# Dibenzopentarylenebis(dicarboximide)s: Novel near-infrared absorbing dyes†

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**The facile synthesis of the new class of core-extended rylene chromophores, dibenzopentarylenebis(dicarboximide)s, having an intense absorption at 1020–1040 nm, is presented.**

Sunlight possesses around 50% of its intensity in the near-infrared (NIR) region that covers wavelengths from 700 to 2000 nm. Broad band infrared absorbers acting over this invisible spectral range are required for efficient heat-ray blocking.[1] Another field of interest is energy conversion:[2] NIR-absorbing dyes convert infrared radiation into heat to initiate thermally driven processes, such as laser welding of polymers, flash fusion of toners and optical data storage. These processes are initiated by low power semiconductor lasers (emission at 780 and 830 nm) and high-power Nd:YAG lasers (1064 nm).[2,3] Commercially available NIR dyes, such as polymethyne dyes, possess low thermal and photostabilities that restrict their application in this field. A significant bathochromic shift can be obtained using strong donor–acceptor interactions in the molecule,[4–6] or by the extending the π-system of the chromophores.[7]

Rylenebis(dicarboximide)s, **1** (Fig. 1), are photochemically and thermally stable dyes, which absorb in the visible ($n$ = 0, 1) and the NIR ranges ($n$ = 2–4). Whereas perylenebis(dicarboximide)s ($n$ = 0, $\lambda_{max}$ = 524 nm) with a variety of applications[8] are well described, the effective synthesis of terrylene- ($n$ = 1, $\lambda_{max}$ = 660 nm)[9] and quaterrylenebis(dicarboximide)s[10] ($n$ = 2, $\lambda_{max}$ = 760 nm) was described only in the last decade. Very recently our group reported the synthesis of even higher rylene homologues,[11] which have an intensive absorption in NIR region: pentarylene- ($n$ = 3, $\lambda_{max}$ = 877 nm) and hexarylenebis(dicarboximide)s ($n$ = 4, $\lambda_{max}$ = 950 nm). Alternatively, coupling and fusion of a perylenedicarboximide with a 1,5-diaminoanthraquinone afforded bis(perylenedicarboximide)-*a,d*-1,5-diaminoanthraquinone **2**, an NIR absorber with a remarkably strong absorption around 1100 nm and a strong thermal and photochemical inertness.[4] The introduction of amines into the bay-region of perylene dyes is also known to shift the absorption of peryleneimides to the NIR region.[6]

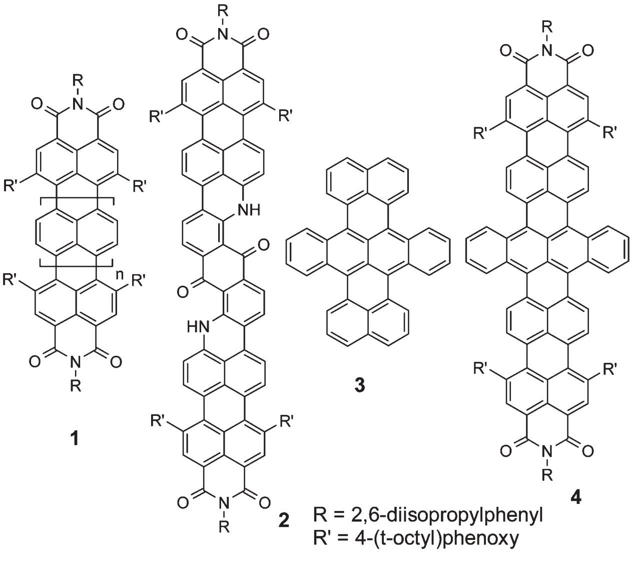

**Fig. 1** Rylene-based NIR dyes.

By extending the π-system of perylenebis(dicarboximide)s along the short molecular axis, two types of molecules can be obtained. Whereas coronene- and dibenzocoronenebis(dicarboximide)s were hypsochromically shifted,[12] the introduction of an acene structure into the rylene moiety caused a significant bathochromic shift.[13,14] Thus, an absorption of dibenzoterrylene **3** is shifted bathochromically by 180 nm,[14] in comparison to terrylene ($\lambda_{max}$ = 560 nm).

Herein, we report an efficient synthesis of a new class of core-extended rylene chromophores—9,10:21,22-dibenzopentarylene-3,4:15,16-bis(dicarboximide)s (DB5DI) **4**, which possess an intensive absorption at 1020–1040 nm.

The synthetic strategy towards dibenzopentarylenebis(dicarboximide)s utilised a 2 + 1 + 2 principle:[11] this includes the synthesis of a perylene–tetracene–perylene triad followed by either one-step, or two-step cyclodehydrogenation (Scheme 1). The active boronic esters of perylenedicarboximides (PMIs), **6** and **7**, were synthesised as described elsewere.[11,15] Although the synthesis of the other building block, 5,11-dibromotetracene **5**, is known,[16] we have elaborated an alternative efficient route to tetracene bromination. Thereby, the NBS bromination of tetracene in chloroform–DMF mixture afforded **5** in 92% yield.

The reaction of **5** with **6** or **7** under Suzuki conditions afforded bis-PMI-tetracene triads **8** and **9** only in low yields (~10%), when tetrakis(triphenylphosphino)palladium(0) was used as a catalyst. The combination of $Pd_2(dba)_3$ with DPEPhos (bis(2-(diphenylphosphino)phenyl)ether) as a ligand was reported to be an efficient catalyst for the Suzuki coupling of the sterically hindered, *ortho*-disubstituted benzenes.[17] Indeed, the application of this catalytic system to the Suzuki coupling of **5** with **6** or **7** significantly improved the yields of **8** and **9** (67 and 59%). Triads **8** and **9** exhibited absorption behaviour, similar to that of parent PMIs **6**[15] and **7**[11] (Fig. 2).

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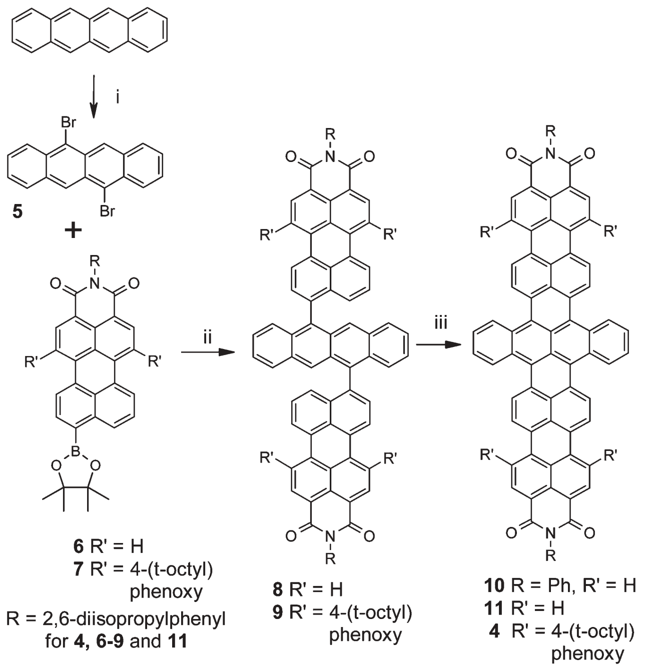

**Scheme 1** *Reagents, conditions and yields*: (i) NBS, DMF–chloroform, 60 °C, 3 h, 92%; (ii) $Pd_2(dba)_3$ , DPEPhos, toluene, $K_2CO_3$ (aq), 85 °C, 67% (for **8**), 59% (for **9**); (iii) $FeCl_3$, dichloromethane, nitromethane, 25 °C, 4 h, then $K_2CO_3$, ethanolamine, DMF, 130 °C, 2 h, 58% (for **11**), 53% (for **4**).

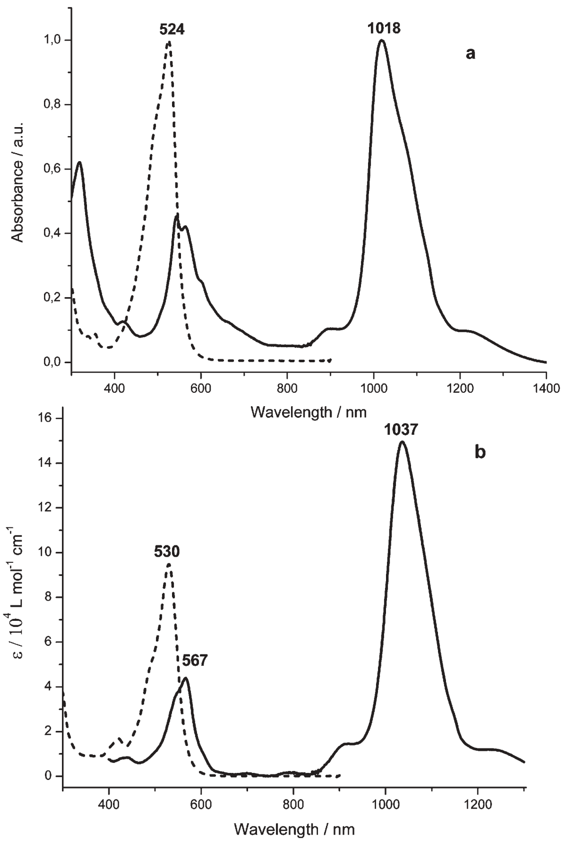

**Fig. 2** UV/vis/NIR spectra of: a) NIR dye **11** (solid line) and its precursor **8** (dashed line); b) NIR dye **4** (solid line) and its precursor **9** (dashed line).

One-step oxidative cyclodehydrogenation of **8** with $AlCl_3$ afforded a product that absorbs at $\lambda_{max}$ = 1010 nm. The MALDI-TOF mass-spectrum showed main peak at $M$ = 1015, that corresponded to completely dealkylated DB5DI **10**.[18] This compound is only slightly soluble in organic solvents (<0.1 mg $mL^{-1}$, PhCl) at room temperature and is better regarded as a pigment than a dye. To avoid dealkylation by strong Lewis acids, the cyclisation of **8** to the DB5DI derivative **11** was achieved under milder conditions in a two-step process. The first cyclisation was performed with $FeCl_3$–nitromethane in $CH_2Cl_2$ at room temperature; the second one was a base-promoted reaction with $K_2CO_3$–ethanolamine. This method provided **11** in an overall yield of 58%. The solubility of **11** was higher than that of **10**, since the two 2,6-diisopropylphenyl groups in imides prevent π–π stacking.[19] However, the solubility of **11** was not sufficient for purification and NMR characterisation. The same two-step approach was applied to triad **9** to obtain tetraphenoxyDB5DI **4** in 53% yield. Due to the high solubility, the dye **4** could be purified by column chromatography and characterised.

The optical spectrum of **11** (Fig. 2a) shows two absorption bands at 560 and 1018 nm. Only the band at 560 nm absorbs in the visible range that causes the violet color of the dye in solution. In the case of the tetraphenoxy dye **4**, the NIR absorption maximum is additionally influenced by the four phenoxy substituents in the bay region of the chromophore ($\lambda_{max}$ = 567 and 1037 nm, Fig. 2b, $\varepsilon_{1037}$ = 149500). These wavelengths are in the range of the emission spectrum of Nd-YAG laser (**4** possesses an 84% of the maximal absorbance at 1064 nm, **11** −75%). According to a thermogravimetric analysis, the NIR absorber **11** is thermally stable up to 441 °C, dye **4** −330 °C. This is important for its use as an energy converter for blending with thermoplastics during processing. Comparison of the NIR absorbance of dye **4** ($\lambda_{max}$ = 1037 nm) and pentarylenebis(dicarboximide) **1** ($n$ = 3, $\lambda_{max}$ = 877 nm)[11] reveals bathochromic shift of 160 nm. Therefore, benzannulation of rylenebis(dicarboximide)s with the introduction of tetracene structure orthogonal to the long axis appears to be an effective method for bathochromic shift of the absorbance.

Rylenebis(dicarboximide) NIR dyes **1** ($n$ = 2–4) are optically transparent in the visible range. The absorbance of DB5DI dyes **4** and **11** in the visible range (530–560 nm) can be caused by their non-planar structure. Quantum-chemical calculations predict the existence of three geometric isomers for parent DB5DI (Fig. 3). In all cases, the planar rylene structure is strongly twisted due to the steric repulsion of hydrogen atoms. This twisted structure increased the susceptibility of the non-degassed solution of **4** and **11** towards photooxidation: the extinction coefficient of their chlorobenzene solutions under UV-irradiation decreased to *ca.* 10% of initial values after 5 h.[20] Since the NIR light does not result in rapid photooxidation, the photostability of blends of **4** and **11** with thermoplastics should be higher under the working conditions.[21] The red-shifted residual absorbance of the PMI dye is maintained in the extended chromophore, since the PMI aromatic system is likely incompletely conjugated with the tetracene part of the molecule.

The facile synthesis of a new class of NIR dyes, 9,10:21,22-dibenzopentarylene-3,4:15,16-bis(dicarboximide)s, has been described. Their UV/vis/NIR spectra are characterised by an intense absorption in the NIR region (1000–1100 nm) together

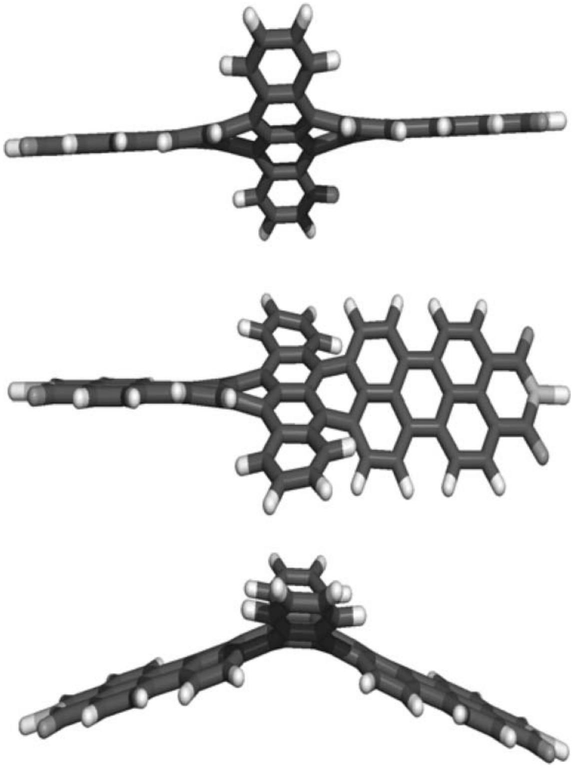

**Fig. 3** Optimised geometries of dibenzopentarylene-bis(dicarboximide) isomers (HyperChem 6, AM1).

with relatively low absorption in the visible range. These properties, as well as their high thermal stabilities, enable laser-induced applications, such as laser welding of polymers. Further, these dyes can be useful as heat-ray blockers[1] with applications in car windscreens, architectural glasses, and agricultural films.

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20 Quartz cuvettes, $\lambda_{max}$ = 254 nm, $c = 10^{-5}$ M.

21 The detailed study of this topic is in progress.