

# Bis(rylenedicarboximide)-*a,d*-1,5-diaminoanthraquinones as unique infrared absorbing dyes†

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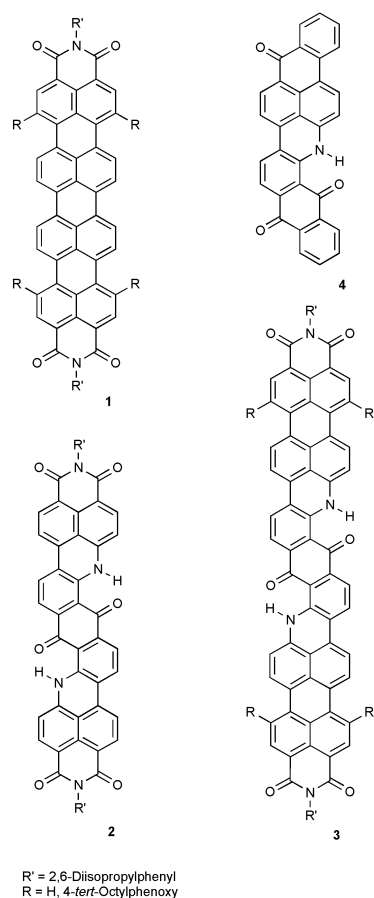
A hitherto unknown class of dyestuff compounds exhibiting three key characteristics, namely absorption in the near infrared (NIR) region, high photostability and good processability, is described.

Sunlight possesses about 50% of its radiation intensity in the near infrared region ranging from 700 nm to 2000 nm. NIR dyes are required for efficient heat-ray blocking and in energy conversion.<sup>1,2,3</sup> Many thermally driven processes such as optical data storage utilise low power semiconductor lasers (emission at 780 nm and 830 nm), high-power Nd-YAG lasers (1064 nm) or a xenon flash.<sup>2–5</sup> A serious drawback of commercially available NIR dyes such as cyanines, phthalocyanines or metal dithiolenes is their low photostability. We have recently synthesised the NIR dye quaterylenetetra-carboxy-dimide **1** with absorption maxima at 780 nm and a high photostability.<sup>6</sup> This was achieved by extending the  $\pi$ -system of perylene dyes, which are widely used as colorants.<sup>7,8</sup> Herein we introduce an alternative and surprisingly facile approach toward

NIR absorbers. The new bis(rylenedicarboximide)-*a,d*-1,5-diaminoanthraquinone **2** and **3** pick up the structural principle of the well known CI Vat Green 3 dye **4** which can be synthesised from benzanthrone and 1-aminoanthraquinone (Fig. 1).<sup>1,9</sup>

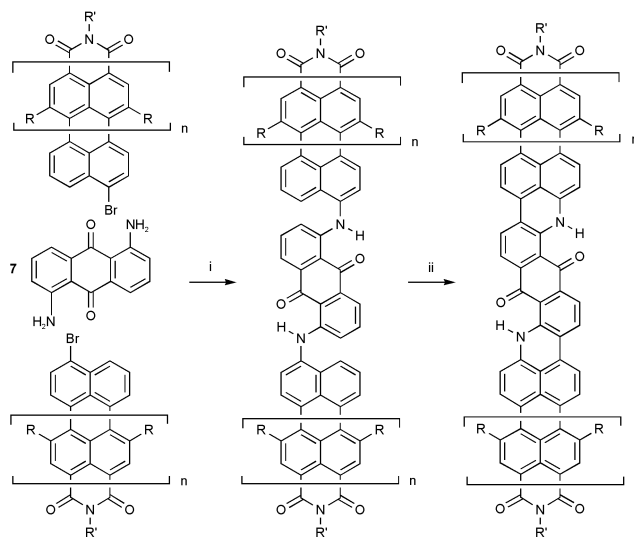
Toward more extended  $\pi$ -systems two equivalents of the rylenedicarboximide **5** and **6** (bromo-substituted in the peri-position), respectively, are treated with 1,5-diaminoanthraquinone under addition of a palladium catalyst (Scheme 1). The products **8** and **9** are obtained in yields >90% when using catalyst loadings of BINAP-ligated palladium of 0.5%.<sup>10–12</sup> They can be obtained pure upon crystallisation with dichloromethylene-methanol in yields >75%. In the second step of the synthesis, the title compounds are formed by mild base-promoted cyclization.<sup>13</sup> Whereas this type of reaction is traditionally performed in molten alkaline salts at very high temperatures (> 200 °C), we have chosen K<sub>2</sub>CO<sub>3</sub>-ethanolamine (for **2**) or sodium *tert*-butoxide-1,5-diazabicyclo[4.3.0]non-5-ene (for **3**) as base. This method provides the NIR absorbers **2** and **3** in high purities with yields >70%. Furthermore, the undesirable effects of the molten alkaline procedure such as extensive corrosion of reaction vessels and demanding work-up are avoided.

The dyes **2** and **3** are well soluble in common organic solvents and can be identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and FD mass spectrometry. The solubility of **2** is due to the introduction of two 2,6-diisopropylphenyl groups at the imide units of the chromophore which inhibit the formation of  $\pi$ -stacks.<sup>14</sup> In the case of **3** we used the 2,6-diisopropylphenyl substituted perylenedicarboximide **6** bearing two phenoxy groups in the bay region which enhance the solubility of perylenedicarboximide by a factor of ten. According to a thermogravimetric analysis, NIR absorbers **2** and **3** exhibit a high thermal stability



R' = 2,6-Diisopropylphenyl  
R = H, 4-*tert*-Octylphenoxy

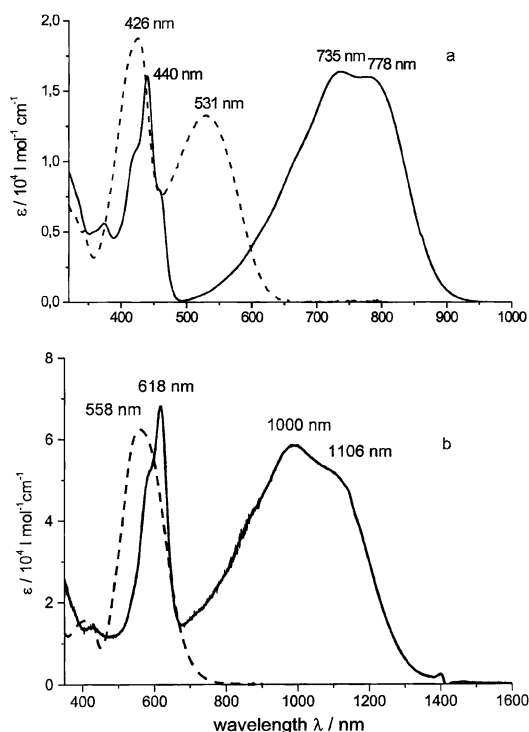
Fig. 1 Novel NIR absorbing dyes and their structural analogues.



**5:** n = 0  
**6:** n = 1, R = 4-*tert*-Octylphenoxy  
**8:** n = 0  
**9:** n = 1, R = 4-*tert*-Octylphenoxy  
**2:** n = 0  
**3:** n = 1, R = 4-*tert*-Octylphenoxy

**Scheme 1** Reagents, conditions and yields: (i) BINAP, Pd<sub>2</sub>(dba)<sub>3</sub>, NaOrBu, toluene, 80 °C, overnight; >90%. (ii) K<sub>2</sub>CO<sub>3</sub>, ethanolamine, 130 °C, 5 d; 72% (for **2**); NaOrBu, DBN, diglyme, 130 °C, 16 h; 74% (for **3**).

† Electronic supplementary information (ESI) available: experimental section. See <http://www.rsc.org/suppdata/cc/b2/b208855j/>



**Fig. 2** a: Absorption spectrum of NIR dye **2** (solid line) and its precursor **8** (dashed line) in  $\text{CHCl}_3$ . b: Absorption spectrum of NIR dye **3** (solid line) and its precursor **9** (dashed line) in  $\text{CHCl}_3$ .

> 400 °C. This is important for their use as energy converters along with their incorporation into various thermoplastics during processing.

The absorption spectrum of the deep green dye **2** (Fig. 2a) shows two absorption bands ( $\lambda_{\text{max}}$  ( $\epsilon$ ) = 440 nm ( $15800 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 778 nm ( $15900 \text{ M}^{-1} \text{ cm}^{-1}$ )) compound **3** (Fig. 2b) has a similar absorption profile ( $\lambda_{\text{max}}$  ( $\epsilon$ ) = 618 nm ( $49500 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 1106 nm ( $37500 \text{ M}^{-1} \text{ cm}^{-1}$ )) only the sharp band at  $\lambda_{\text{max}} = 618 \text{ nm}$  absorbs in the visible range of the spectrum and gives rise to the blue colour. The fact that it is clearly separated from the NIR bands contributes to the brilliance in colour of **3**. Further, the blue colour of the NIR dye allows ubiquitous applications under the overall aspect of customer compliance considering that blue is experienced as 'agreeable' for the perception of colour by the human eye. The absorptions of both dyes are well within the emission wavelength spectrum of the low-power semiconductor laser (dye **2**) and the high-power Nd-YAG laser (dye **3**).

The high wavelength bands of **2** and **3** are broad and almost structureless, as expected for a charge-transfer (CT) transition, whereas the low wavelength bands have the typical fine structure of rylene-dicarboximides. 1,5-Diaminoanthraquinones give rise to bands involving the electron lone pairs of the amino

groups. In addition they form intramolecular hydrogen bonds leading only to negligible solvatochromism. Compared to the absorption spectrum of the uncyclised precursor **8**, that of the product **2** reveals a very small bathochromic shift of the first absorption band due to the amino substituted naphthalene and a dramatic bathochromic shift of the second band due to the extended anthraquinone unit. The spectra of **3** and its precursor **9** show the same effect except that the bands of 1,5-diaminoanthraquinone and 9-aminoperylene-dicarboximide units overlap. In solutions of concentrated sulfuric acid of **3** the CT band disappears and the extinction of the band at 624 nm increases significantly due to the protonation of the amino function.

The photostability of **2** and **3** appears to be very high. Their solutions in 1,2,4-trichlorobenzene remain unchanged in sunlight after 4 weeks. Under the same conditions commercially available cyanine dye IR 140 ( $\lambda = 790 \text{ nm}$ ) has only one tenth of the initial absorption left after two days. Photostability testing (UV light,  $\lambda_{\text{max}} = 360 \text{ nm}$ ) using poly(methylmethacrylate) films (10  $\mu\text{m}$ , 0.5 wt % of **2** or **3**) is even more striking since the spectra remain unaffected after a week.

In summary we have described the synthesis of a new class of NIR dyes *via* a short and efficient route. Their UV/Vis/NIR-spectra are characterised by a remarkably high absorption at the laser outputs of low and high power lasers. This property together with the high photostability and thermal inertness enables laser induced processes like thermal imaging and optical data storage with high efficiencies. Further, one can envisage use as heat-ray blockers in car windscreens, architectural glasses and agricultural films.

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