



Overview of Perylene Bisimide Dyestuff: Synthesis and Properties

Tawfik A. Khattab* and Meram S. Abdelrahman

Dyeing, Printing and Auxiliaries Department, National Research Centre, Cairo 12622, Egypt.



CrossMark

Abstract

Perylene-3,4,9,10-tetracarboxylic acid diimides (PDI) have been widely considered as efficient industrial colorants. Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) has been used as starting material for the synthesis of PDI colorants. PDI dyes have been distinguished with various colorimetric shades, photostability, and good physical and chemical properties. A variety of perylene bisimide derivatives with different characteristics have been developed by tuning the functional groups at the four bay and two imide positions in the PDI structure.

Keywords: Perylene dianhydride; Perylene diimid; Luminescence properties.

1. Introduction

Dyes are compounds that have been employed to impart color to various materials, such as paper, textile and leather [1-8]. Functional dyes can be defined as colorants that provide a new function upon exposure to external stimuli, such as light and heat [9-17]. Functional dyes have been used in various fields, such as sensors and biosensors, bioimaging, UV protection, and antimicrobial agents [18-33]. Rylene dyes exhibit rylene molecular skeleton of naphthalene units connected in peri-positions. The addition of extra naphthalene moieties forms poly(peri-naphthalene)s, such as perylene dyes [34-41]. Perylene dyes have been useful for a variety of applications due to their intense absorption in the visible light spectrum, excellent quantum yield and high stability [42-50]. The four bay positions in perylene bisimide derivatives are displayed in **Figure 1**, Perylene bisimide colorants are distinguished by their high performance as pigments.

They are available in various colorimetric shades ranging between red and violet, in addition to their shades of black [51, 52]. They exhibit very good physical and chemical properties such as their outstanding resettlement stability in plastic based products, simple over-painting, chemical stability, higher thermal stability, and admirable photostability [53]. Numerous perylene bisimide colorants (**Figure 2**) have accordingly found their way to industry. Economically, applying perylene bisimide pigments in disposable commercial items is relatively restricted because of their relatively high cost [51]. Nowadays,

peryene bisimides have been used mainly in fiber technologies and industrial coatings, especially in carpets and vehicles industries [53].

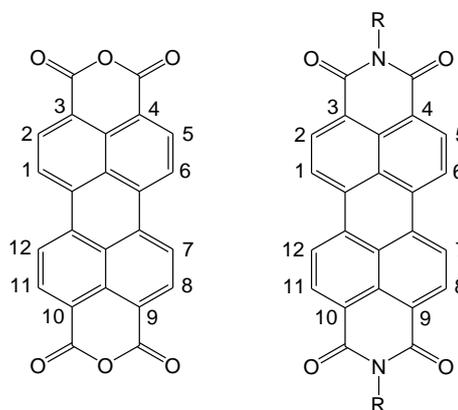


Figure 1. Molecular structures of PDA (*left*) and the corresponding perylene bisimide (*right*); the bay positions include the 1, 6, 7, and 12 positions.

In addition to their use as significant industrial colorants, PDI have combined a high absorbance coefficient in the visible light range with approximately unity emission quantum yield. PDI are also characterized by elevated photo-chemical stability, and numerous attractive physical and chemical characteristics [54, 55]. Perylene bisimides have a comparatively low reduction potential allowing their function as electronic acceptors for organic photoelectric applications [56]. Both perylene

*Corresponding author e-mail: ta.khattab@nrc.sci.eg; (Tawfik A. Khattab).

Receive Date: 12 July 2022, **Revise Date:** 24 July 2022, **Accept Date:** 01 August 2022, **First Publish Date:** 01 August 2022

DOI: 10.21608/EJCHEM.2022.150082.6501

©2022 National Information and Documentation Center (NIDOC)

mono-imide and bisimide have been used in a variety of optical purposes like dye synthesized solar cells, heterojunction solar cells, transistors, electro-photographic devices, laser dyes, light emitting diodes. This could be attributed to their attractive optical, photophysical, and photo-electric characteristics [57-61]. In addition to the research work of perylene mono-imide and perylene bisimide derivatives in photovoltaics, functionalized perylene bisimides have also been widely considered in essential investigation of photo-induced electron and energy transfer operations as a result of their simply recognizable excited state and anion absorption. This research work affords facts to understand the electron and energy transfer interactions. It also profits numerous connected research fields especially in the area of organic photovoltaics that have benefited from investigating the light-induced charge transfer. The research considerations have recently paying attention on utilizing perylene bisimide derivatives as energetically interactive semiconductors for organic photoelectric applications [62, 63]. Perylene bisimide pigments are still considered as one of the high potentially active electron transport compounds with a low electron affinity (-3.9 eV) for unmodified perylene bisimides, which is comparable to that of Carbon-60 (C₆₀) and its different derivatives, the possibility for high quality packing of molecules, and simple chemical functioning in comparison to fullerenes-based acceptors [64].

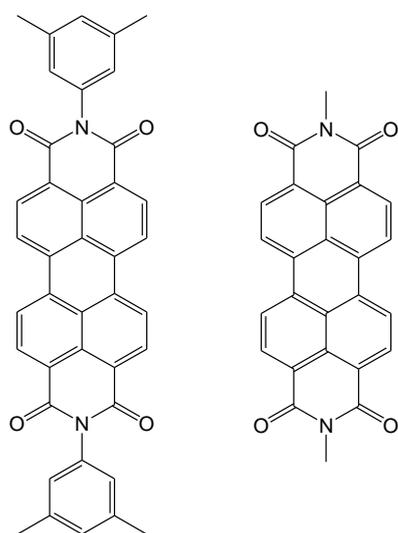


Figure 2. Molecular structures of industrially used perylene bisimides; Pigment Red 149 (left), and Pigment Red 179 (right).

2. Synthesis of perylene bisimides

2.1. Imide-positions substitution

The key start material for the preparation of PDI materials is PDA, which undergoes a condensation reaction with alkyl amine or aromatic amine to afford

the corresponding perylene bisimide derivatives in high yield. PDA was synthesized on industrial scale by oxidizing acenaphthene using air to provide naphthalic anhydride. The provided product is consequently subjected to NH₃ to afford the imide form of 1, 8-naphthalene dicarboxylic acid, which has been fused with a strong base at 190-200 °C, and then air-oxidized to obtain the corresponding perylene bisimide derivatives as shown in **Figure 3**. PDA can be obtained by acid hydrolyses of the prepared perylene bisimide using concentrated sulfuric acid at 220 °C [51-53].

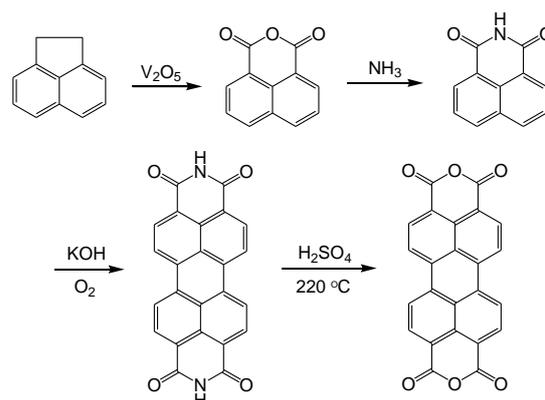


Figure 3. Synthesis of perylene bisimide with different imide substituents.

In addition to the preparation of insoluble and high melting point perylene bisimide pigments for coating and other related applications, the majority of the present research work on perylene bisimides is correlated to organic photo-electric applications, photo-induced operations, and supramolecular chemistry, which necessitate the preparation of perylene bisimide materials with rational solubility in regular known solvents. Accordingly, different synthetic techniques to prepare high solubility perylene bisimide derivatives were reported. In the 1990s, Langhals and coworkers reported an approach that is successful in the preparation of soluble symmetrical PDI by the use of solubilizing alkyl imide substituents. Another successful approach has been reported by means of using aromatic substitution at the bay sites of the PDI core, leading to twisting and consequently the rupture of the strong π - π interaction toward improved solubility. Additionally, water-soluble perylene bisimides were synthesized by means of water soluble substituents, such as carboxylates, phosphates, polyglycerols and cyclodextrins, at the imide positions via strategy equal to that explained by Langhals [65, 66].

As shown in **Figure 4**, a number of methods have been reported to produce soluble perylene bisimide pigments by adding functional groups at the imide sites. The most familiar process for the preparation of symmetrical PDI is the condensation of PDA with

aromatic amine derivatives and alkyl primary amines in high boiling point solvents such as quinoline or imidazole, and using anhydrous zinc acetate (~10-30%) as a catalytic agent. The produced yield of this reaction reaches 95%, with comparatively straightforward purification process [64]. Another significant technique for symmetrical perylene bisimide derivatives is by reacting PDA with active amines in a refluxed mixture of butanol, propionic acid and acetic acid, or in a mixture of butanol and distilled water to afford high yields higher than 90%. In contrast to the first synthetic approach, the second is further appropriate for the preparation of dibromo or tetrachloro substituted perylene bisimides, as less side reactions were detected, including nucleophilic substitutions at the halogenated sites of PDA. Moreover, it was established that perylene benzoimidazole materials could be gained by the analogous condensation of PDA with the corresponding *o*-phenylenediamine derivatives. Commonly, a combination of two isomers could be afforded in the preparation of perylene benzoimidazoles. The separation of the produced isomeric forms is difficult with ordinary purification techniques like recrystallization and column chromatography [65].

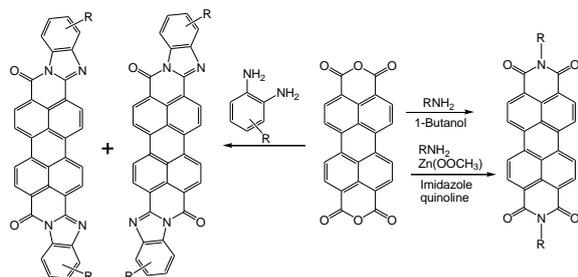


Figure 4. Synthesis of perylene bisimides with a variety of substituents at imide areas.

Asymmetrical perylene bisimides with diverse substituents at the two imide sites have been investigated. Efforts to *one-pot* synthesis of asymmetrical perylene bisimide derivatives by running the reaction process with either concurrent or sequential addition of two different organic amines are frequently ineffective due to the small distinctions in reactivity of the employed amines with PDA. Generally, traces of the targeted product are obtained, with the main product being the corresponding symmetrical perylene bisimide derivatives. There are presently two common synthetic techniques to afford perylene bisimide materials with different functional groups at the imide sites [65]. As shown in **Figure 5**, the first approach for asymmetrical perylene bisimides essentially begins from the synthesis of the corresponding symmetrical derivatives. Hydrolysis of symmetrical PDI affords the corresponding perylene mono-imide-mono-anhydride product in a yield of

~50%. Additional imidization of the produced perylene mono-imide-mono-anhydride derivative with another alkylamine or aromatic amine was utilized to establish the other substituent in producing the aimed asymmetrical PDI. It has been a challenge to prepare perylene mono-anhydride-mono-imide derivatives from PDA using the corresponding primary amine since it has been difficult to guarantee that the condensation reaction takes place at one of the two anhydride sides. Commonly, symmetrical PDI are usually the main product as soon as only one equivalent or less of the corresponding amine is used to the reaction system [67]. An additional convenient method to asymmetrical perylene bisimides was initially established by Tam-Chang et al., in which the target asymmetrical perylene bisimides were obtained through the perylene mono-anhydride salt from the hydrolysis of PDA, followed by additional imidization reactions as shown in **Figure 5** [68].

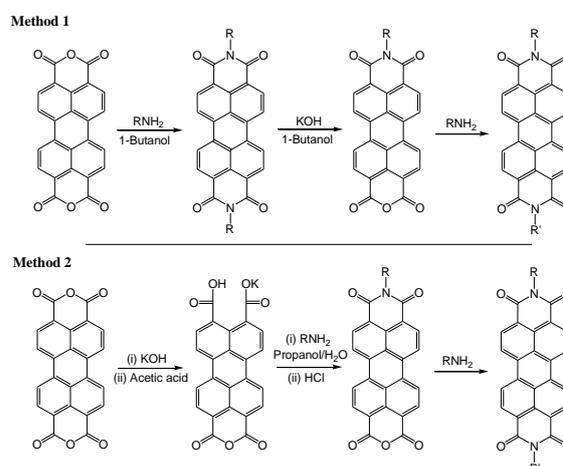


Figure 5. Two synthetic approaches for asymmetrical perylene bisimides.

The asymmetrical perylene bisimides synthesized using the synthetic methods (**Figure 5**) by the addition of different substituents at the imide positions typically display the same absorbance and emission characteristics from the corresponding symmetrical bisimides, especially in solutions at low contents when the molecular aggregates is restricted. This could be due to the nodes in the HOMO and LUMO energy levels at the imide sites of PDI decrease the electronic coupling of the imide groups with the perylene bisimide aromatic core to a least value [53]. The main electronic effect from the imide moiety is only inductive. Thus, there is a slight alteration in the electronic characteristics of PDI with a variety of imide functional groups. It has been valuable to manage the solubility and solid state molecular packing by including various side chains at the imide sites of perylene bisimides without considerably affecting on their electronic and optical characteristics [64]. Wurthner et al. reported recently

efficient, three-steps, multigram-scale synthetic methodology to perylene bisimides with sensitive substituents like aldehyde, which are not reachable by conventional imidization approaches. Two new functional dibromo-substituted perylene bisimides have been prepared employing Suzuki coupling, establishing non-aggregating, high solubility and highly luminescent (near unity quantum yield) bay unsubstituted perylene bisimide derivatives [69]. Centore et al. described the preparation of two thiadiazole-bearing perylene bisimide derivatives by the inclusion of 1, 3, 4-thiadiazole at the imide nitrogen of the perylene core (**Figure 6**). The produced perylene bisimides were employed to develop *n*-type organic thin-film transistors [70].

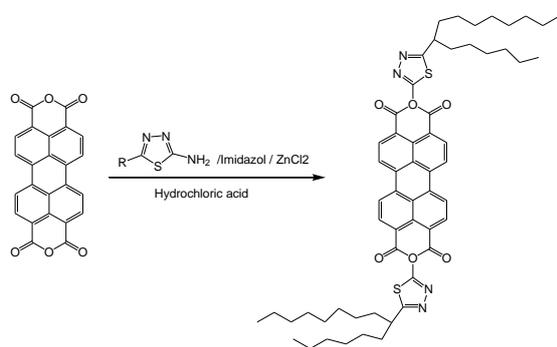


Figure 6. Synthesis perylene bisimides functionalized with *N*-thiadiazole substituents.

Recently, Gao et al. described the design, preparation and properties of fluorescent and water soluble perylene bisimide probes with a dendritic polyethylene glycol substituents. The produced dyes were divided into two categories, namely, head–tail and core–shell PDI dyes. Both categories are water soluble with similar aggregation, optical, and cyto-compatibility characteristics. Increasing the dendron generation was observed to suppress the aggregation of PDI in aqueous solution due to the hydrophilic effect of the bulky dendritic polyethylene glycol moieties. Higher dendron generation also increased the fluorescence quantum yield from 4% to 93%. The improved fluorescence quantum yield, water solubility, photostability and low cytotoxicity make these dyes excellent probes for live cell imaging [71]. Raj et al. reported the design and synthesis of conjugated *n*-type PDI-based copolymer comprising 5,5'-bis(4-aminophenyl)-2,2'-bifuryl fragment as an active agent for heterojunction photovoltaic devices. The produced acceptor low molecular weight copolymer displays extended UV-Vis absorption from the near-infrared region with relatively high extinction coefficient. The experimental findings and theoretical calculation for the produced copolymer indicates low-lying LUMO and high-lying HOMO energy levels leading to lowered HOMO and LUMO energy gap able to deliver high open circuit voltage

(0.92 V) for the fabricated bulk-heterojunction photovoltaics with a power conversion efficiency (PCE) of 0.34% [72]. Wang et al. reported *one-pot* synthesis of asymmetric tetrachlorinated PDI by reacting tetrachlorinated PDA with admixture of 2-amino-ethanol and dodecanamine or 2-decyl-1-tetradecanamine. Then, the hydroxyl group of the produced perylene bisimide was reacted with methacryloyl chloride to afford the corresponding methacrylate derivatives bearing long alkyl tails (**Figure 7**). A series of functionalized homopolymers were prepared via radical polymerization [73].

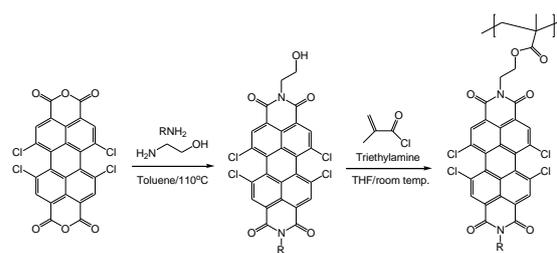


Figure 7. Structures of perylene bisimide based polymers from tetrachloro perylene bisimide; R is an alkyl group.

2.2. Bay-positions substitution

An additional approach for the preparation of soluble PDI is to set up substituents at the bay sites. The chemistry of establishing functional groups at the bay region of perylene bisimides was originally reported by Seybold and coworkers. [74] According to the work reported by Seybold et al., four phenoxy groups were built-in onto the tetrachlorinated perylene bisimide through nucleophilic substitution. Recently, Wurthner and coworkers have recently reported the preparation of the tetrafluoro-substituted perylene bisimide in practical yields from the corresponding tetrachlorinated start material [53, 75]. However, introducing numerous other nucleophilic substituents on the perylene bisimide aromatic core were verified to be difficult. Despite the process toward four folds of chlorination of PDA had previously been identified since 1985, only recently it was revealed that the bromination process of PDA could introduce dibromo-substituted PDA, which can be transformed into dibrominated perylene bisimides [76]. Nonetheless, the extracted material from the bromination process is highly complicated compared to that of the chlorination process of PDA, because of one- and three-fold bromination products, in addition to formation of considerable amounts (10-20 %) of another dibrominated perylene bisimide regio-isomer (1,6-dibromo-perylene bisimide). Moreover, each of these dibromo-substituted perylene bisimide regio-isomers from the latter dibromo-substituted PDA cannot be easily isolated from the crude mixture [77]. Yu et al. described the preparation of novel furan functionalized PDI as efficient building blocks for

supramolecular structures to build one dimensional micro- and nano-structures via controlling employed solvents. Different structural aggregates were produced including nanospheres, nanorods, and nanovesicles supramolecular architectures displaying attractive optical properties for potential micro-scale photonic applications [78]. Weissman et al. reported the synthesis of an oligoarylacetylene bearing amphiphilic perylene bisimide as shown in **Figure 8**. This oligomer is able to self-assemble into 2D porous networks in both of aqueous solution and casted films with 4 nm thickness. They were able to cast the 2D porous networks on a variety of solid surfaces, while maintaining its solution phase structure [79].

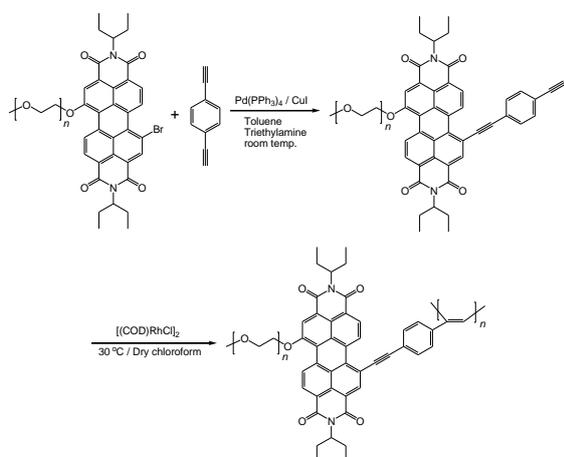


Figure 8. Synthesis of perylene bisimide phenylacetylene oligomer.

2.3. Other-positions substitution

A simple bromination reaction of perylene bisimides under controlled conditions has been reported as a promising reaction method, despite mono-, di- and tri-brominated products were also afforded together with two isomeric products of the dibrominated bisimide. Harsh reaction conditions permit the bromination to introduce the bay-dibrominated derivatives as the main product with high yield and lower reaction time. Wurthner and coworkers have recently reported that a number of isomerically pure 1, 7-dibrominated perylene bisimides can be produced in low yields after multiple crystallizations [80]. Substitution of the halogen atoms at the aromatic cores by means of nucleophilic substitution on those dibrominated or tetrachlorinated perylene bisimides is comparatively simple, and usually products can be isolated in comparatively high yields. Fluorides, cyanides, thiophenols, alcohols, phenols, and amines have been incorporated at the perylene bisimide bay regions to afford a variety of perylene bisimides dyes with attractive optical and photoelectric properties [53, 55, 57, 65, 75]. Furthermore, metal-catalyzed C-C coupling reactions have been reported in the synthesis of functionalized

perylene bisimides from the dibromo-substituted perylene bisimides [81, 82]. Moreover, Mullen and coworkers have also described that from the perylene bisimide ethynyl derivatives obtained by Sonogashira coupling reaction, corene bisimide derivatives, with extended conjugated scaffolds, can be prepared by straightforward reactions [83].

Another synthetic method for the preparation of 2, 5, 8, 11-substituted perylene bisimides has been reported. Ruthenium-catalyzed C-H bond activation has been an efficient reaction for arylation or alkylation of perylene bisimides at the 2, 5, 8, 11-positions as shown in **Figure 9**. Introducing an alkyl group at the 2, 5, 8, 11-positions considerably improves the solid state fluorescence and solubility in different known organic solvents without causing any severe distortions in the produced perylene bisimide aromatic core. Both of electron donating and withdrawing aryl moieties can be included in PDI with reasonable yields. The electronic properties of the aryl moieties has an important effect on their electrochemical characteristics since both HOMO and LUMO energy levels are considerably affected by those aryl moieties at the 2,5,8,11-sites of PDI structure [84].

1, 2, 5, 6, 7, 8, 11, 12-Octachloroperylene-3, 4:9, 10-tetracarboxylic bisimide has been prepared in a good yield through chlorination process of PDI using chlorosulfonic acid as a solvent at 80 °C. However, because of the low solubility of the introduced product, multiple crystallizations in a mixture of acetic acid and *N*-methylpyrrolidone followed by sublimation are necessary to guarantee enough purity for different photoelectric purposes [53]. The solubility of perylene bisimides is affected mainly by both of imide and bay substituents. It was established that PDI with long tails or *o*-substituted phenyl moieties usually demonstrate high solubility. The common interpretation is that the bulk functional groups are pushed out of the perylene bisimide molecular plane; thus hampering the face-to-face π - π molecular stacks, leading to better solubility. In the same way, substituents at the bay position of the aromatic core could force the molecular structure to a propeller like twisting of both naphthalene half fragments. This has been also established to be an effective technique to avoid the face-to-face π - π molecular stacks, and enhancing solubility [85].

3. Physical characteristics of perylene bisimides

Perylene bisimides display a mixture of attractive absorbance, physical, emission and redox characteristics, resulting in important research work on this type of materials for a variety of photoelectric applications [57-62].

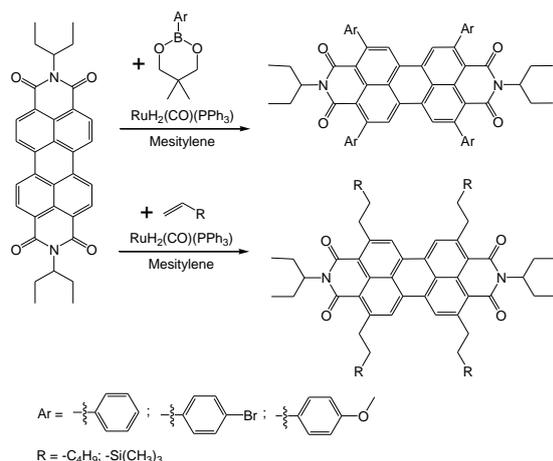


Figure 9. Synthesis of perylene bisimide with substitution at the 2,5,8,11-positions.

3.1. Optical characteristics

The majority of perylene bisimide pigments are red solid materials with high melting point, and high thermal and photostability. Nonetheless, other perylene bisimide derivatives with orange, maroon, blue-black, and black colors were recognized as a result of the aggregation effect, leading to differences in the absorbance spectra and their extinction coefficients. Perylene bisimides have been reported as a collection of superb organic colorants with high extinction coefficient in the visible spectrum ranging from 400 nm to 600 nm with approximately unity quantum yield, and longer excited state lifetime which reaches four nanoseconds in many ordinary organic solvents [64]. In general, perylene bisimides are distinguished by a vibronic structural band with high absorbance coefficient with a powerful yellow-green fluorescence. Moving the absorption and emission by about 5 nm can be experienced by varying the N-terminal substituent. On the other hand, groups at the bay regions demonstrate an apparent effect on the absorbance and emission spectra as a result of high electronic coupling of perylene bisimide π -orbitals and the bay-substituted groups. This property is obvious in many cases; for example, two phenoxy groups at the bay regions of perylene bisimide results in a 20–40 nm red shift in the absorbance and emission spectra producing a change in color of the orange emission [86]. More obvious spectral variations take place upon the addition of electron rich substituents to the bay positions to produce perylene bisimides with dark green colors as a result of the 150 nm bathochromic shift. As a result of a high spectral shift related to the amino to perylene bisimide internal charge transfer property, some solvatochromism characteristics are displayed with reduced fluorescence quantum yield. Restricted spectral variations and solvatochromism effects are indicated if electron deficient groups are added into perylene bisimides at the bay position due

to the inductive effect of these σ -acceptors reducing both LUMO and HOMO energy levels in the same style which also leads to stabilization of the LUMO to some extent higher than the HOMO, and therefore decreasing the energy gap [81–83].

The optical properties of perylene bisimides are extremely reliant on their concentration and the surrounding conditions like temperature and polarity of solvent. UV-Vis absorbance spectra depend on concentration of these dyes with less polar solvents showing major variations of the absorption spectra [53, 64]. Comparable remarks were established for perylene bisimide emission spectra as a function of growing concentration. The activity of PDI was studied in toluene to indicate that the aggregation-induced emission and reduced quantum yields were indicated with higher concentrations in toluene. Aggregation of PDI was extensively investigated and used for a variety of photoelectric applications [86]. As referred previously, functionalized perylene bisimides are frequently applied for essential photo-induced charge transfer applications due to the simply known perylene bisimide radical anion absorption spectra. The absorbance of PDI and its corresponding chemically produced anions were studied. Substituent groups at the imide regions demonstrate restricted affects on the anion absorbance spectra, whereas the bay-located substituent groups produce a significant change in the shape and position of the absorbance band. The distinct absorption properties simplify the establishment of the electron transfer reaction rate in functionalized perylene bisimides [87].

3.2. Redox characteristics

The electrochemical characteristics of perylene bisimides were extensively studied [88]. Perylene bisimides with no substituents at the bay sites are excellent electron acceptors with a simple reduction and hard oxidation in solution. In general, perylene bisimides display the first reduction potential similar to Carbon-60 and its analogues making them interesting acceptors in place of fullerenes in photoelectric applications with a comparatively lower cost and higher light harvesting [88]. Similar to the optical performance of perylene bisimide dyes, moderately little effects on redox characteristics of PDI in solutions are indicated from changing of the substituent groups at the imide regions. However, the substituent groups at the bay regions have marked effects on the redox potentials as a result of the induction effects from the electron-withdrawing substituents, which can stabilize these perylene bisimide derivatives by reducing the energy of HOMO and LUMO molecular orbitals to the same extent. In the case of electron-donating groups at the bay regions, a quasi reversible oxidation wave can be indicated [64]. Perylene bisimides with conjugated

substituent groups at the bay regions are usually easier to be subject for reduction in comparison to perylene bisimides with free bay region. This is most likely to be a result of the extended conjugation. Because substituent groups at the imide area demonstrate only little effect on both of the optical and redox characteristics, a variety of imide groups have been involved to adjust the solubility and solid state molecular packing. However, much more research work on introducing perylene bisimides with a variety of photoelectric properties have been reported using different substituents at the bay regions [89].

3.3. Molecular self-assembly

The molecular self-assembly performance of perylene bisimides in the solid state has been extensively studied to control colors for different industrial purposes. Perylene bisimide crystal configurations usually display flat parallel π -arrangements, similar to that in graphite [90]. The imide substituent groups can have an effect on the stacking distance, which affects on the intermolecular interactions of these π -arrangements in the crystal lattice, producing a variety of colors of perylene bisimide powders ranging from red to dark. However, the bay substitution can produce distortion of the flat π -arrangements as a result of steric strain. Materials with attractive photoelectric characteristics have been established by Mullen, Wurthner, and Meijer through controlling the spatial arrangements of perylene bisimides via molecular stacking methods such as metal coordination and H-bonding driven stacking to produce meso and nanoscopic supramolecular architectures. The ease of this approach to build a range of different size structures is attractive with lower needs for multistep organic synthesis [91].

3.4. Liquid crystals and photodynamic therapy

Lee and co-worker demonstrated the preparation of the first green and optically active lyotropic liquid crystal based on perylene bisimides. The color tuning of the produced perylene bisimides was accomplished by the bulk and electron-donor dipyrrolidine fragments at the bay position. The optical activity was achieved by introducing chiral amine periphery as proved by circular dichroism spectroscopy. The resulting materials display high thermal stability with reasonable solubility in water and different organic solvents. The aqueous solutions of the hydrochloride salts of the produced perylene bisimides display liquid crystal phases as proved by Polarizing Optical Microscopy at room temperature [92]. Gao et al. reported the synthesis of perylene bisimides as columnar liquid crystals via introducing dendritic peptide terminals at the two imide positions. The mesomorphic behavior displayed an ordered columnar mesophases at room temperature [93].

Highly luminescent core twisted perylene bisimides were reported by Wurthner et al. These dyes are distinguished by distortion of the perylene plane with dihedral angle ranging between 15° and 40° as indicated by crystallography. The aggregation of this PDI group is limited to π - π stacked dimers in apolar solvents as a result of the distorted aromatic core. Numerous perylene bisimide dyes have luminescence and mesogenic phase behavior. Thus, they display thermotropic columnar mesophases. The twisted aromatic core exhibits a considerable impact on the π - π stacking style in both of solution and columnar stacking of the liquid crystal phases. The highly twisted tetra-substituted perylene bisimides favor longitudinal slipped stacks, while for the less twisted di-substituted perylene bisimides, the property of rotational displacement accomplished among molecules in cofacial aggregations. The relation between the distortion level of the aromatic core and self-assembly feature that established for those perylene bisimides introduces helpful explanation for the supramolecular controlling of optical characteristics of their aggregations [94]. Akkaya et al. demonstrated the preparation of a series of water soluble green perylene bisimides as potential sensitizers in photodynamic therapy (**Figure 10**). When excited by red-light, PDI were able to efficiently generate singlet oxygen in cell culture medium, displaying photo-induced cytotoxic effect on the human cell line of erythroleukemia [95].

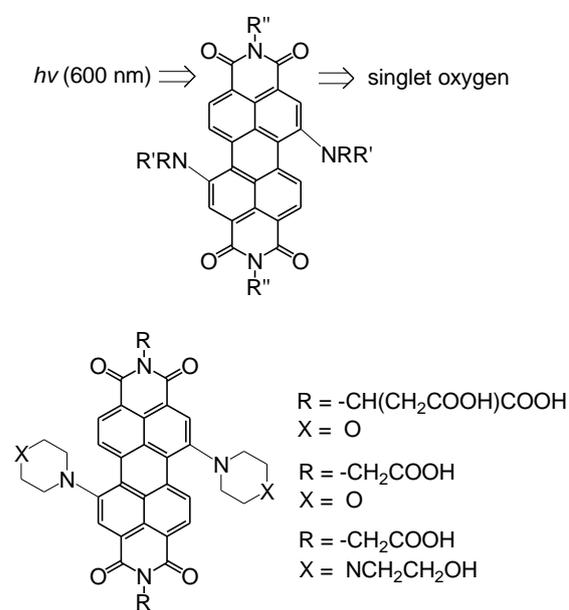


Figure 10. Water soluble perylene bisimide as potential sensitizers in photodynamic therapy.

4. Conclusion and future outlook

Perylene bisimide pigments have established significant consideration in both research and

industrial work. They were primarily used for industrial applications as red vat pigments. Numerous members of perylene bisimides have found high technology industrial applications particularly in automotive coatings as a result of their preferred combination of properties such as low solubility, chemical and weather stability, thermal and photostability and high extinction coefficient. Current applications of perylene bisimides are in the field of photoelectric purposes as they are considered as the best n-type semiconductor accessible. The precedent years have witnessed an increasing attention to this group of chromophores as a result of their favorable characteristics.

5. References

- [1] T. Khattab, H. Mashaly, H. Ahmed, M. Rehan, Multi-stimuli Responsive Natural Fibers Immobilized with Silver Nanoparticles via Plasma-activated Generation of Polyaniline, *Egyptian Journal of Chemistry* 65 (2022) 1-2.
- [2] D. Hamdy, A. G. Hassabo, H. Othman, Recent use of natural thickeners in the printing process, *Journal of Textiles, Coloration and Polymer Science* 18 (2021) 75-81.
- [3] T.A. Khattab, S. Kamel, Recent advances in sensitizer dyes for photodynamic therapy, *Egyptian Journal of Chemistry* 64 (2021) 4037-4052.
- [4] M. Diaa, H. Othman, A.G. Hassabo, Printing wool fabrics with natural dyes curcuma and alkanet (A Critique), *Journal of Textiles, Coloration and Polymer Science* 19 (2022) 11-16.
- [5] T.A. Khattab, S. Kamel, A Concise Review on Synthesis and Applications of Helicenes, *Egyptian Journal of Chemistry* 64 (2021) 593-604.
- [6] S. Abdelmoez, M. Abdelrahman, T. Khattab, Synthesis, solvatochromic properties and pH sensory of novel symmetrical bis (tricyanofuran) hydrazone chromophore, *Egyptian Journal of Chemistry* 62 (2019) 1197-1206.
- [7] T. Khattab, K.M. Haggag, Synthesis and spectral properties of symmetrical and asymmetrical 3-cyano-1, 5-diarylformazan dyestuffs for dyeing polyester fabrics, *Egyptian Journal of Chemistry* 60 (2017) 33-40.
- [8] M. Abdelrahman, H. Ali, Boron Difluoride Complex Dyes: Synthesis and Photophysical Properties, *Journal of Textiles, Coloration and Polymer Science* 17 (2020) 43-55.
- [9] T.A. Khattab, H.E. Gaffer, Sherif Abdelmoez Aly, Thomas M. Klapötke, Synthesis, solvatochromism, antibacterial activity and dyeing performance of tricyanofuran-hydrazone analogues, *ChemistrySelect* 1 (2016) 6805-6809.
- [10] T.A. Khattab, S.A. Aly, T.M. Klapötke, Naked-eye facile colorimetric detection of alkylphenols using Fe (III)-impregnated silica-based strips, *Chemical Papers* 72 (2018) 1553-1559.
- [11] T.A. Khattab, Novel solvatochromic and halochromic sulfahydrazone molecular switch, *Journal of Molecular structure* 1169 (2018) 96-102.
- [12] T.A. Khattab, K.M. Haggag, M.H. Elnagdi, A.A. Abdelrahman, S.A. Aly, Microwave-assisted synthesis of arylazoaminopyrazoles as disperse dyes for textile printing, *Zeitschrift für anorganische und allgemeine Chemie* 642 13 (2016) 766-772.
- [13] T.A. Khattab, M.H. Elnagdi, K.M. Haggaga, A.A. Abdelrahmana, S.A. Aly, Green synthesis, printing performance, and antibacterial activity of disperse dyes incorporating arylazopyrazolopyrimidines, *AATCC Journal of Research* 4 (2017) 1-8.
- [14] M.S. Abdelrahman, M.M.G. Fouda, J.S. Ajarem, S.N. Maodaa, A.A. Allam, T.A. Khattab, Development of colorimetric cotton swab using molecular switching hydrazone probe in calcium alginate, *Journal of Molecular Structure* 1216 (2020) 128301.
- [15] M.S. Abdelrahman, S.H. Nassar, H. Mashaly, S. Mahmoud, D. Maamoun, M. El-Sakhawy, T.A. Khattab, S. Kamel, Studies of polylactic acid and metal oxide nanoparticles-based composites for multifunctional textile prints, *Coatings* 10 (2020) 58.
- [16] T.A. Khattab, E. Tolba, H. Gaffer, S. Kamel, Development of electrospun nanofibrous-walled tubes for potential production of photoluminescent endoscopes, *Industrial & Engineering Chemistry Research* 60 (2021) 10044-10055.
- [17] T.A. Khattab, M.M.G. Fouda, A.A. Allam, S.I. Othman, M. Bin-Jumah, H.M. Al-Harbi, M. Rehan, Selective Colorimetric Detection of Fe (III) Using Metallochromic Tannin-Impregnated Silica Strips, *ChemistrySelect* 3 (2018) 12065-12071.
- [18] T.A. Khattab, Synthesis and Self-assembly of Novel s-Tetrazine-based Gelator, *Helvetica Chimica Acta* 101 (2018) e1800009.
- [19] O.M. Mokhtar, Y.A. Attia, A.R. Wassel, T.A. Khattab, Production of photochromic nanocomposite film via spray-coating of rare-earth strontium aluminate for anti-counterfeit applications, *Luminescence* 36 (2021) 1933-1944.
- [20] T.A. Khattab, A.A. Allam, S.I. Othman, M. Bin-Jumah, H.M. Al-Harbi, M.M.G. Fouda, Synthesis, solvatochromic performance, pH

- sensing, dyeing ability, and antimicrobial activity of novel hydrazone dyestuffs, *Journal of Chemistry* 2019 (2019).
- [21] M.S. Abdelrahman, S.H. Nassar, H. Mashaly, S. Mahmoud, D. Maamoun, T.A. Khattab, Polymerization products of lactic acid as synthetic thickening agents for textile printing, *Journal of Molecular structure* 1203 (2020) 127421.
- [22] M.S. Abdelrahman, T.A. Khattab, S. Kamel, Hydrazone-Based Supramolecular Organogel for Selective Chromogenic Detection of Organophosphorus Nerve Agent Mimic, *ChemistrySelect* 6 (2021) 2002-2009.
- [23] T.A. Khattab, M.S. Abdelrahman, From smart materials to chromic textiles, In *Advances in functional finishing of textiles*, pp. 257-274. Springer, Singapore, 2020.
- [24] T.A. Khattab, M.S. Abdelrahman, H.B. Ahmed, H.E. Emam, Molecularly imprinted cellulose sensor strips for selective determination of phenols in aqueous environment, *Fibers and Polymers* 21 (2020) 2195-2203.
- [25] M.S. Abdelrahman, T.A. Khattab, S. Kamel, Development of a novel colorimetric thermometer based on poly (N-vinylcaprolactam) with push- π -pull tricyanofuran hydrazone anion dye, *New Journal of Chemistry* 45 (2021) 5382-5390.
- [26] N.A. Alhakamy, A.O. Noor, K.M. Hosny, J.J. Nasr, M.M.G. Fouda, T.A. Khattab, H.E. Gaffer, Synthesis of new cyanopyridine scaffolds and their biological activities, *Current Organic Synthesis* 17 (2020) 567-575.
- [27] T.A. Khattab, M. Rehan, Synthesis and characterization of bis-azo 1, 2, 4, 5-tetrazine dyestuff, *Journal of Textiles, Coloration and Polymer Science* 15 (2018) 33-36.
- [28] A. Aldalbahi, M.E. El-Naggar, T.A. Khattab, M. Hossain, Preparation of flame-retardant, hydrophobic, ultraviolet protective, and luminescent transparent wood, *Luminescence* 36 (2021) 1922-1932.
- [29] T.A. Khattab, M.E. El-Naggar, A.G. Al-Sehemi, M. Pannipara, M.A. Abu-Saied, M.F. Abou Taleb, Facile preparation strategy of photochromic dual-mode authentication nanofibers by solution blowing spinning of cellulose nanowhiskers-supported polyacrylonitrile, *Cellulose* 29 (2022) 6181-6192.
- [30] H. Abou-Yousef, T.A. Khattab, Y.A. Youssef, N. Al-Balakocy, S. Kamel, Novel cellulose-based halochromic test strips for naked-eye detection of alkaline vapors and analytes, *Talanta* 170 (2017) 137-145.
- [31] T.A. Khattab, H.E. Gaffer, Synthesis and application of novel tricyanofuran hydrazone dyes as sensors for detection of microbes, *Coloration Technology* 132 (2016) 460-465.
- [32] A. Saini, C.W. Christenson, T.A. Khattab, R. Wang, R.J. Twieg, K.D. Singer, Threshold response using modulated continuous wave illumination for multilayer 3D optical data storage, *Journal of Applied Physics* 121 (2017) 043101.
- [33] M.H. El-Newehy, H.Y. Kim, T.A. Khattab, M.E. El-Naggar, Production of photoluminescent transparent poly (methyl methacrylate) for smart windows, *Luminescence* 37 (2022) 97-107.
- [34] M.A. Martínez, A. Doncel-Giménez, J. Cerdá, J. Calbo, R. Rodríguez, J. Aragón, J. Crassous, E. Ortí, L. Sánchez, Distance matters: biasing mechanism, transfer of asymmetry, and stereomutation in N-Annulated perylene bisimide supramolecular polymers, *Journal of the American Chemical Society* 143 (2021) 13281-13291.
- [35] R. Renner, M. Stolte, J. Heitmüller, T. Brixner, C. Lambert, F. Würthner, Substituent-dependent absorption and fluorescence properties of perylene bisimide radical anions and dianions, *Materials Horizons* 9 (2022) 350-359.
- [36] Q. Jiang, H. Sun, D. Zhao, F. Zhang, D. Hu, F. Jiao, L. Qin et al., High Thermoelectric Performance in n-Type Perylene Bisimide Induced by the Soret Effect, *Advanced Materials* 32 (2020) 2002752.
- [37] S. Hayakawa, K. Matsuo, H. Yamada, N. Fukui, H. Shinokubo, Dinaphthothiepine bisimide and its sulfoxide: soluble precursors for perylene bisimide, *Journal of the American Chemical Society* 142 (2020) 11663-11668.
- [38] Q. Liu, T. Liu, Y. Fang, Perylene Bisimide derivative-based fluorescent film sensors: from sensory materials to device fabrication, *Langmuir* 36 (2020) 2155-2169.
- [39] V. Grande, B. Soberats, S. Herbst, V. Stepanenko, F. Würthner, Hydrogen-bonded perylene bisimide J-aggregate aqua material, *Chemical science* 9 (2018) 6904-6911.
- [40] S. Abdelmoez, R.A. Abd El Azeem, A.A. Nada, T.A. Khattab, Electrospun PDA-CA nanofibers toward hydrophobic coatings, *Zeitschrift für anorganische und allgemeine Chemie* 642 (2016) 219-221.
- [41] D. McDowall, B.J. Greeves, R. Clowes, K. McAulay, A.M. Fuentes-Caparrós, L. Thomson, N. Khunti et al., Controlling Photocatalytic Activity by Self-Assembly-Tuning Perylene Bisimide Photocatalysts for the Hydrogen Evolution Reaction, *Advanced Energy Materials* 10 (2020) 2002469.
- [42] M. Hecht, F. Würthner, Supramolecularly engineered J-aggregates based on perylene

- bisimide dyes, *Accounts of Chemical Research* 54 (2020) 642-653.
- [43] S. Hayakawa, A. Kawasaki, Y. Hong, D. Uruguchi, T. Ooi, D. Kim, T. Akutagawa, N. Fukui, H. Shinokubo, Inserting nitrogen: An effective concept to create nonplanar and stimuli-responsive perylene bisimide analogues, *Journal of the American Chemical Society* 141 (2019) 19807-19816.
- [44] F. Segatta, M. Russo, D.R. Nascimento, D. Presti, F. Rigodanza, A. Nenov, A. Bonvicini et al., In Silico Ultrafast Nonlinear Spectroscopy Meets Experiments: The Case of Perylene Bisimide Dye, *Journal of chemical theory and computation* 17 (2021) 7134-7145.
- [45] M. Bonchio, Z. Syrgiannis, M. Burian, N. Marino, E. Pizzolato, K. Dirian, F. Rigodanza et al., Hierarchical organization of perylene bisimides and polyoxometalates for photo-assisted water oxidation, *Nature chemistry* 11 (2019) 146-153.
- [46] Y. Xu, J. Zheng, J. O. Lindner, X. Wen, N. Jiang, Z. Hu, L. Liu, F. Huang, F. Würthner, Z. Xie, Consecutive Charging of a Perylene Bisimide Dye by Multistep Low-Energy Solar-Light-Induced Electron Transfer Towards H₂ Evolution, *Angewandte Chemie International Edition* 59 (2020) 10363-10367.
- [47] J. Huang, H. Ren, R. Zhang, L. Wu, Y. Zhai, Q. Meng, J. Wang et al., Supramolecular self-assembly of perylene bisimide-based rigid giant tetrahedral, *ACS Nano* 14 (2020) 8266-8275.
- [48] K. Ma, R. Wang, Y. Rao, W. Zhao, S. Liu, T. Jiao, Langmuir-Blodgett films of two chiral perylene bisimide-based molecules: aggregation and supramolecular chirality, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 591 (2020) 124563.
- [49] A. Nowak-Król, F. Würthner, Progress in the synthesis of perylene bisimide dyes, *Organic Chemistry Frontiers* 6 (2019) 1272-1318.
- [50] A.G. Hassabo, A.L. Mohamed, T.A. Khattab, Preparation of cellulose-based electrospun fluorescent nanofibres doped with perylene encapsulated in silica nanoparticles for potential flexible electronics, *Luminescence* 37 (2022) 21-27.
- [51] W. Herbst, K. Hunger, Industrial Organic Pigments, 2nd completely revised ed., (1997).
- [52] P.M. Kazmaier, R. Hoffmann, A theoretical study of crystallochromy. Quantum interference effects in the spectra of perylene pigments, *Journal of the American Chemical Society* 116 (1994) 9684-9691.
- [53] F. Würthner, Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures, *Chemical communications* 14 (2004) 1564-1579.
- [54] B.A. Jones, A. Facchetti, M.R. Wasielewski, T.J. Marks, Tuning orbital energetics in arylene diimide semiconductors. Materials design for ambient stability of n-type charge transport, *Journal of the American chemical society* 129 (2007) 15259-15278.
- [55] M.J. Ahrens, M.J. Fuller, M.R. Wasielewski, Cyanated perylene-3, 4-dicarboximides and perylene-3, 4: 9, 10-bis (dicarboximide): Facile chromophoric oxidants for organic photonics and electronics, *Chemistry of materials* 15 (2003) 2684-2686.
- [56] B.A. Jones, M.J. Ahrens, M.-H. Yoon, A. Facchetti, T.J. Marks, M.R. Wasielewski, High-mobility air-stable n-type semiconductors with processing versatility: dicyanoperylene-3, 4: 9, 10-bis (dicarboximides), *Angewandte Chemie International Edition* 43 (2004) 6363-6366.
- [57] Á.J. Jiménez, F. Spänig, M. Salome Rodriguez-Morgade, K. Ohkubo, S. Fukuzumi, D.M. Guldi, T. Torres, A tightly coupled bis (zinc (II) phthalocyanine)- perylenediimide ensemble to yield long-lived radical ion pair states, *Organic letters* 9 (2007) 2481-2484.
- [58] H.Z. Chen, M.M. Ling, X. Mo, M.M. Shi, M. Wang, Z. Bao, Air stable n-channel organic semiconductors for thin film transistors based on fluorinated derivatives of perylene diimides, *Chemistry of Materials* 19 (2007) 816-824.
- [59] W. Hongyu, P. Bo, W. Wei, Solar cells based on perylene bisimide derivatives, *Huaxue Jinchuan/Progress in Chemistry* 20 (2008) 1751-1760.
- [60] Z. Tan, E. Zhou, X. Zhan, X. Wang, Y. Li, S. Barlow, S.R. Marder, Efficient all-polymer solar cells based on blend of tris (thienylenevinylene)-substituted polythiophene and poly [perylene diimide-alt-bis (dithienothiophene)], *Applied Physics Letters* 93 (2008) 307.
- [61] K.D. Belfield, M.V. Bondar, F.E. Hernandez, O.V. Przhonska, Photophysical characterization, two-photon absorption and optical power limiting of two fluorenylperylene diimides, *The Journal of Physical Chemistry C* 112 (2008) 5618-5622.
- [62] Z. An, S.A. Odom, R.F. Kelley, C. Huang, X. Zhang, S. Barlow, L.A. Padilha et al., Synthesis and Photophysical Properties of Donor-and Acceptor-Substituted 1, 7-Bis (arylalkynyl) perylene-3, 4: 9, 10-bis(dicarboximide)s, *The Journal of Physical Chemistry A* 113 (2009) 5585-5593.
- [63] B.C. Thompson, J.M.J. Fréchet, Polymer-fullerene composite solar cells, *Angewandte chemie international edition* 47 (2008) 58-77.

- [64] Y. Nagao, Synthesis and properties of perylene pigments, *Progress in organic coatings* 31 (1997) 43-49.
- [65] H. Langhals, Cyclic carboxylic imide structures as structure elements of high stability. Novel developments in perylene dye chemistry, *Heterocycles* 1 (1995) 477-500.
- [66] T. Heek, C. Fasting, C. Rest, X. Zhang, F. Würthner, R. Haag, Highly fluorescent water-soluble polyglycerol-dendronized perylene bisimide dyes, *Chemical communications* 46 (2010) 1884-1886.
- [67] A. Wicklein, P. Kohn, L. Ghazaryan, T. Thurn-Albrecht, M. Thelakkat, Synthesis and structure elucidation of discotic liquid crystalline perylene imide benzimidazole, *Chemical communications* 46 (2010) 2328-2330.
- [68] I.K. Iverson, Cascade of molecular order by sequential self-organization, induced orientation, and order transfer processes, *J. Am. Chem. Soc.* 121 (1999) 5801-5802.
- [69] P.D. Frischmann, F. Würthner, Synthesis of a non-aggregating bay-unsubstituted perylene bisimide dye with latent bromo groups for C-C cross coupling, *Organic letters* 15 (2013) 4674-4677.
- [70] R. Centore, L. Ricciotti, A. Carella, A. Roviello, M. Causà, M. Barra, F. Ciccullo, A. Cassinese, Perylene diimides functionalized with N-thiadiazole substituents: Synthesis and electronic properties in OFET devices, *Organic Electronics* 13 (2012) 2083-2093.
- [71] H. Liu, Y. Wang, C. Liu, H. Li, B. Gao, L. Zhang, F. Bo, Q. Bai, X. Ba, Fluorescent water-soluble probes based on dendritic PEG substituted perylene bisimides: synthesis, photophysical properties, and live cell images, *Journal of Materials Chemistry* 22 (2012) 6176-6181.
- [72] M.R. Raj, S. Anandan, R.V. Solomon, P. Venuvanalingam, S.S.K. Iyer, M. Ashokkumar, Synthesis of conjugated perylene diimide-based copolymer with 5, 5'-bis (4-aminophenyl)-2-2'-bifuryl moiety as an active material for organic photovoltaics, *Journal of Photochemistry and Photobiology A: Chemistry* 247 (2012) 52-62.
- [73] Y. Cui, D. Yao, Y. Chen, Z. Wang, Synthesis and properties of novel functional polymers from tetrachlorinated perylene bisimide, *Journal of Polymer Science Part A: Polymer Chemistry* 50 (2012) 3485-3492.
- [74] G. Seybold, G. Wagenblast, New perylene and violanthrone dyestuffs for fluorescent collectors, *Dyes and Pigments* 11 (1989) 303-317.
- [75] F. Würthner, P. Osswald, R. Schmidt, T.E. Kaiser, H. Mansikkamäki, M. Könemann, Synthesis and optical and electrochemical properties of core-fluorinated perylene bisimides, *Organic letters* 8 (2006) 3765-3768.
- [76] A. Böhm, H. Arms, G. Henning, P. Blaschka, BASF AG, German Pat. DE 19547209 A1, 1997, In *Chem. Abstr.*, vol. 127, p. 96569g. 1997.
- [77] F. Würthner, V. Stepanenko, Z. Chen, C.R. Saha-Möller, N. Kocher, D. Stalke, Preparation and characterization of regioisomerically pure 1, 7-disubstituted perylene bisimide dyes, *The Journal of organic chemistry* 69 (2004) 7933-7939.
- [78] Y. Yu, Y. Li, Z. Qin, R. Jiang, H. Liu, Y. Li, Designed synthesis and supramolecular architectures of furan-substituted perylene diimide, *Journal of colloid and interface science* 399 (2013) 13-18.
- [79] H. Weissman, A. Ustinov, E. Shimoni, S.R. Cohen, B. Rybtchinski, Self-assembled two-dimensional porous network in aqueous solution based on perylene diimide phenylacetylene oligomer, *Polymers for Advanced Technologies* 22 (2011) 133-138.
- [80] P. Rajasingh, R. Cohen, E. Shirman, L.J.W. Shimon, B. Rybtchinski, Selective bromination of perylene diimides under mild conditions, *The Journal of organic chemistry* 72 (2007) 5973-5979.
- [81] M.J. Ahrens, M.J. Fuller, M.R. Wasielewski, Cyanated perylene-3, 4-dicarboximides and perylene-3, 4: 9, 10-bis (dicarboximide): Facile chromophoric oxidants for organic photonics and electronics, *Chemistry of materials* 15 (2003) 2684-2686.
- [82] A. de Craats, Liquid crystalline coronene derivatives, *Journal of Materials Chemistry* 11 (2001) 1789-1799.
- [83] U. Rohr, P. Schlichting, A. Böhm, M. Gross, K. Meerholz, C. Bräuchle, K. Müllen, Liquid crystalline coronene derivatives with extraordinary fluorescence properties, *Angewandte Chemie International Edition* 37 (1998) 1434-1437.
- [84] S. Nakazono, S. Easwaramoorthi, D. Kim, H. Shinokubo, A. Osuka, Synthesis of arylated perylene bisimides through C-H bond cleavage under ruthenium catalysis, *Organic letters* 11 (2009) 5426-5429.
- [85] M. Gsänger, J.H. Oh, M. Könemann, H.W. Höffken, A.-M. Krause, Z. Bao, F. Würthner, A crystal-engineered hydrogen-bonded octachloroperylene diimide with a twisted core: an n-channel organic semiconductor, *Angewandte Chemie International Edition* 49 (2010) 740-743.
- [86] F. Würthner, C. Thalacker, S. Diele, C. Tschierske, Fluorescent J-type aggregates and thermotropic columnar mesophases of perylene

- bisimide dyes, *Chemistry–A European Journal* 7 (2001) 2245-2253.
- [87] W.E. Ford, H. Hiratsuka, P.V. Kamat, Photochemistry of 3, 4, 9, 10-perylenetetracarboxylic dianhydride dyes. 4. Spectroscopic and redox properties of oxidized and reduced forms of the bis (2, 5-di-tert-butylphenyl) imide derivative, *The Journal of Physical Chemistry* 93 (1989) 6692-6696.
- [88] A.S. Lukas, Y. Zhao, S.E. Miller, M.R. Wasielewski, Biomimetic electron transfer using low energy excited states: A green perylene-based analogue of chlorophyll a, *The Journal of Physical Chemistry B* 106 (2002) 1299-1306.
- [89] S. Rajaram, P.B. Armstrong, B.J. Kim, J.M.J. Frechet, Effect of addition of a diblock copolymer on blend morphology and performance of poly (3-hexylthiophene): perylene diimide solar cells, *Chemistry of materials* 21 (2009) 1775-1777.
- [90] E. Hädicke, F. Graser, Structures of eleven perylene-3, 4: 9, 10-bis (dicarboximide) pigments, *Acta Crystallographica Section C: Crystal Structure Communications* 42 (1986) 189-195.
- [91] F. Würthner, R. Dobrawa, D.G. Kurth, Electrostatic self-assembly of fluorescent perylene bisimide coordination polymers, In *Abstracts of Papers of the American Chemical Society*, vol. 227, pp. U347-U347. 2004.
- [92] J.J. Naidu, S.-H. Shin, K.-U. Jeong, M.-H. Lee, Optically active lyotropic chromonic liquid crystal based on green perylene bisimide, *Bulletin of the Korean Chemical Society* 31 (2010) 2705-2708.
- [93] B. Gao, D. Xia, L. Zhang, Q. Bai, L. Bai, T. Yang, X. Ba, Helical columnar liquid crystals based on dendritic peptides substituted perylene bisimides, *Journal of Materials Chemistry* 21 (2011) 15975-15980.
- [94] Z. Chen, U. Baumeister, C. Tschierske, F. Würthner, Effect of core twisting on self-assembly and optical properties of perylene bisimide dyes in solution and columnar liquid crystalline phases, *Chemistry–A European Journal* 13 (2007) 450-465.
- [95] F. Yukruk, A.L. Dogan, H. Canpinar, D. Guc, E.U. Akkaya, Water-soluble green perylenediimide (PDI) dyes as potential sensitizers for photodynamic therapy, *Organic letters* 7 (2005) 2885-2887.