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A bifunctional smart material: the synthesis of a metal-free black pigment for optoelectronic applications from an organic semiconducting molecular rod

Abstract

Purpose – To synthesise and evaluate the properties of a novel smart material consisting of a metal-free organic black pigment with a unique chromophore for bifunctional applications in optoelectronics.

Design/methodology/approach – A robust and highly efficient organic reaction, namely, a double [2 + 2] cycloaddition, was deployed to transform a rod-like structure for charge-transfer applications to a strongly-conjugated light-absorbing molecule for both optical and electronic applications.

Findings - The synthesis and characterisation of an air-stable metal-free black pigment is reported which contains an unconventional donor-acceptor panchromatic chromophore with an absorption window spanning 600 nm; the compound was synthetically converted from an organic semiconducting molecular rod and retains strong charge-transfer properties. The chromophore is comprised of tetracyanoquinodimethane (TCNQ) adduct either side of a dithienothiophenyl (DTT) core, capped with hexyl thiophenes that ensures solubility in common organic solvents. Its propensity to form excellent thin-films on different substrates such as glass and paper, with a total opacity in organic solvent, gives it the potential for wide-ranging applications in organic optoelectronics.

Research limitations/implications – The synthetic chemistry and fundamental properties are investigated in the present study, with more detailed treatments and analysis to be soon developed. One leading smart material is presented, with further derivatives under investigation.

Practical implications – The work presented shows the possibility of converting structures from one application to another with relative ease, but retain properties for both, using well-known and facile conditions.

Originality / value – The structures are novel, and an enhanced air-stable organic panchromatic chromophore is reported for processing in common organic solvents.

Keywords – Pigment, Black, Panchromatic chromophore, Optoelectronics, Smart material

Paper type – Research paper

Introduction

There is a growing interest in black dyes and pigments, due to their varied optoelectronic applications from colorants to dye-sensitised solar cells (Grätzel, 2003; Grätzel, 2004). There are few chromophores that give a truly black colour and these can be split into inorganic and organic structures. To date, the inorganic complexes are based either on chromium (Du *et al*., 2010; Chai and Leibman, 2004) or ruthenium (Grätzel, 2003; Nazeeruddin *et al*., 1999), as illustrated in Figure 1A. These consist of a metal center and various derivatised aromatic ligands. Due to toxicity concerns, there has been a shift towards metal-free or purely organic structures, which acquire their black colour from strong electron-donating or withdrawing groups.

There are two common types of organic chromophores, as shown in Figure 1B and include i) the azo species Acid Black 1 (Grzechulska and Morawski, 2002) and substituted amino-arylazothiazoles (Griffiths, 1998) and ii) the indoline-thiazole Indoline Dye 4 (Horiuchi *et al*., 2004) and phenoxazine-thiazole (Tian *et al*., 2009) TH304; these structures are strongly inter-related. The Acid Black-based dyes are widely used throughout industrial colouration and solar cell technology, while the least designed and worst performing are the amino-arylazothiazoles, in strong contrast to the rationally-designed Indoline Dye 4. Acid Black 1 has a typical diazo-based dye structure with electron donating NH_2/OH groups and SO_3Na/NO_2 withdrawing groups, while the substituted amino-arylazothiazoles mixes azo and thiazole units. The Indoline Dye 4 utilises electron-rich phenyl units for the donating group with the highly conjugated thiazoline units for the withdrawing group. The TH304 is only a slight variant of Indoline Dye 4, with a different electron-donating octyl-phenoxazine unit. These typical structures and their many derivatives are widely reported for the design of strongly-absorbing chromophores.

(Take in Figure 1)

Many derivatives of both the inorganic and organic structures in Figure 1A and 1B include sulphate or acidic groups that have a second role of binding to a given substrate. Their polar nature and acidity enables the colorants to be water soluble, and unfortunately, extremely hygroscopic once in the solid state or thin-film. While water solubility is desirable for eluent processing in dyeing textiles or thin-film formation on a substrate, it has significant disadvantages in organic electronic device applications. It is highly desirable for structures to operate on substrates or in devices such as dye-sensitised solar cells without them being sensitive to environment variables. The challenge is to synthesise a strongly-conjugated chromophore that absorbs light across hundreds of nanometers and be soluble in the solvent of choice. In stark contrast to the structures presented in Figure 1, the pigment synthesised in this work, hereby designated Leeds Black 154 or (LB154, Figure 1C), has a unique chromophore, comprised of dithienothiophenyl (DTT), tetracyanoquinodimethane (TCNQ), and two hexylthiophenes which facilitate excellent solubility in common organic solvents and optoelectronic properties. Herein, we report a bifunctional smart material consisting of a water-repellent organic black pigment with a novel and strongly-absorbing panchromatic chromophore.

Experimental

Materials

All chemicals were used as acquired from Sigma Aldrich without further purification.

General Procedures for Products 3 and 6

Under nitrogen a flame-dried flask was evacuated and backfilled three times, which was then charged with a solution of 2,2'-dibromodithieno[2,3-b:3′,2′-d]thiophene (0.732 g, 2.08 mmol), copper iodide (0.0093 g, 0.048 mmol) and tetrakistriphenylphosphine palladium (0) (0.120 g, 0.104 mmol) in tetrahydrofuran (20 mL) and diisopropylamine (2 mL). The solution was bubbled with nitrogen for 15 min. The selected alkyne (1.00 g, 5.21 mmol) was added dropwise and the mixture stirred for 17 hours at room temperature. The mixture was filtered and the solvent evaporated giving a crude residue which was purified with flash column chromatography (40 % dichloromethane in petroleum ether 40-60 °C) then recrystallised from hexane giving target compound.

Synthesis

Compounds 2-4 were synthesised according to reference (Shaik *et al.*, 2013).

2-bromo-5-hexylthiophene (2)

Pale yellow oil, 6.65 g, 26.9 mmol, 91.5 % yield; δ_H (500 MHz, $CDCl_3$): 6.82 (d, 1H, 3.6), 6.51 (d, 1H, 3.6), 2.73 (t, 2H, 7.6), 1.62 (h, 2H), 1.30 (m, 6H), 0.88 (t, 3H, 6.9); δ_C (500 MHz, $CDCl_3$): 147.7, 129.2, 124.3, 108.6, 31.5, 31.4, 30.3, 28.6, 22.6, 14.08, m/z (EI+): calc. 247.1951; found 246.0078 (M+H).

2-trimethylsilylethynyl-5-hexylthiophene (3)

Pale yellow oil (1.93 g, 7.30 mol, 90 %); ^{1}H-NMR (500 MHz, $CDCl_3$): 6.86 (d, *J* = 3.6, 1H), 6.42 (d, *J* = 3.6, 1H), 2.57 (t, *J* = 7.5, 2H), 1.45 (t, *J* = 7.3, 2H), 1.10 (m, 6H), 0.69 (t, *J* = 6.8, 3H), 0.04 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): 148.5, 132.8, 124.0, 120.5, 98.2, 97.8, 31.6, 31.6, 30.2, 28.7, 22.6, 14.1, 0.01.

2-ethynyl-5-hexylthiophene (4)

Pale orange oil (1.17 g, 6.08 mmol, 84.6 %); ^{1}H (500 MHz, $CDCl_3$): 6.86 (d, *J* = 3.6, 1H), 6.42 (d, *J* = 3.6, 1H), 3.03 (s, 1H), 2.57 (t, *J* = 7.5, 2H), 1.45 (p, *J* = 7.3, 2H), 1.10 (m, 6H), 0.69 (t, *J* = 6.8, 3H), 0.04 (s, 9H) ; ^{13}C-NMR (125 MHz, $CDCl_3$): 148.5, 132.8, 124.0, 120.5, 98.2, 97.8, 31.6, 31.6, 30.2, 28.7, 22.6, 14.1.

DTT-Br$_2$ (5)

Synthesis of 2,2'-dibromodithieno[2,3-b:3′,2′-d]thiophene (DTT-Br$_2$) (5) was carried out according to reference (Kwon *et al.*, 2011).

White powder (1.59 g, 80 %) ^{1}H-NMR (500 MHz, $CDCl_3$): 7.28 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): 123.2, 112.4; micro calc. (%) C 27.13, H 0.57, S 27.17, Br 45.13, found C 27.10, H 0.60, S 26.60, Br 45.45.

Bis-2-(2-ethynyl-5-hexylthiophenyl)-dithienothiophene (6)

Synthesis according to reference (Yanpeng *et al.*, 2016).

Orange fibrous powder (0.74 g, 62 %); ^{1}H-NMR (500 MHz, $CDCl_3$): 7.41 (s, 1H), 7.14 (d, *J*=3.6, 1H), 6.70 (d, *J*=3.6, 1H), 2.81 (t, *J*=7.5, 2H), 1.68 (p, *J*=7.3, 7.4, 2H), 1.34 (m, 6H), 0.89 (t, *J*=6.8, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): 149.5, 141.8, 132.7, 131.4, 125.0, 124.5, 124.2, 119.6, 88.84, 85.9, 31.5, 31.5, 30.3, 28.7, 22.6, 14.1; IR (CΞC, neat, cm^{-1}): 2136.9; HRMS (ES+, m/z): calc. 576.1108, found: 577.1102; micro calc.(%): C 66.62, H 5.59, S 27.79; found: C 66.40, H 5.50, S 27.60; m.p. 90 °C.

Leeds Black 154 (LB154)

A mixture of compound 6 (0.100 g, 0.173 mmol), 7,7,8,8-tetracyanoquinodimethane (TCNQ) (0.106 g, 0.52 mmol) and dimethylformamide (10 mL) was stirred at 70 °C for 17 hours in air. Once cool, the mixture was poured onto water (50 mL) and the aqueous phase extracted with ethyl acetate (150 mL × 3). The organic layers were collected together and washed with brine, dried and evaporated giving a dark crude residue. The crude was purified (silica, 1:1 dichloromethane: petroleum ether (40-60°C)) affording a black powder (0.074 g, 0.075 mmol, 43 %); ^{1}H (500 MHz, $CDCl_3$): 7.96 (d, *J* = 7.6, 1H), 7.79 (d, *J* = 3.9, 1H), 7.62 (s, 1H), 7.45 (d, *J* = 7.6, 1H), 7.28 (d, *J* = 9.6, 1H), 7.01 (d, *J* = 9.6, 1H), 6.98 (d, *J* = 3.9, 1H; HRMS: calculated 985.2954; found 924.2728 ($M-C_6H_{13}+Na$). Structure was assigned with COSY NMR (supporting information).

Quantum chemical calculations

Density functional theory (DFT) with the B3LYP (Becke, 1993) functional and 6-31G(d) basis set were used to calculate the optimised geometry, frontier molecular orbitals and energies of LB154, utilising the Gaussian 09 program (Frisch *et al.*, 2009). The results were visualised in Avogadro (Hanwell *et al.*, 2012).

Reflectance and CIELAB measurements

The sample was measured by an X-Rite 504 (interface 86) spectrophotometer with D65 illumination at 10° viewing angle. The colour of the sample is reported in the CIELAB colour space.

Results and discussion

Scheme 1 shows the high-yielding five-step synthetic route to the target product LB154. These steps include a thiophene derivatisation (Shaik *et al.*, 2013) which include a Sonogashira coupling with trimethylsilylacetylene (TMSA) under mild conditions and deprotection with tributylammonium fluoride (TBAF) (85-92 %), followed by a second Sonogashira to a dibromo (Kwon *et al.*, 2011) DTT giving the previously synthesised and characterised compound (Yanpeng *et al.*, 2016) 6 in 62 % yield. This compound was designed for organic transistor applications but its electron-rich nature is perfectly suited to electron-poor adducts such as nitriles and formed the basis for the work on the novel panchromatic chromophore investigated in this study. Following the extensive work by Diederich (Michinobu *et al.*, 2006) and Shoji (Shoji *et al.*, 2008; Shoji *et al.*, 2009; Shoji *et al.*, 2011) on single and double alkyne cycloadditions with nitrile adducts *via* a ring-opening of tetracyanocyclobutene intermediates, 7,7,8,8-tetracyanoquinodimethane (TCNQ) was added in a similar fashion to the electron-rich molecular rod and afford the target material in moderate yield (45 %). The synthetic route was designed to include hexyl chains to ensure solubility of all intermediates in common organic solvents and processability of the final target LB154.

(Take in Scheme 1)

The chromophore absorption is strong enough to absorb all incident light in solution, as illustrated in Figure 2A, which shows total opacity of the pigment in acetonitrile. Figure 2B and C) shows the excellent thin-film formation on both glass and paper substrates respectively.

(Take in Figure 2)

The unique chromophore of LB154 ensures a strong 600 nm absorption across the visible and ultraviolet regions between 200 and 800 nm (Figure 3). The broad lower intensity peak at longer wavelengths (650 nm) is considered to arise from a TCNQ excitation while the sharp intense peak at lower wavelengths (250 nm) and broad shoulder absorption up to 400 nm is due to the DTT absorption unit. This is confirmed with the comparison of the UV-Vis absorption spectrum of **6**, which shows the most intense peak centred at 400 nm and contains vibrational modes at 250 nm. Moreover, LB154 still retains absorption at its lowest intensity around 500 nm, ensuring the structure does not yield any colour in this region.

(Take in Figure 3)

Density functional theory (DFT) calculations were performed to probe the energy gap of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) and elucidate orbital contributions (Figure 4). LB154's strong optical HOMO energy level is localized to one of the TCNQ adducts. The LUMO energy level spreads across the breadth of the backbone of the structure. The overlap of the low energy HOMO/LUMO orbital densities may be a large contributing factor for the strong panchromatic absorption. Moreover, the HOMO-LUMO gap is 2.04 eV, which is greater than that of pentacene (Chang *et al.*, 2010), a well-known organic semiconductor, by 0.204 eV, proving LB154 has strong air stability for processing under ambient conditions.

(Take in Figure 4)

Figure 5 shows the reflectance spectra of dyed paper, and shows an inflection at 560 nm, correlating well with the UV-Vis absorption. It is important to note that the reflectance does not achieve higher than 14.1 % at 700 nm, clearly indicating the strength of the chromophore. The K/S strength value was found to be 4.283 and the colour of the sample was measured in the CIELAB colour space, giving 35.75, -0.22 and -1.56 for L*, a* and b* respectively, in agreement with the literature (Ryu *et al.*, 1992).

(Take in Figure 5)

Figure 6 (Top) illustrates the thermal gravimetric profile of LB154, and shows the initial weight loss most likely arising from the co-crystallised residual hexane at 68.2 °C, the first decomposition onset at 226.6 °C and a second at 370.5 °C; these have been identified as belonging to the hexyl and nitrile units and the core units respectively from the weight derivative profile in Figure 6 (Bottom). Even at 150 °C, the weight still remains at 96.7 %, showing good thermal stability.

(Take in Figure 6)

Conclusions

This work presents the synthesis of a novel air-stable black organic pigment, containing a unique donor-acceptor chromophore. The material is found to be panchromatic and absorbs over a 600 nm window between 200 and 800 nm. The thin-films form excellent adhesion to both glass and paper substrates and in acetonitrile the solution is rendered completely opaque. These results suggest the structure will have wide-ranging applications in organic optoelectronics. These applications are currently under investigation in our laboratories.

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Scheme 1 Synthesis of LB154; 6 was synthesised previously (Yanpeng *et al.* 2016) from compounds 4 and 5 according to references 10 and 11 respectively

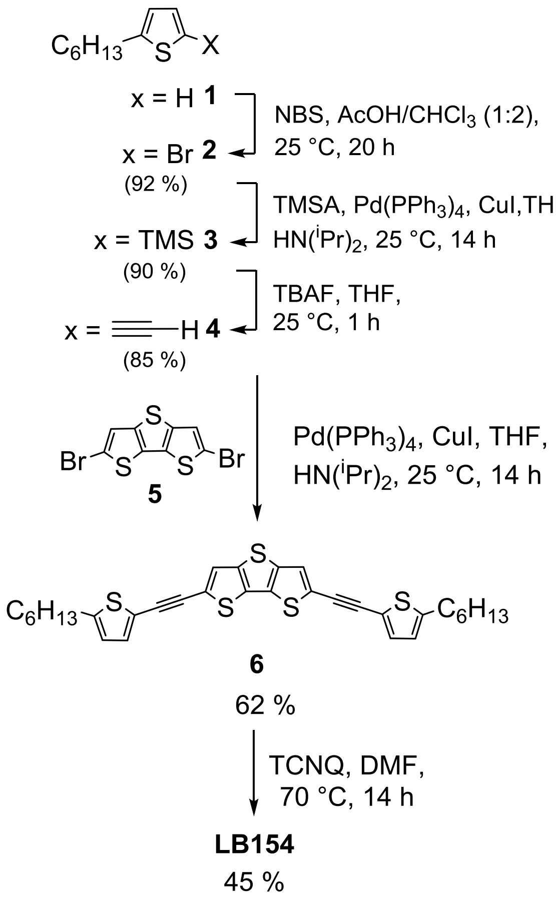

Figure 1 Selected black pigments and their structures, a) conventional inorganic, b) typical organic and c) this work, novel organic chromophore

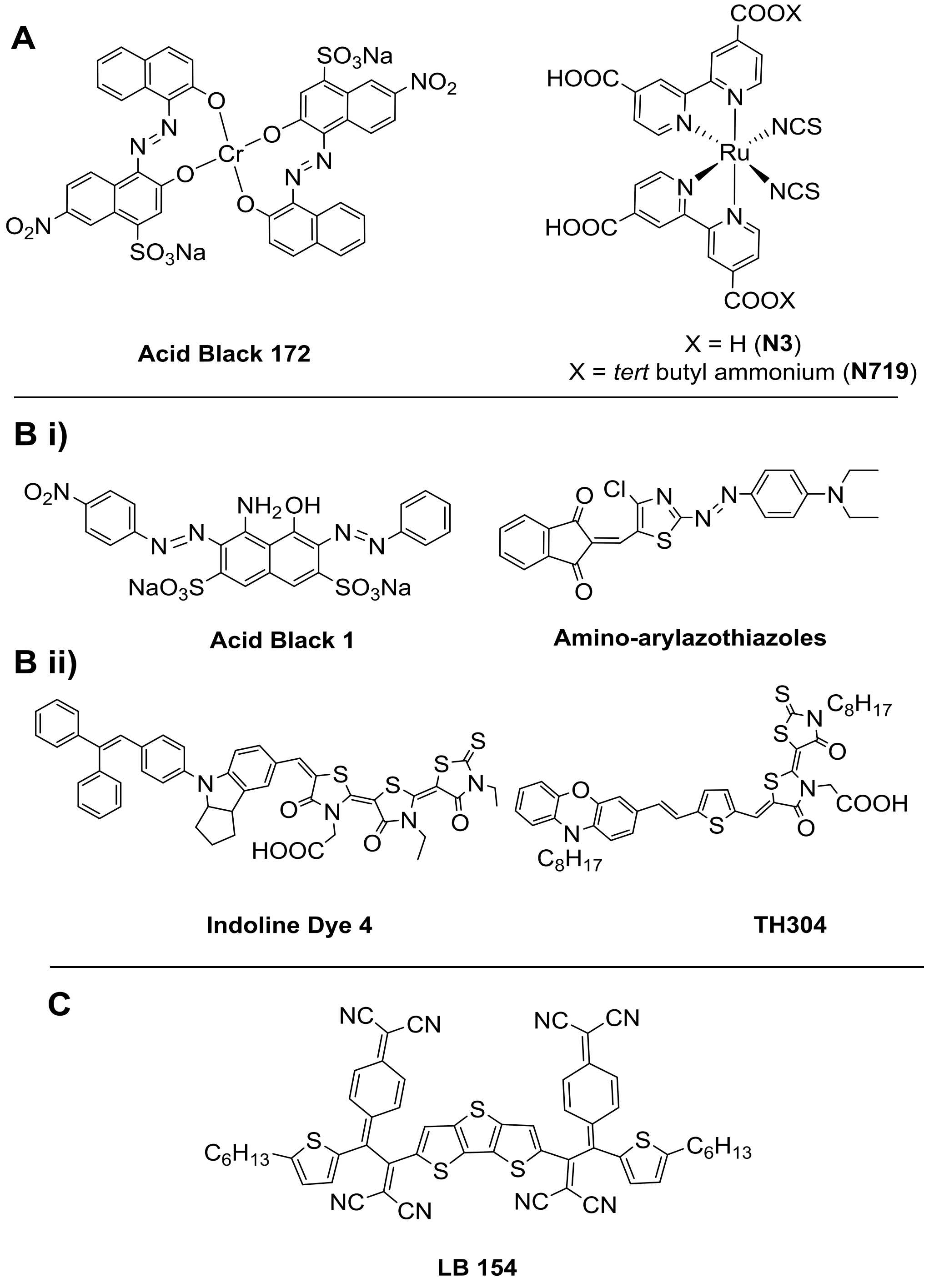

Figure 2 The strong absorption of the compound LB154 as A) total opacity in acetonitrile solution (10.6 mg in 10 mL) and examples of the pigment on B) glass and C) paper showing excellent thin-film formation

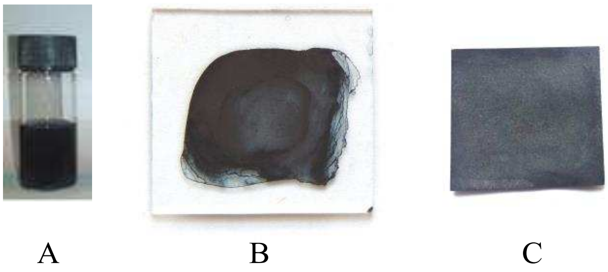

Figure 3 UV-Vis absorption spectra of pure 6 and LB154 in chloroform at 20 °C

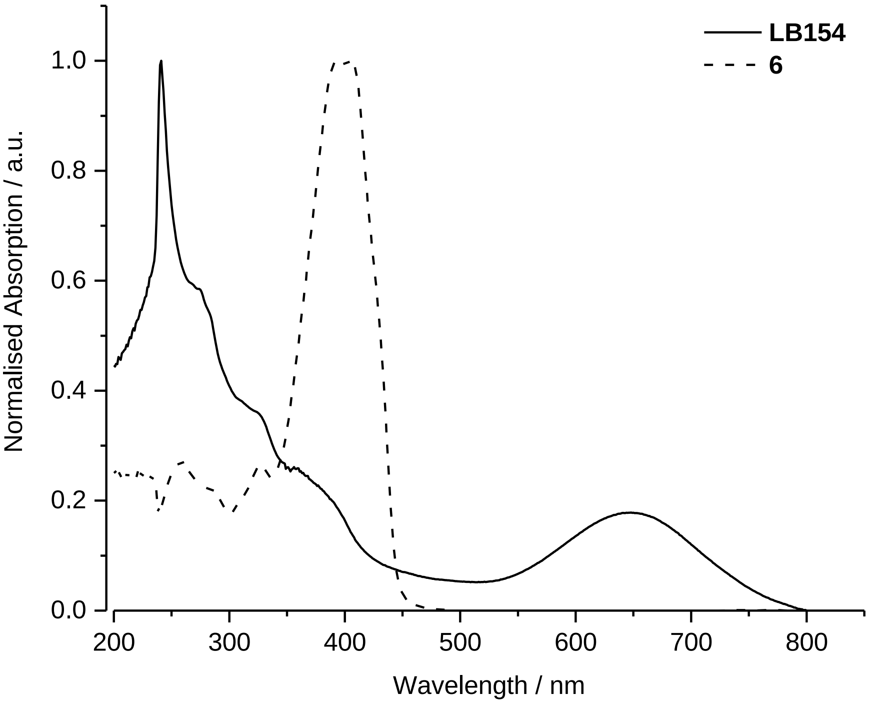

Figure 4 HOMO-LUMO orbital plots and associated energies of LB154 in eV. The overlapping of the low energy HOMO and LUMO orbital densities across the structure and low energy gap suggest significant suitability for both light scavenging and charge-transfer applications. The hexyl units were omitted for computational time

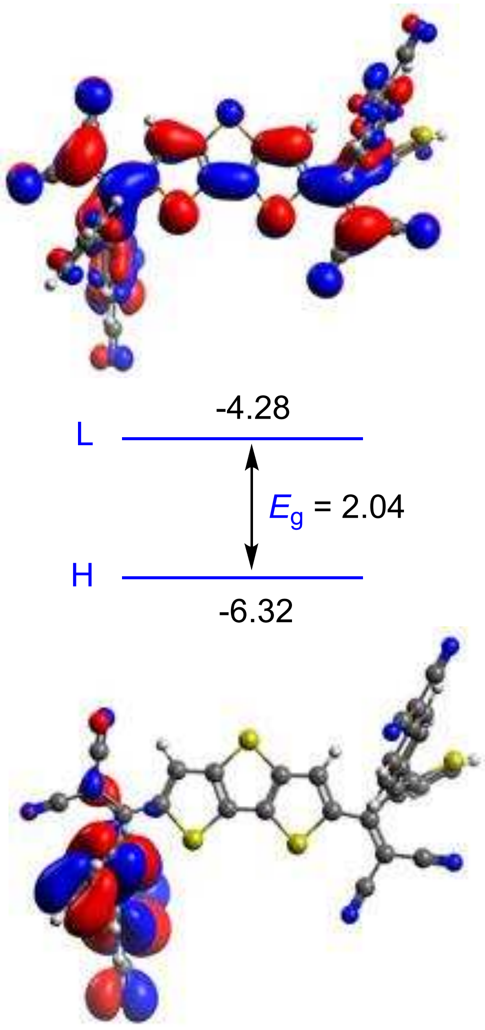

Figure 5 The reflectance spectrum of dyed paper with LB154 showing an inflection at 560 nm

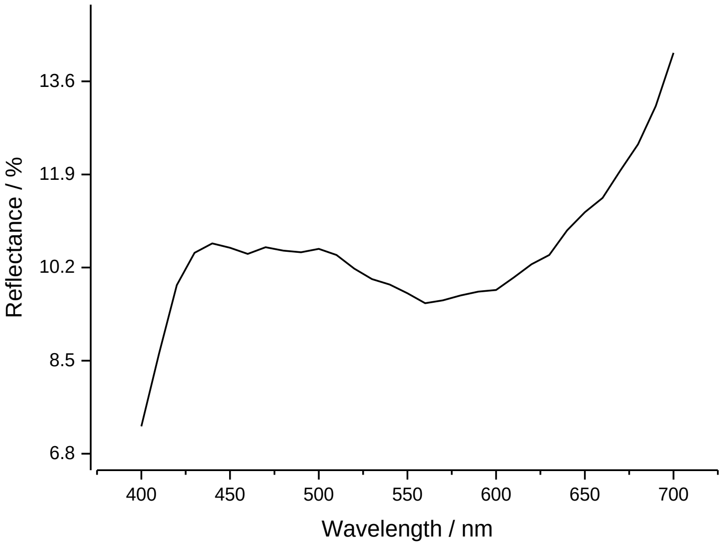

Figure 6 Thermal gravimetric profile of LB154 operated under nitrogen as sample weight (%) between 25 and 500 °C (top); the weight loss derivative showing the initial onset at 68.2 °C arising from the residual co-crystallised hexane, followed by the two stages of decomposition with the first at 226.6 °C for the hexyl and nitrile units and the second at 370.5 °C for the core DTT unit (bottom).