ChemComm

COMMUNICATION

A facile protection–deprotection route for obtaining indigo pigments as thin films and their applications in organic bulk heterojunctions†

Eric Daniel Głowacki,*[a] Gundula Voss,[a] Kadir Demirak,[b] Marek Havlicek,[a] Nevsal Sünger,[b] Aysu Ceren Okur,[c] Uwe Monkowius,[d] Jacek Gąsiorowski,[a] Lucia Leonat[a] and Niyazi Serdar Sariciftci[a]

Indigo and its derivatives are industrially-important dyes known for centuries. The low solubility of these compounds limits their applications and hinders potential synthetic chemistry using indigo as a building-block. Herein we report attachment of the *tert*-butoxy carbonyl (tBOC) thermolabile protecting group to indigos, allowing their processing into neat thin films as well as mixed films with a semiconducting polymer. Photoinduced charge transfer is observed to and from these pigments and the polymer.

Indigo and its derivatives constitute a family of natural-origin dyes and pigments of substantial industrial importance.[1] Indigo is usually processed *via* vat dyeing, exploiting the water-solubility of the reduced *leuco* indigo. Indigo is also used in its hydrogen-bonded pigment form for industrial coloring applications. Recent work exploring indigoids as organic semiconductors has shown that these materials afford ambipolar charge transport with mobilities in the range of 10^{-2}–0.5 cm^2 V^{-1} s^{-1} with substantial operational stability under ambient conditions.[2–4] Both 'old' and new emerging applications motivate us to find a way to work with indigos in organic solvents.

Herein we use the technique of attaching the thermolabile *tert*-butoxy carbonyl (tBOC) protecting group to the indigo amine function, yielding a highly-soluble indigo derivative. These groups can be removed by heat treatment later, regenerating the original pigment (Fig. 1). We observed a variety of different H-bonded crystallites formed using this approach, with potential applications as functional organic nano- and microparticles for organic electronics. Mixing the soluble indigo precursors with a semiconducting polymer, poly-(3-hexylthiophene), P3HT, followed by thermal regeneration of the pigment, yields evidence of photoinduced charge transfer between the polymer and indigo. Starting from the 1990s, researchers at
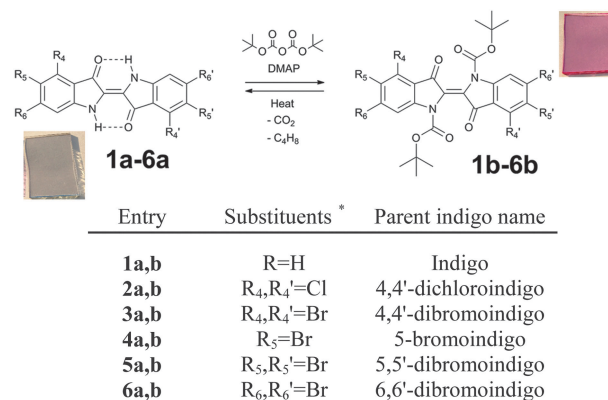

Entry	Substituents[*]	Parent indigo name
1a,b	R=H	Indigo
2a,b	R_4,R_4'=Cl	4,4'-dichloroindigo
3a,b	R_4,R_4'=Br	4,4'-dibromoindigo
4a,b	R_5=Br	5-bromoindigo
5a,b	R_5,R_5'=Br	5,5'-dibromoindigo
6a,b	R_6,R_6'=Br	6,6'-dibromoindigo

Fig. 1 Protection and deprotection of indigo pigments (**1a–6a**) using tBOC to yield protected dyes **1b–6b**. The table shows the compounds used in this study. *Unless otherwise specified, all R = H.

Ciba–Geigy have employed the tBOC group to form soluble latent pigments of diketopyrrolopyrroles, allowing dissolution of the latent pigment in organic matrices followed by heating to yield the stable pigment.[5] This method was disclosed in a 1993 patent for a wide range of pigment-forming molecules, including indigo.[6] Basic chemical data on **1b** were reported for the first time in 2004, however no derivatives of indigo were reported.[7] In the field of organic electronics, the tBOC group has been employed to allow solution-processing of polyaniline[8] and solution-processing of solar cells using tBOC quinacridone[9] and transistor devices using quinacridone and diketo-pyrrolopyrroles.[10] We prepared pigments **1a**–**3a** and **5a**–**6a** from the precursor *o*-nitrobenzaldehyde.[11] Compound **4a** was prepared according to Clark and Cooksey.[12] **1b**–**6b** were prepared by stirring the pigments **1a**–**6a** in dichloromethane at room temperature with ≥2 equivalents of tBOC$_2$O and about one equivalent of dimethyl amino-pyridine (DMAP) for 1–3 days. Experimental details and analytical data for **1**–**6** can be found in the ESI.† This is the first time that indigo mixtures have been separated by column chromatography. To underscore the utility of this method, we obtained a historical sample from the early 1900s (Dyestuff museum, TU Dresden, Prof. Hartmann) consisting of a mixture of unsubstituted indigo, 5-bromoindigo, and
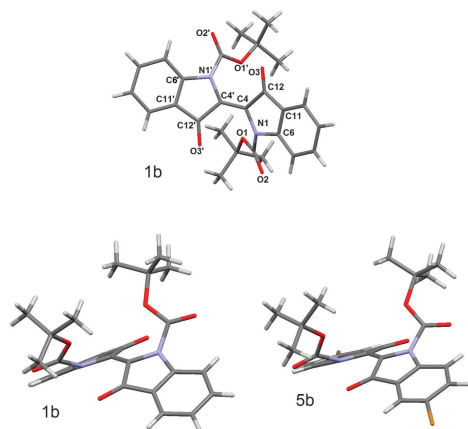
[a] *Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Linz, Austria. E-mail: eric_daniel.glowacki@jku.at*
[b] *Solar Energy Institute, Ege University, Bornova-Izmir, Turkey*
[c] *Dept. of Materials Science and Engineering, Sabanci University, Istanbul, Turkey*
[d] *Institute of Inorganic Chemistry, Johannes Kepler University, Linz, Austria*

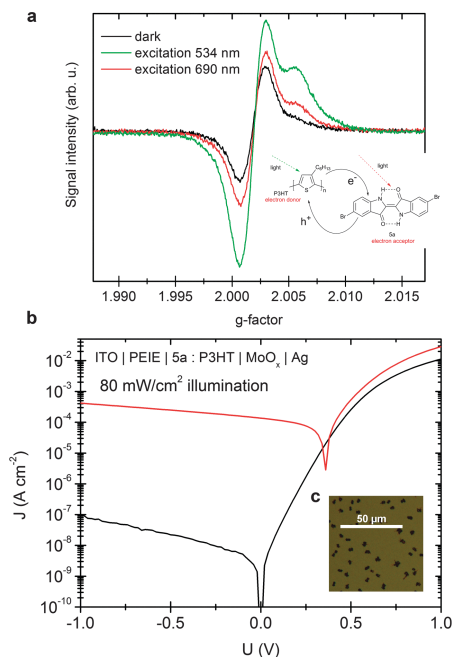**Fig. 2** Molecular structures of **1b** and **5b**. Two views of **1b**, and one of **5b** are shown.

Fig. 4 Photomicrographs of films of **1a–6a** spin-cast from chloroform solutions of **1b–6b** followed by deprotection at 200 °C for 5 minutes. Scale bar = 50 μm.

5,5′-dibromoindigo. The mixture was protected using the *t*BOC reaction and subsequently separated using column chromatography. Products **1b–6b** were further purified by recrystallization from ethyl acetate. This procedure can yield crystals suitable for single crystal X-ray diffraction. We obtained the crystal structures of compounds **1b** and **5b**, which were very similar. The structures of **1b** and **5b** are shown in Fig. 2. The *t*BOC protected indigos are highly-distorted relative to the planar parent compound. Both *t*BOC groups arrange on one face of the C_2-symmetric molecule, pushing the two indole rings away and resulting in a strained central double bond at C4–C4′. This substantial distortion of the molecule is unlike other reported *t*BOC compounds, such as *t*BOC quinacridone, which retains its planarity.[13] The optical absorption of the *t*BOC indigos exhibited a blue-shift in absorption of 40–60 nm, characteristic of indigoids where the intramolecular H-bonding is broken and the 'H-chromophore' is lost.[1,14] UV-Vis spectra are shown in Fig. 3. We found that like other *N,N*′-disubstituted indigos, compounds **1b–6b** exhibited photochemical *trans*–*cis* isomerism. Green irradiation of solutions at 532 nm produced a rapid blue-shift in absorption, turning the solution from violet to orange (ESI†). Keeping the sample in the dark for ∼100 min resulted in restoration of the original violet colour. The existence of isosbestic points at 397 and 494 nm confirms a clean photochemical isomerisation reaction without decomposition. Photoisomerism in indigoids lacking H-bonding has been reported in *N,N*′-substituted indigos,[14] *leuco* indigo,[15] and the related thioindigo dyes.[16] The behaviour observed here resembles closely that of *N,N*′-diacetyl indigo.[16] The parent compounds **1a–6a** did not show photochromic behaviour, as reported before for indigos with intramolecular H-bonding.[16,17]
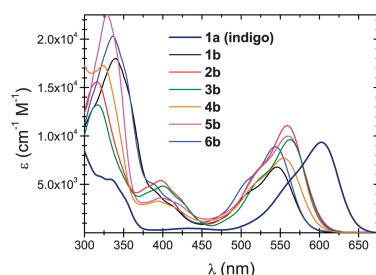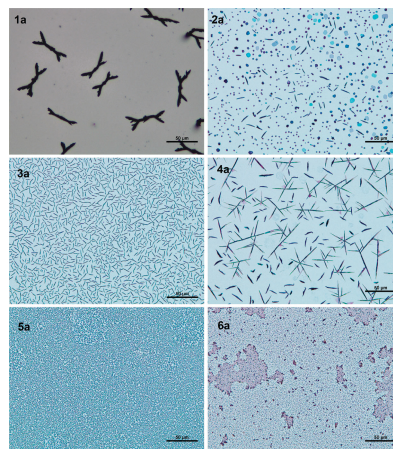
The *t*BOC indigos **1b–6b** could be readily dissolved in chloroform or chlorobenzene with concentrations as high as 100 mg ml^{-1}. We spin-cast such solutions onto glass substrates yielding violet-coloured, uniform and extremely smooth films. Atomic-force microscopy (AFM) measurement showed RMS roughness of such films to be between 1–2 nm (see ESI†). Heating of these films at 200 °C afforded blue-coloured deprotected films of **1a–6a**.

The deprotection mechanism to yield the pigments **1a–6a** was verified by thermogravimetric analysis (TGA). Heating sample powders to 190–200 °C resulted in a loss corresponding to two equiv. of isobutene and CO_2 (ESI†). We found that while films of the protected compounds **1b–6b** were all uniform, following deprotection, the films differed significantly from one another depending on the molecular structure of the **1a–6a** parent indigos.

Photomicrographs of deprotected films are shown in Fig. 4. Heating films of **1b** yielded non-contiguous crystallites. It was found, by placing a slide above the heated sample during deprotection, that some of the indigo sublimed and created a blue residue on the cover-slide. This behaviour is easily rationalized by the fact that the deprotection mechanism from soluble *t*BOC derivatives to the final H-bonded pigment proceeds through deprotected, unassociated indigo dye molecules as an intermediate. These small molecules can readily sublime. Thus film formation during deprotection is governed by the process of non-associated indigo molecules evaporating or migrating to form H-bonded pigment crystals, which are thermally-stable. In the case of all the other substituted indigos **2a–6a**, the individual dye molecules have sufficiently high molecular weight to not sublime during deprotection. In the case of compounds **2a–4a**, we found that films following deprotection featured large micron-sized crystallites. AFM examination (ESI†) revealed that between these large crystallites, a continuous film of much smaller grains of several-hundred nanometers in size existed. In the case of **5a** and **6a**, crystallites in the range of one micron formed, however they are isolated from each other and no continuous film of smaller grains was observed. Compounds **2a** and **4a** clearly demonstrate that at least two distinctly different types of crystallites exist following deprotection, as can be seen in Fig. 4.

Despite their long history in the chemical literature, H-bonded indigos have not been studied with respect to photoinduced

Fig. 3 UV-Vis absorption spectra of *t*BOC compounds in CHCl₃ with indigo shown for comparison.

This journal is © The Royal Society of Chemistry 2013

Fig. 5 (a) L-ESR signal at 60 K for a 1 : 1 blend of **5a**:P3HT. (b) *J–V* characteristics of a bulk heterojunction diode using **5a**:P3HT as the active layer. (c) Photomicrograph of the **5a**:P3HT blend.

electron transfer reactions. We conducted experiments to verify the existence of photoinduced charge transfer between thermally-regenerated particles of compound **5a** and the semiconducting polymer P3HT. Films were prepared by spin casting mixtures of P3HT:**5b** in $CHCl_3$, followed by heating to 185 °C for 5 minutes. Such films were tested using light-induced electron paramagnetic resonance (L-ESR) and also used as the active layer of an organic solar cell. L-ESR is a well-established technique for measuring photoinduced charge transfer in organic donor–acceptor blends.[18] Upon exciting the P3HT polymer with green light at 60 K, we observed a double-signal originating from the uncoupled spins of the positive polaron on the P3HT and the radical anion on the indigo (Fig. 5a). The *g*-value of the radical anion of **5b** was found to be 2.005. P3HT showed a *g*-value of 2.002, consistent with the literature.[19] Excitation with red light at wavelengths greater than 650 nm where P3HT does not absorb but **5a** does also yielded a double-signal, indicating that photoinduced hole transfer from **5a** to P3HT occurs. L-ESR experimental details can be found in the ESI.† The presence of photoinduced charge transfer suggests that donor–acceptor solar cells can be prepared from such a blend. Solar cells fabricated with the structure shown in Fig. 5b yielded working devices with good diode characteristics, nevertheless photocurrents remained low, on the order of 200–500 μA cm^{-2} under simulated solar illumination. This is attributed to the large size of **5a** crystals, which were on the order of 2–3 μm (Fig. 5c). It is known that the domain size of donor–acceptor blends should ideally be on the order of tens of nanometers,[20] and photocurrents on the order we measured for our devices are consistent with bulk heterojunctions with very rough mixing. Additionally, we underline that photocurrents for P3HT-only devices are about two orders of magnitude lower. Therefore we believe that optimizing the morphology of the bulk heterojunction during the deprotection

reaction is critical for increasing the device performance. Fabrication details can be found in the ESI.†

We find that the *t*BOC protection–deprotection procedure allows indigo to be solubilized in organic solvents, and the protected compound can be heated to regenerate the parent pigment. This technique allows simple solution-processing of indigo films. The deprotection behaviour of films of *t*BOC protected indigos yields a variety of different H-bonded crystallites. We found that indigo processed in this way together with P3HT yields evidence of photoinduced charge transfer and offers a potential avenue for fabricating donor–acceptor solar cells where indigo pigments function as electron acceptors.

Notes and references

1 H. Zollinger, *Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments*, Wiley-VCH, Weinheim, 3rd edn 2003; P. F. Gordon and P. Gregory, *Organic Chemistry in Colour*, Springer-Verlag, Berlin, 1987.
2 M. Irimia-Vladu, E. D. Głowacki, P. A. Troshin, G. Schwabegger, L. Leonat, D. K. Susarova, O. Krystal, M. Ullah, Y. Kanbur, M. A. Bodea, V. F. Razumov, H. Sitter, S. Bauer and N. S. Sariciftci, *Adv. Mater.*, 2012, **24**, 375–380.
3 E. D. Głowacki, L. Leonat, G. Voss, M.-A. Bodea, Z. Bozkurt, A. M. Ramil, M. Irimia-Vladu, S. Bauer and N. S. Sariciftci, *AIP Adv.*, 2011, **1**, 042132–042137.
4 E. D. Głowacki, G. Voss, L. Leonat, M. Irimia-Vladu, S. Bauer and N. S. Sariciftci, *Isr. J. Chem.*, 2012, **52**, 540–551.
5 J. S. Zambounis, Z. Hao and A. Iqbal, *Nature*, 1997, **388**, 131–132.
6 U. Schaedeli, J. S. Zambounis, A. Iqbal, Z. Hao and H. Dubas, EP 0654711, 1993.
7 K. Ichimura, K. Arimitsu and M. Tahara, *J. Mater. Chem.*, 2004, **14**, 1164–1172.
8 C. Lee, Y. Seo and S. Lee, *Macromolecules*, 2004, **37**, 4070–4074.
9 T. L. Chen, J. J.-A. Chen, L. Catane and B. Ma, *Org. Electron.*, 2011, **12**, 1126–1131.
10 H. Yanagisawa, J. Mizuguchi, S. Aramaki and Y. Sakai, *Jpn. J. Appl. Phys.*, 2008, **47**, 4728–4731.
11 A. Baeyer and V. Drewsen, *Ber. Dtsch. Chem. Ges.*, 1882, **15**, 2856–2864.
12 R. J. H. Clark and C. J. Cooksey, *New J. Chem.*, 1999, **23**, 323–328.
13 J. Mizuguchi, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, o474–o475.
14 J. Weinstein and G. M. Wyman, *J. Org. Chem.*, 1956, **78**, 4007–4010; W. Lüttke, H. Hermann and M. Klessinger, *Angew. Chem., Int. Ed.*, 1966, **5**, 598–599.
15 R. Rondão, J. Seixas de Melo, M. J. Melo and A. J. Parola, *J. Phys. Chem. A*, 2012, **116**, 2826–2832.
16 G. M. Wyman, *Chem. Rev.*, 1956, **55**, 625–657.
17 J. Seixas de Melo, A. P. Moura and M. J. Melo, *J. Phys. Chem. A*, 2004, **108**, 6975–6981.
18 V. Dyakonov, G. Zoriniants, M. Scharber, C. Brabec, R. Janssen, J. Hummelen and N. Sariciftci, *Phys. Rev. B*, 1999, **59**, 8019–8025; N. Schultz, M. Scharber, C. Brabec and N. Sariciftci, *Phys. Rev. B*, 2001, **64**, 245210.
19 V. I. Krinichnyi and E. I. Yudanova, *J. Renewable Sustainable Energy*, 2009, **1**, 043110.
20 G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323–1338.