of time. With water soluble rylene dyes single molecule measurements regarding biological problems can now be addressed as well. The same set of favorable properties also makes the rylene dyes excellent candidates for applications in organic electronic devices.

◆ Introduction

Colors have always appealed to human beings. Colors not only influence emotions of individuals but are also an instrument of communication. Therefore, colorants have played an important role in the development of cultural history, and the synthetic manufacturing of dyestuffs was a major driving force in the industrial revolution of the 19th century. In recent times, the use of organic dyes and pigments for coloring textiles and other consumer goods was expanded to the field of the so called "functional dyes." In this context, the most important role is not played by the aesthetic appearance, but by the physical or chemical properties of the dyes such as light emission, photoelectric and photochemical activity as well as light-induced polarization. Some of the resulting applications which make use of this new type of chromophore are fluorescent labels in biochemistry and medicine, laserdyes, electrophotography, xerography, data storage, and sensitizers in photovoltaic devices. The integration of dyes in diverse high-technology fields dictates new and fascinating challenges for a materials-oriented organic synthesis. However, the classical topics in dyestuff research remain valid. These consist of molecular and supramolecular control of the absorption and emission behavior or the brilliance and the stability of the dye.

In the community of organic chemists, dyestuff chemistry is often considered to be somewhat old-fashioned, since its classical topics have fizzled out; there is a lack of new types of chromophores and industrial manufacture of dyestuffs is confronted with well known problems regarding costs and public acceptance. Also fitting within this context is the fact that the synthesis of a natural product, even if achieved via just an alternative route, is scientifically more appreciated than the generation of an "artificial" dye. However, the motivation for a synthetic target molecule can not only arise from the number of difficult steps and newly created stereogenic centers involved but should be fuelled by the function, either biological or physical, of a compound. Exploring the function of a molecule means applying a large variety of different techniques to a complex micro- or macroscopic system. Important questions regarding the future of information technology and energy conversion on the first view seem only to be of concern to physicists and engineers. It is much less obvious that the solution of future problems starts with the availability of suitable materials, among which dyes continue to play an important role.

The following text is divided in two parts. In the first part, the synthetic tools are described that are necessary to guarantee the optimal performance of functional dyes in a complex environment. In the second part, the focus lies on describing particular notable examples of functional dyes. These examples have been selected to represent a well balanced mix of relevance for basic research and industrial importance. The basic structures of the materials described in this text consist of perylene (**1**) and the much more photostable perylenetetracarboxdiimide **2** (PDI), first prepared in 1912 (Figure 1).[1] Particularly, severe requirements for functional dyes are nowadays defined by single molecule spectroscopy (SMS) where the fluorescence of single emitter molecules rather than of their ensemble is recorded. The chromophores presented here have



1 **2**

Figure 1.

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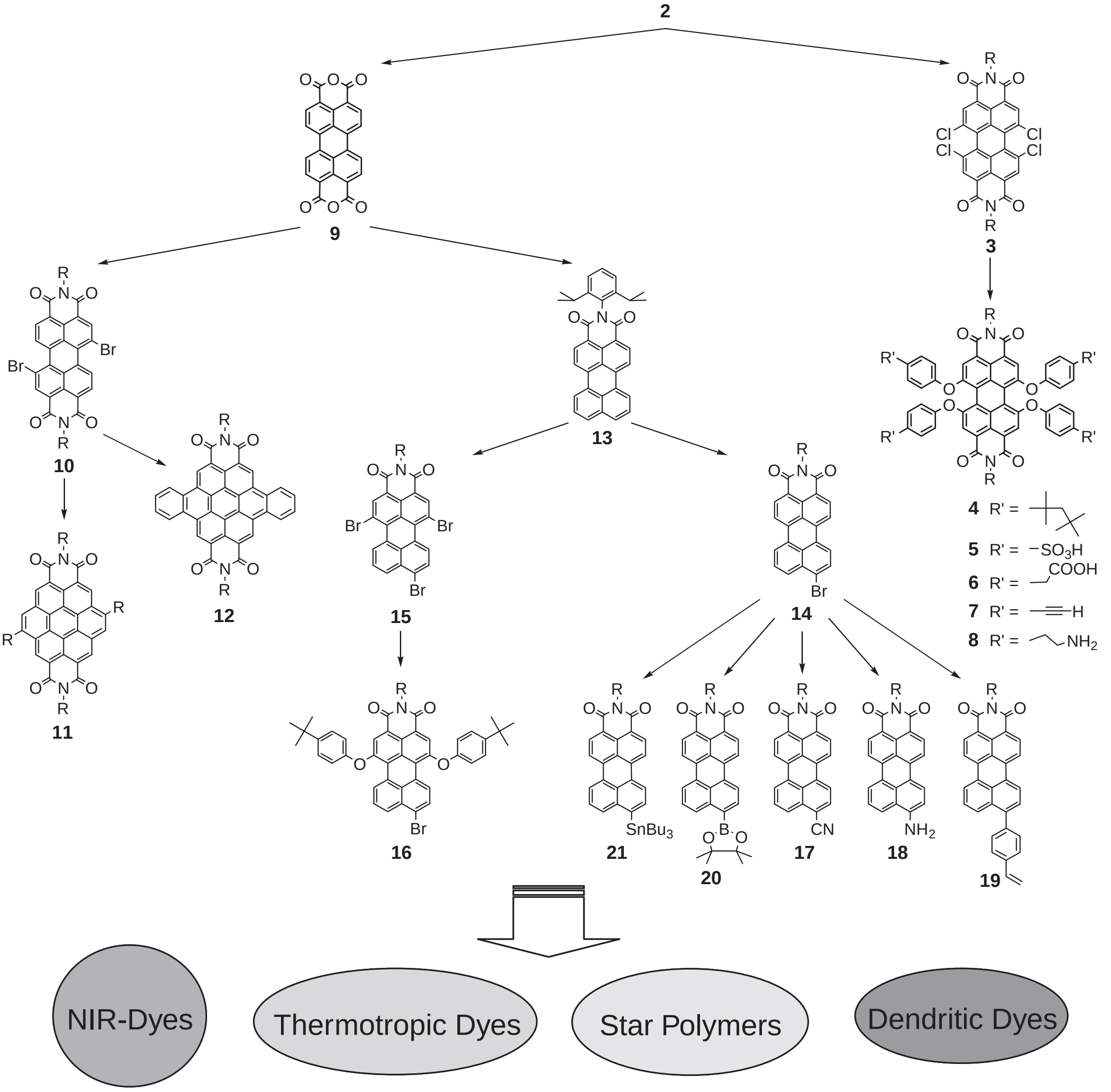
proved to be of outstanding value for SMS, so that this text extends classical dyestuff chemistry into the age of nanoscience and nanotechnology.

Chemical Modification of Perylenetetracarboxdiimides

The role of **2** as an industrially important dye is well known. However, PDI **2** represents also the key structure from which new types of chromophores, important intermediates and different functional perylene dyes are derived. The genealogical tree for a large variety of perylene derivatives originating from **2** is shown in Scheme 1. PDI **2** is chlorinated in nitrobenzene with thionyl chloride introducing four halogen atoms into the bay-positions.[2] The tetrachloro derivative **3** is then further reacted in a nucleophilic replacement with various phenol derivatives. Phenoxylation with 4-isooctylphenol bearing sterically demanding alkyl groups is not only accompanied by a bathochromic shift of the absorption maximum from ca. 520 to 580 nm but also by a 10 to 50-fold increase in the solubility of **4** in organic solvents.[3] Solubility in aqueous medium is achieved by introducing sulfonyl or carboxyl groups in the phenol units of the bay-positions as realized for **5** and **6**, respectively.[4,5] It is important to note that **5** retains its high fluorescence quantum yield in water (60%), easily penetrates living cells and exhibits improved photostability on the single molecule level compared with other water soluble dyes.[6]

Functionalization of the bay positions also enables an effective shielding of the chromophore, which otherwise exhibits a high tendency towards π-stacking. This encapsulation is realized by creating four terminal alkynes at the phenoxy groups, which are used for the build up of polyphenylene dendrimers around compound **7** acting as a core molecule.[7–10] Aggregation of chromophores in the solid state commonly causes undesirable red shifts in the emission spectra and/or emission quenching. The lack of a bathochro-



Scheme 1. The genealogical tree of perylene compounds.

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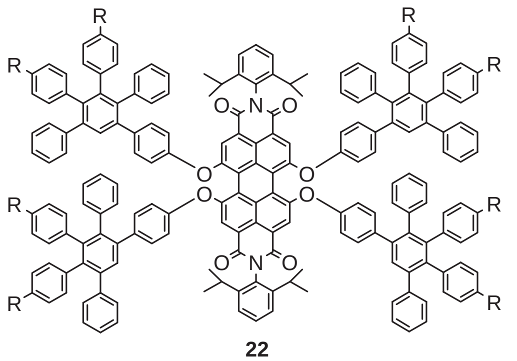

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R = H, n-Alkyl, Triphenylamine

Figure 2.

mic shift in emission upon going from solution to the solid state indicates that the stiff polyphenylene dendrons as present, e.g. in the G1-dendrimers **22** (Figure 2) efficiently suppress interaction of the emissive cores, leading to pure red-orange emission in solid state and even in single-layer light emission devices (LEDs). The periphery of the dendrimers with a PDI as emissive core can additionally be functionalized with long alkyl chains introducing good film-forming properties to the otherwise microcrystalline material.[7] When instead of alkyl chains triphenyl amine moieties are attached to the dendritic surface, intramolecular energy transfer is demonstrated by the observation of PDI emission on excitation of the triphenylamines, and electron transfer is detected by comparing fluorescence quenching in solvents of different polarity.[10]

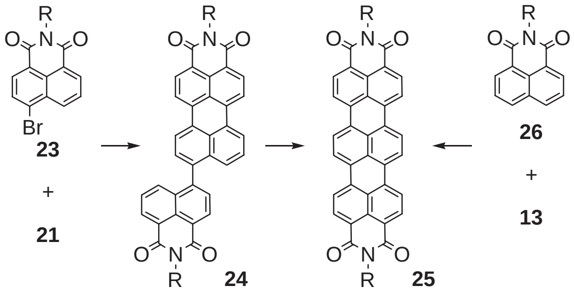
Attaching dendritic arms around the PDI core requires an iterative process for the build-up of higher dendrimer generations. However, it is also possible to use the tetraphenoxy PDI **8** as an initiator to create pH-responsive star polypeptides.[11] In a similar way, star-shaped polystyrenes[12] and polyesters were prepared.[13]

Instead of four halogen atoms as realized in **3**, the bay positions can be functionalized with two bromine atoms by reacting perylenedianhydride **9** in 100% sulphuric acid with bromine.[14] After an imidization reaction with alkyl or arylamines, the dibromo PDI **10** is obtained. This compound allows easy access to a different class of chromophores, the coronenediimides.[14] In this synthesis, **10** was reacted in a palladium(0)-catalyzed Hagihara–Sonogashira reaction with various 1-alkynes to afford the bis(alkynyl)-substituted perylene-3,4:9,10-bis(dicarboximide)s, which upon treatment with strong, non-nucleophilic bases underwent an almost quantitative cyclization reaction to yield **11**. When **11** is substituted with appropriate alkyl chains the coronenediimides form discotic mesophases and combine the properties of both dyes and liquid crystals. After incorporation into a polymer matrix, the corresponding films exhibit a remarkable feature. Upon tempering a significant shift of the emission wavelength is detected within a few seconds. This effect might be of use for the fabrication of multicolor displays. The coronene scaffold can be further extended by an alternative route. Instead of reacting terminal alkynes with **10**, the Suzuki coupling using 2-bromophenylboronic acid and subsequent palladium-catalyzed dehydrohalogenation yields dibenzocoronene tetracarboxdiimide **12**.[15]

So far, bis- and tetra-functionalized perylene derivatives have been described. How can mono- and tris-functionalization in the context of peryleneimides be achieved? For that purpose, the perylenedianhydride **9** is subjected to an imidization reaction with 2,6-dialkylanilines, preferentially 2,6-diisopropylaniline, during which one of the two anhydride structures decarboxylates and the perylenemonoimide **13** is formed.[16] The reaction conditions involve very high temperatures and the solvent quinoline, whereupon the thermally less stable imide-anhydride spontaneously looses the anhydride structure. Not surprisingly, the absorption spectrum of monoimide **13** with maxima at 487 and 507 nm exhibits a hypsochromic shift compared to the PDI **2**. More important are the facile routes by which **13** can be chemically functionalized as summarized in Scheme 1. **13** is selectively brominated in the 9-position by applying a five-fold excess of bromine at 50 °C to yield **14**.[17,18] More drastic reaction conditions and a larger excess of bromine result in the corresponding tribrominated perylenemonoimide **15**.[17,18] In the case of **15**, introducing phenoxy groups with sterically demanding alkyl substituents as discussed for **4** leads to improved solubility of **16**, which is of major importance for the preparation of more extended π-systems as described in regard to NIR absorbing dyes later in this contribution. The compounds **14** and **16** bearing one bromine atom attached to the perylene core open the way for fast and easy functionalization of the chromophore. A representative example is the conversion of **14** into the cyano derivative **17** applying the Rosemund von Braun reaction, which exhibits a brilliant yellow-orange color shade and a strong fluorescence in the solid state so that it is produced commercially for use as a signal dye.[19] An elegant way of introducing an amino group in the 9-position consists of palladium-mediated Buchwald coupling of **14** with benzophenonimine and subsequent deprotection of the amine **18** under acidic conditions.[20] Likewise applying the palladium-catalyzed Suzuki reaction, a polymerizable group can be attached to the chromophore by coupling with vinylphenylboronic acid to give the styrene-modified perylene derivative **19**. Since metal-catalyzed cross-coupling reactions have been proven a powerful tool for the functionalization of perylene dyes, the chromophore itself is derivatized into the boronic ester **20**[21] and the stannane **21**[22,23] to have building blocks readily available which can be applied in these type of reactions. The important role of **20** and **21** as intermediates for the construction of multichromophoric systems and for the extension of the perylene chromophore into its higher homologues will be outlined in the following paragraphs.

Higher Rylenes and New NIR Absorbing Dyes

The first attempts to shift the absorption maximum of PDI **2** to longer wavelengths relied on condensation of perylenedianhydride **9** with *o*-diaminoarene compounds, which produced the corresponding imidazole derivatives as a mixture of syn- and anti-isomers.[24,25] Bathochromic shifts of up to 100 nm were achieved. An alternative concept to obtain long wavelength absorbing perylene dyes is the successive incorporation of additional naphthalene units between the imide structures leading to the homologous series of rylenetetracarboxdiimides. Extension of PDI by one naphthalene results in the terrylenediimide **25** (TDI). The synthesis of this compound is realized by applying tin compound **21** and 4-bromonaphthaleneimide **23** in a Stille coupling to yield the terrylene precursor **24**, which can be fused by KOH and an oxidation reagent to the TDI **25** (Scheme 2).[23] To avoid toxic stannyl compounds, alternatively **20** is reacted with **23** in a Suzuki coupling to form **24**.[26] This reaction proceeds even more efficiently with yields of up to 90%. Due to the high demand for TDIs, a third route has been established. This is based on coupling perylenemonoimide **13** with naphthalenemonoimide **26** in a one-pot reaction in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and *t*-BuONa. The advantages of this route are that it can be easily carried out on the 100 g scale and purification by column chromatography is avoided.[26]

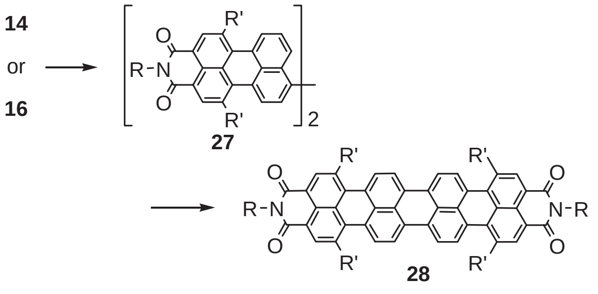


Scheme 2. Synthesis of terrylenediimide **25**.

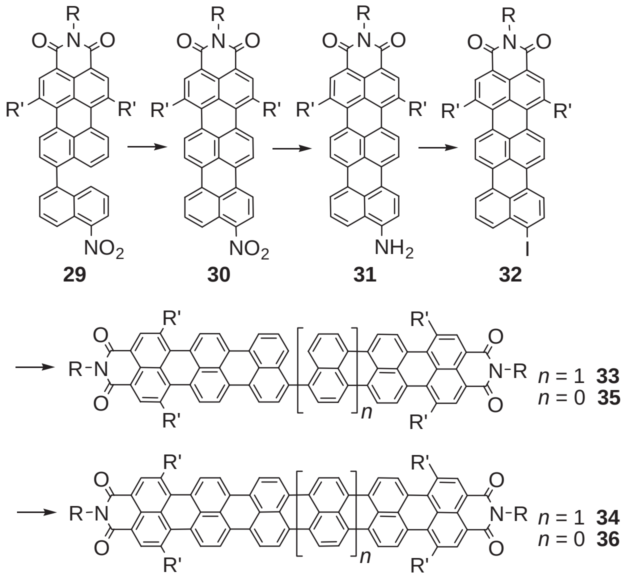
The next higher homologue in the series of rylenetetracarboxdiimides is the quaterrylenediimide (QDI). The synthesis of this dye is even more straightforward since instead of a heterocoupling a homocoupling leads to the target molecule **28** (Scheme 3). Starting from brominated perylenemonoimides **14** or **16** nickel(0)-induced dimerization leads to the bisperylenyl **27**, which can be planarized to **28** under the same conditions as described for the TDI **25**.[17,18]

Further extension along the long axis of the rylenediimides has been achieved and two synthetic routes towards the penta- and hexarylenediimide have been developed.[27] The first one, the so called "nitronaphthalene method," starts from the coupling product of the boronic ester of 1-bromo-5-nitronaphthalene and **16**. The bisaryl compound **29** is then cyclized to **30**, reduced to the amine **31** and finally transformed into the iodo terrylenemonoimide **32** by a Sandmeyer reaction. From this building block the hexarylenediimide **34** is obtained by homocoupling and subsequent cyclodehydrogenation. Similarly, the coupling of **32** with **16** yields the perylenemonoimide–terrylenemonoimide bichromophore **35** and subsequent planarization results in the pentarylenediimide **36** (Scheme 4). An alternative access to penta- and hexarylene, which will not be discussed any further here, the so called "bisbromorylene method" is based on building up triaryl precursor molecules consisting of three perylene units or two perylenes and a naphthalene which after cyclodehydrogenation result in the hexa- and pentarylenediimides, respectively.[27]

Upon inspecting the absorption spectra of PDI **2** and TDI **25** a bathochromic shift of the absorption maxima of around 100 nm is detected (Figure 3). **25**, which is deeply blue colored, absorbs at 650 nm whereas **2** has a brilliant red color (abs. max. 550 nm). Even more important in the context of functional dyes is that upon going from PDI to TDI the fluorescence quantum yield remains almost unchanged at 90% for **25**. The emission maxima of TDI derivatives lie in the range from 670 to 710 nm depending on the substitution pattern in the bay regions.[23] Thus, they are NIR emitting dyes, which is an important region of the electromagnetic spectrum for biological applications. In the case of the QDI **28** the quantum yield drops to 5% (em. max. 800 nm). The absorption maxima of QDI dyes with varying degree of phenoxylation are detected between 760 and 790 nm (Figure 3). In strong contrast to PDI and TDI, solutions of quaterrylenediimide appear to be almost colorless having a light greenish appearance which is caused by the rising absorption band at around 600 nm. The absorption spectra of penta- and hexarylene derivatives **36** and **34** exhibit absorption maxima at 830–880 and 950 nm, respectively (Figure 3). As a result the penta- and hexarylenediimide are completely colorless in solution.[27]



Scheme 3.



Scheme 4. Synthesis of higher rylene dyes: Pentarylenediimide **36** ($n = 0$) and hexarylenediimide **34** ($n = 1$).

By extending the aromatic π-system also the absorption coefficients increase from $\varepsilon = 60{,}000\,\mathrm{M^{-1}\,cm^{-1}}$ (PDI), $\varepsilon = 93{,}000\,\mathrm{M^{-1}\,cm^{-1}}$ (TDI), $\varepsilon = 167{,}000\,\mathrm{M^{-1}\,cm^{-1}}$ (QDI) over $\varepsilon = 235{,}000\,\mathrm{M^{-1}\,cm^{-1}}$ (pentarylenediimide) to $\varepsilon = 293{,}000\,\mathrm{M^{-1}\,cm^{-1}}$ for the hexarylenediimide. For organic NIR-dyes such high absorption coefficients are unprecedented. In addition to these remarkable photophysical properties, all the presented NIR-absorbers still display the excellent chemical, photochemical and thermal stability seen for their smaller counterparts the PDIs. For this reason the pentarylene **36** and the hexarylene **34** are very well suited for a new technique for joining polymers called laser welding. In the process of overlap welding, the laser penetrates the upper

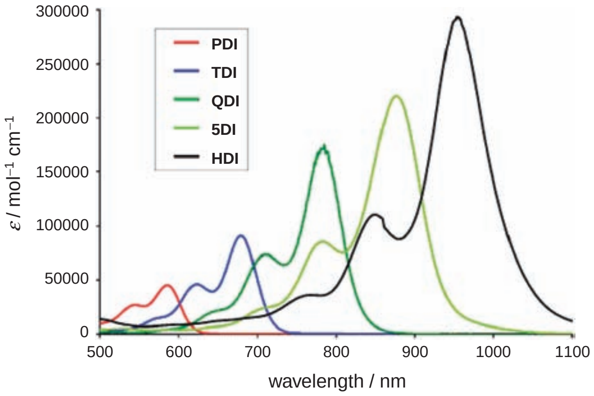
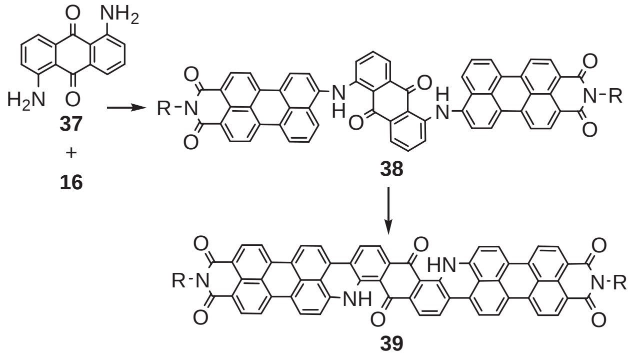


Figure 3. UV–vis absorption spectra of rylenediimides: Perylenediimide **2** (PDI), terrylenediimide **25** (TDI), quaterrylenediimide **28** (QDI), pentarylendiimide **36** (5DI), hexarylenediimide **34** (HDI).



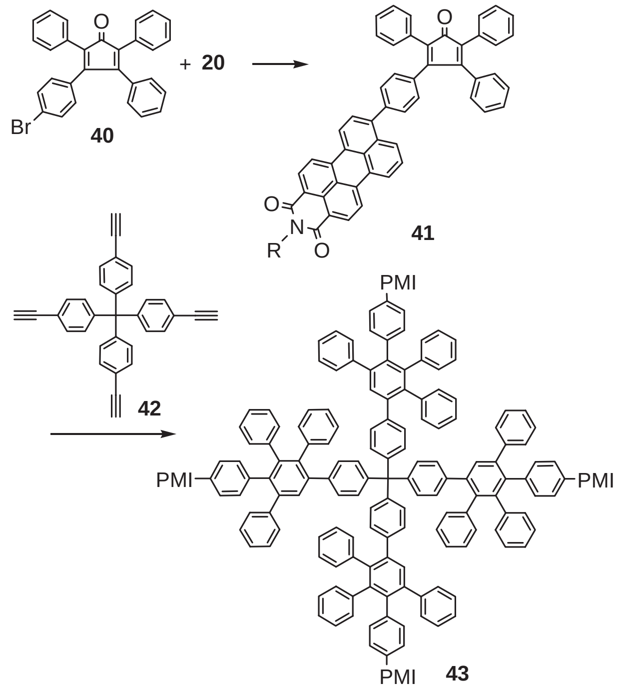
Scheme 5.

workpiece and is absorbed by the lower part. The generated heat is transferred by heat conduction. The mutual melt pool achieves almost base material strength after solidification. For effective heat absorption within the polymer, absorbing additives are needed, which mostly exhibit an intrinsic color in the visible limiting the color range of components. The most striking advantage of the NIR absorbing rylenecarboxdiimides for that purpose is that they do not absorb in the visible so that the process of laser welding would not be restricted anymore to the use of transparent or colored components.

An alternative strategy to achieve absorption in the NIR-region relies on combining different chromophore topologies. Treatment of bromo perylenemonoimide **16** with 1,5-diaminoanthraquinone (**37**) in the presence of a palladium catalyst results in formation of the triaryl compound **38** which can be planarized by exposure with base to produce the NIR absorber **39** (Scheme 5).[28] The absorption of this dye is even further shifted to longer wavelengths in comparison to hexarylenediimide **34**. Absorption maxima appear in the NIR region at 1000 and 1106 nm. The application of such NIR chromophores for laser marking will be described later in this text.

Multichromophoric Systems Based on Perylene Dyes

The NIR absorber **39** is build up from three chromophores including two perylenemonoimides. For the construction of multichromophores containing a much larger number of chromophores a dendritic approach has been chosen. As mentioned in the context of encapsulation of perylene dyes, polyphenylene dendrimers are build up around multiethynyl-functionalized core molecules in an iterative process applying a Diels–Alder reaction and deprotection of alkyne functions.[29,30] The resulting dendritic structures consists of highly twisted pentaphenyl motifs, which are chemically and photochemically inert and, even more important, shape persistent. Due to these properties the polyphenylene dendritic scaffold is ideally suited for the functionalization with chromophoric units since perfect spatial control over several dyes within such a scaffold is achieved. The parameters permitting the adjusting of the number of dyes, interchromophoric distances and dipole orientations are the symmetry of the core molecules, branching reagents and generation number meaning that the spatial definition of chromophores is encoded by synthesis.



Scheme 6.

One possible synthetic route among others[31] relies on functionalizing tetraphenylcyclopentadienone **40**, with the boronic ester of perylenemonoimide **20** by Suzuki coupling to yield **41**. This dye-labeled terminating reagent allows the preparation of multichromophoric systems with a large number of chromophores.[21] The first dendrimer generation **43** after applying **41** in a Diels–Alder reaction with the tetraethynyl core **42** already contains 4 chromophores (Scheme 6). The next higher second generation contains 8 perylenemonoimide units at the periphery of the dendrimer and even a third generation with 16 chromophores has been achieved. In these multichromophoric dendritic systems the high fluorescence quantum yield of each chromophore is retained, so that these materials can rightly be regarded as highly fluorescent and photostable nanoparticles. Other methods to build up defined nano-objects containing perylene dyes rely on metal-ligand-coordination-directed self assembly[32,33] or covalent coupling of the dyes to multifunctional building blocks[34] and aggregation of such multichromophoric systems.[35]

Beside decorating the surface of polyphenylene dendrimers with only one type of chromophore, the desymmetrization approach[36] allows the introduction of donor–acceptor pairs derived from the family of rylene dyes at different hemispheres at the rim of the dendrimers.[37,38] Intramolecular Förster-type excitation energy transfer (FRET) between three peryleneimide chromophores and a terryleneimide chromophore is detected. More than 95% of the energy harvested by the peryleneimide chromophores is transferred and trapped in the acceptor. To further develop the concept of light harvesting in dendritic systems, two synthetic strategies have been combined. Instead of just encapsulating a PDI with a bare polyphenylene dendritic shell, TDI is applied as a core molecule. Subsequently, dendrons are attached which carry peryleneimide chromophores. Finally, a dendritic surface layer containing naphthaleneimides is introduced.[39] By this multistep synthesis a dendritic triad **44** (Figure 4) is generated containing a central TDI as energy acceptor, four peryleneimides as "transmitters" within the dendritic scaffold and eight naphthaleneimides as antennae at the rim. Detailed photophysical measurements reveal that FRET occurs from peryleneimide to terrylenediimide with an efficiency of 99.5%. On excitation of the naphthalenes, they transfer their excitation energy either directly or in a cascade-type fashion to the core, the latter case involving scaffold-substituted

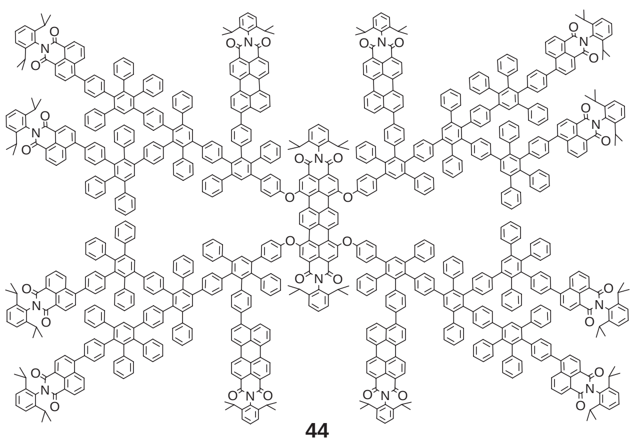


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Figure 4.

PMIs as intermediate acceptors. The spatial positioning and the spectral properties of the chosen rylene chromophores make this multichromophoric system an efficient light collector, able to capture light over the whole visible spectral range and to transfer it finally to the TDI, the latter releasing it as red fluorescence.[40] In addition to generating light-harvesting systems from exclusively synthetic units, a bioorganic hybrid combining a natural antenna system and a terryleneimide dye have been constructed. Energy transfer occurs from the chlorophyll units as donors to the terrylene acceptor, which is covalently attached close to the *N*-terminus of the protein scaffold.[41]

Nanocolorants

The star polymers build around PDI as mentioned above have advantages in comparison to their low molecular weight counterparts concerning their migration fastness and their compatibility with a polymer matrix. In contrast to pigments, however, they do not exhibit a well defined particle size distribution, instead they form amorphous materials. To combine the favorable properties of dyes and pigments in a cost effective way colored latex dispersions have been developed.[42] In a miniemulsion process the styrene derivative **19** is copolymerized with styrene as monomer which results in colored, narrowly dispersed nanoparticles wherein dyes are covalently attached. A dye concentration of up to 5 wt % can be adjusted without observing aggregation of the dyes. When coloring polymeric matrices with "nanocolorants" less chromophore is needed to attain the same color impression than for classical pigments. The reason therefore is that each dye molecule contributes equally to the absorption. As a consequence of this, the absorption bands are not broadened or weakened as occurs for transitions in the solid state. Also remarkable is the high migration fastness in HD-PE and PMMA, which underline the practical importance of the concept. When the identical chromophore **13** is only physically incorporated into the latex beads significant leaching of the chromophore out of the polymer matrix is observed.

Laser Marking of Polymers

On top of imparting polymer matrices with stable colors it is also desired to change these by external stimuli, e.g. light or heat, for writing purposes. Before the process of laser marking is described in more detail, a novel class of thermotropic perylene dyes needs to be introduced. The amino-functionalized peryleneimide **18** in contrast to its non-modified counterpart **13** (Scheme 1) is characterized by a deep blue color with structureless absorption bands whereas **13** appears to be brilliant orange with a fine structured spectrum. Responsible for this significant color change is charge transfer from the electron-donating amine group to the imide structure. The charge transfer can be blocked by introducing alkoxycarbonyl substituents to form **45**. These thermally unstable moieties undergo elimination into an alkene and carbon dioxide upon heating almost quantitatively regenerating **18** (Figure 5). This process is accompanied by a color change from orange to blue. Variations in the alkoxycarbonyl substitution lead to different reaction temperatures for this color switch between two photostable color states.[20]

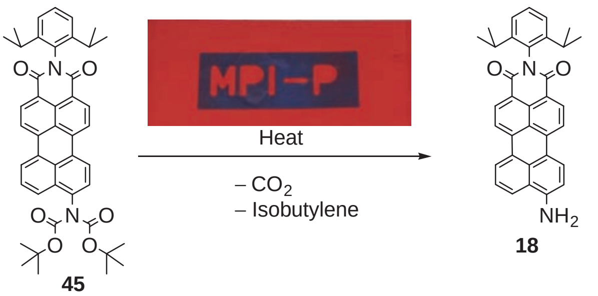

Figure 5. Thermochromic perylene dyes: In peryleneimide **45** the donor properties of the amine group are masked by carbamoyl groups. Heating of **45** leads to removal of the masking groups which results in a color change from red to blue.

Laser marking is a thermographic process which uses a laser as a heat source for the inscription of polymeric matrices.[43] The advantage of this technique arises from the speed and flexibility for the generation of different markings or complex graphical representations. Due to the high energy density of laser light the velocity for inscriptions reaches 2 m/s allowing also its application on rough surfaces and on places which are difficult to access. Moreover, masks and solvents are not needed. Usually, the marking is achieved by evaporation, foaming or carbonisation of the polymeric matrix induced by the heat of the laser. To date, large difficulties remain in the preparation of multi-colored markings of different color shades, good color strength and brilliance.

For that reason, the thermochromic dye **45** and the NIR absorber composed of aminoanthraquinone and two peryleneimides **39** are incorporated into a polystyrene polymer matrix. Indeed, heating with a Nd:YAG laser (1064 nm) leads to the decomposition of **45** accompanied by the expected color change. Spot sizes within the polystyrene film down to a few micrometers are achieved which also suggests the possible use of a combination of functional rylene dyes for data storage purposes in such a configuration.

Perylene and Terrylene Dyes for SMS

So far all presented applications of ryleneteracarboxdiimides are related to a polymeric environment. Also for experiments where the emission behavior of single chromophores is investigated the dyes are usually embedded in a polymeric matrix but at very low concentrations.[44] Looking at single molecules, in contrast to ensemble measurements which yield information on average properties, provides information on individuals such as distributions and time trajectories of properties that would otherwise be hidden. In this way, static disorder or dynamic disorder of individual molecules can be detected, which is not possible by averaging the observable of a bulk system. A good fluorophore for such experiments exhibits a high extinction coefficient, a high fluorescence quantum yield and good chemical and photochemical stability. Photobleaching severely limits the observation time, and thus, the amount of collected information during the experiment. Since most PDI and TDI chromophores excellently fulfill these requirements they have been established as key chromophores for SMS. Investigating the amino-functionalized peryleneimide **18** in a polystyrene matrix revealed different conformations of the amine group relative to the chromophore. Even transitions between these spectrally defined conformers can be detected in real time.[45,46] For PDI with four phenoxy groups in the bay positions, similar to **4**, SMS shows conformational changes of the bay substituents which are related to twisting of the single molecule around the central PDI long axis.[47] Beside detecting intrinsic changes within the perylene chromophores these dyes can also be used to probe their polymeric environment, e.g. measuring the free volume of polymers.[48] In addition to single chromophores, also multichromophoric systems have been studied on the single molecule level.[49] In dendrimers with multiple identical chromophores, energy hopping and transfer to the chromophore with the energetically lowest singlet state is observed.[50,51] If more than one chromophore is in an excited state in one molecule either singlet–triplet-[51–53] or singlet–singlet annihilation,[54] can occur. These annihilation processes are also observed in peryleneimide dimers and are not restricted to dendritic systems.[55] The investigation of singlet–singlet and singlet–triplet annihilation is of great importance for constructing single photon sources from organic molecules since their performance strongly relies on these parameters.[56,57] In the future, single photon sources might be applied in quantum computing and quantum cryptography. In addition to study photophysical processes in multichromophoric systems with identical chromophores, energy transfer on the single molecule level in donor–acceptor systems constructed from rylene dyes similar to the chromophoric triade **44** has been investigated.[40,58,59] When the polyphenylene dendrimers at the periphery are functionalized with electron donors instead of energy-donating moieties, reversible electron transfer is observed in single dendritic molecules.[60]

Single molecule methods play a growing role in biophysical studies[61,62] and in "live cell imaging" experiments where single proteins, virions, drugs or other single bio-particles are labeled in order to follow the pathway and/or the interactions of these particles inside the living cell.[63] For such experiments, dyes are favorable which emit outside the region of autofluorescence of living cells (>600 nm). Up to now, the number of water-soluble fluorophores available in this spectral region with high photostability is rather limited.

To fill this gap, water-soluble TDI derivatives carrying sulfonated phenoxy groups have been synthesized. At the single molecule level a much higher photostability of these dyes in comparison with other well known water-soluble dyes is detected. Furthermore, labeling of single proteins has been achieved. The dye–protein conjugates have been characterized by FCS and photostability measurements. The uptake of the TDIs in liposomes and in living HeLa cells demonstrates the outstanding capability to label artificial and natural lipid membrane containing compartments. The most striking result in this context is that cellular trafficking of membrane containing compartments, e.g. endosomes in living cells can be observed over very long periods of time (more than 30 min). Control experiments with known dyes acting as fluid phase markers show complete photobleaching after almost 10 s underlining the outstanding properties and future potential of water-soluble TDIs for biological applications.

◆ Rylene Dyes in Devices

Due to their outstanding properties rylene dyes are not only suited for SMS but are also applied in the field of organic semiconductors in electronic devices such as field-effect transistors,[64] photovoltaic cells[65] or LEDs. The electron-withdrawing imide structures are responsible for their n-type character[66] so that in liquid-crystalline phase forming *N*,*N*′-alkyl-PDI the majority of charge carriers are electrons reaching mobilities of up to $0.6\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in thin-film transistors.[67] A significant step towards organic thin film photovoltaic devices has been made with a combination of the liquid-crystalline hexa-*peri*-hexabenzocoronene (HBC) and a PDI with branched alkyl chains.[68] Using a blending technique, these materials have been allowed to self-assemble into a two-phase photovoltaic material which shows an extraordinary performance. For such photovoltaic cells, a quantum efficiency (the ratio of light absorbed to electrical energy produced) of 34% using 490 nm light has been achieved. In order to increase the efficiency of organic solar cells and to cover light also in the NIR region, perylene-, terrylene-, and quaterrylenetetracarboxdiimide derivatives with branched alkyl chains have been synthesized. They exhibit a high degree of order in the bulk since they form discotic columnar phases with large and highly ordered domains which ensure an undisturbed percolation pathway for charge carriers between electrodes in photovoltaic devices. A high degree of order is also found in blends of these materials with HBC.[69] Besides using HBC as p-type semiconductor, efficient photovoltaic cells have been obtained using perylenediimide blended with a polycarbazole.[70] A promising approach to obtain organic photovoltaic materials consists of covalent coupling of peryleneimide with oligothiophenes.[71]

The concept of covalent coupling of peryleneimide derivatives to polymers has also been successfully applied in the context of organic LEDs.[72] The emission color of fluorene-based polymers can be facilely tuned across the whole visible spectrum by copolymerization with perylene dyes. Incorporation of the dyes is realized in the polymer mainchain, at the chain termini, or as side chains. Energy transfer causes the emission to come solely from the dye units which results in efficient LEDs. These polymers are suitable to act as efficient red, green, or blue emitters for full color displays or might be blended to produce other emission colors including pure white light.

◆ Summary and Outlook

Perylene dyes can be functionalized by a large variety of organic reactions to control their solubility, absorption and emission behavior, whereby PDI, perylenedianhydride and tetrachloro PDI act as starting materials. Especially, metal-catalyzed cross-coupling reactions have proven as powerful synthetic tools in perylene chemistry. These types of reactions, beside functionalization, allow the build up of the homologous series of the rylenetetracarboxdiimides up to the hexarylene consisting of six naphthalene units connected via their *peri*-positions leading to strong absorption in the NIR region. For the construction of multichromophoric systems an approach relying on polyphenylene dendrimers leads to highly fluorescent and shape persistent nanoparticles. When a perylene dye is incorporated into the core of these dendrimers their aggregation is efficiently suppressed. Taking advantage of both synthetic strategies leads to artificial light-harvesting systems. By combining the novel ryleneimide chromophores with concepts applied in polymer chemistry or different polymeric matrices high tech applications can be realized. These range from nanocolorants, which combine the advantages of dyes and pigments, over laser marking of polymers to efficient photovoltaic and light-emitting devices. Due to their outstanding chemical and photochemical stabilities as well as their high fluorescent quantum yields, perylene and terrylene chromophores have been established as key chromophores for SMS. Photophysical processes like energy and electron transfer can now be investigated on the single molecule level over long observation times. Beside labelling and visualization of single proteins, terrylene dyes have been applied to study events taking place in living cells.

In the future, the rylene dyes will be further investigated in the context of biological systems including the visualization of protein–protein interactions or enzyme catalysis. A great challenge for the future also lies in improving photovoltaic devices and field-effect transistors applying rylene dyes now that both the synthetic tools and the methods of processing have been improved. Problems still to be solved in this regard are the interfacing with electrode materials and achieving even larger control over macroscopic order without defects. A solution to the latter issue might be self-healing self-assembled rylene derivatives.

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