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A Novel Profluorescent Dinitroxide for Imaging Polypropylene Degradation

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ABSTRACT

A new profluorescent dinitroxide, 9,10-bis(1,1,3,3-tetramethylisoindolin-2-yloxy-5-yl)anthracene (BTMIOA), was synthesized and shown to be a powerful probe for detecting changes during the initial stages of thermo-oxidative polypropylene degradation. This probe, which contains a 9,10-diphenylanthracene core linked to two nitroxides, possesses strongly suppressed fluorescence due to quenching by the nitroxide groups. Upon reaction with polymer alkyl radicals, this suppression is removed and fluorescence may readily be observed. Thus, in addition to stabilizing polypropylene, this new probe allows polymer breakdown during the induction period to be monitored by spectrofluorimetry. Most importantly, BTMIOA was found to be a valuable tool for imaging and

mapping free-radical generation in thermo-oxidatively degraded polypropylene using fluorescence microscopy.

MANUSCRIPT TEXT

Free-radical processes underpin the thermo and photo-oxidative degradation of polyolefins. Thus, to extend the lifetime of these polymers, stabilizers are generally added during processing to scavenge the free-radicals formed as the polymer degrades. Nitroxide radical precursors, such as hindered amine stabilizers (HAS),^{1,2} are common polypropylene additives, as the nitroxide moiety is a potent scavenger of polymer alkyl radicals (R^{\bullet}). Oxidation of HAS by radicals formed during polypropylene degradation yields nitroxide radicals ($RR'NO^{\bullet}$), which rapidly trap the polymer degradation species to produce alkoxyamines, thus retarding oxidative polymer degradation. This increase in polymer stability is demonstrated by a lengthening of the “induction period” of the polymer (the time prior to a sharp rise in the oxidation of the polymer). Instrumental techniques such as chemiluminescence or infrared spectroscopy are somewhat limited in detecting changes in the polymer during the initial stages of degradation. Therefore, other methods for observing polymer degradation have been sought as the useful life of a polymer does not extend far beyond its “induction period”.³

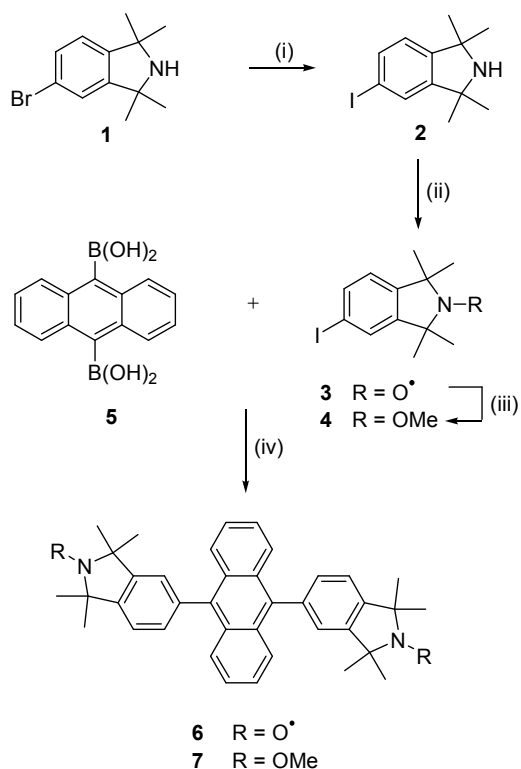
A sensitive technique for monitoring the alkyl radical precursors to polymer degradation involves spin-trapping by profluorescent nitroxides. These compounds, which possess a fluorophore tethered by a short covalent link to a nitroxide moiety, are effective scavengers of carbon centered radicals and quenchers of excited electronic states. They exhibit low fluorescence due to enhanced intersystem crossing from the first excited singlet state to the triplet state via electron exchange interactions of the nitroxide radical. Upon radical trapping to form a diamagnetic alkoxyamine, normal fluorophore emission is enabled and thus, these nitroxide-fluorophore adducts can be employed as extremely responsive fluorescent probes for the detection of free-radical species.⁴ This property has been previously applied to evaluate radical formation in various polymer contexts,⁵⁻⁷ however these probes possess nitroxide-containing piperidine or pyrrolidine units tethered through ester or amide linkages to a

fluorophore. For monitoring polymer degradation, linkages that are susceptible to hydrolysis and subsequent scission of the nitroxide moiety from the fluorophore, are not ideal.

Nitroxides based on the more rigid isoindoline structure exhibit somewhat superior chemical and thermal stability in polymers.^{8,9} Herein, we describe the synthesis and properties of the novel dinitroxide, 9,10-bis(1,1,3,3-tetramethylisoindolin-2-yloxy-5-yl)anthracene (BTMIOA) **6**, a markedly superior, enhanced stability profluorescent nitroxide probe analogous to 9,10-diphenylanthracene. This new probe possesses a (masked) high quantum yield and so is more sensitively able to detect free-radical formation during polymer degradation. The high quantum yield facilitates monitoring by spectrofluorimetry, but also allows degradation to be readily imaged using fluorescence microscopy.

The new probe was synthesized by a Suzuki cross coupling reaction between 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxy **3** and anthracene-9,10-diboronic acid **5** in a modest yield (29%) (Scheme 1). The more reactive iodo-nitroxide **3** was preferred over its bromo analogue as a coupling partner. Preparation of **3** was achieved by lithiation of 5-bromo-1,1,3,3-tetramethylisoindoline **1**, followed by treatment with iodine and subsequent oxidation with hydrogen peroxide in the presence of a tungstate catalyst. The alkylated diamagnetic dinitroxide analogue, 9,10-bis(2-methoxy-1,1,3,3-tetramethylisoindolin-5-yl)anthracene **7**, was obtained by Suzuki coupling of 5-iodo-2-methoxy-1,1,3,3-tetramethylisoindoline **4** (formed using Fenton chemistry by reaction of 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxy **3** with methyl radicals generated from dimethylsulfoxide and hydrogen peroxide) and anthracene-9,10-diboronic acid **5** in a more moderate yield (43%). A comparison of the fluorescence of dinitroxide **6** and its methoxyamine derivative **7** reveals the substantial suppression of the fluorescence of the 9,10-diphenylanthracene core in compound **6** arising from the presence of the two nitroxides. This effect is evident from the quantum yields (Φ_F) of 2.9×10^{-3} and 0.89 obtained for compounds **6** and **7** respectively, following excitation at 375 nm (ϵ 14 500 M⁻¹cm⁻¹).

Scheme 1. Synthesis of BTMIOA **6** and BTMIOA-Me **7**.



Reagents and conditions: (i) (a) $nBuLi$, THF, $-78^\circ C$, 15 min, (b) I_2 , THF, $-78^\circ C$ to RT, (c) $NaHCO_3$, H_2O_2 , MeOH-DCM; (ii) $NaHCO_3$, $Na_2WO_4 \cdot 2H_2O$, H_2O_2 , MeOH, 3 days; (iii) $FeSO_4 \cdot 7H_2O$, H_2O_2 , DMSO, 15 min; (iv) $Pd(PPh_3)_4$, Na_2CO_3 , THF- H_2O , $80^\circ C$, 3 days.

Polypropylene plaques containing dinitroxide **6** or methoxyamine **7** were obtained by swelling the polymer in 5 mM toluene solutions of **6** or **7**. The amount of compound present in each plaque was quantified using UV-vis spectroscopy (assuming that the concentration in solution is comparable to that in a solid plaque for a set absorbance). The maximum concentration of BTMIOA **6** or BTMIOA-Me **7** in a doped plaque was found to be ~ 0.17 mM, corresponding to ~ 0.009 wt% (assuming a polypropylene density of 0.9 g cm^{-3}). The plaques were thermally degraded at $150^\circ C$ in a 100 % O_2 environment. Samples were removed from the oven periodically and their fluorescence spectra recorded (excitation - 260 nm). Figure 1 shows the fluorescence emission of the BTMIOA **6** doped plaque subjected to oxidation under oxygen for 10 hours. The fluorescence of the degrading plaque was found to slowly increase over the first 300 minutes and then rise more rapidly between 400 and 500 minutes, indicating

the trapping of alkyl radicals and formation of fluorescent alkoxyamines. Interestingly, the fluorescence profile appears to indicate two stages involving sequential trapping of the two nitroxides.

We have previously reported the use of 1,1,3,3-tetramethyldibenzo[*e,g*]isoindolin-2-yloxy (TMDBIO) as a probe for monitoring the thermo-oxidative degradation of polypropylene.^{10,11} The new profluorescent probe **6** reported here markedly stabilizes the polymer, as demonstrated by the extended induction period before observed chemiluminescence (Figure 1), and is a significant advance over TMDBIO. This new probe allows the monitoring of the thermal degradation of polypropylene for longer periods than TMDBIO, which reaches a maximum fluorescence and then decreases due to secondary oxidation of the TMDBIO adducts. Notably, the oxidative stability of the model alkyl adduct, BTMIOA-Me **7** is much improved over TMDBIO-Me, with a plaque containing **7** maintaining fluorescence after oxidation for 120 minutes at 150°C under oxygen. Under the same conditions TMDBIO-Me samples returned rapidly to background fluorescence levels.

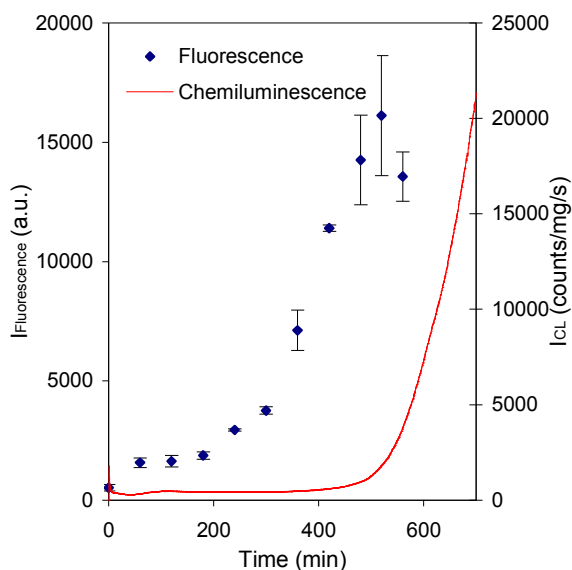


Figure 1. Fluorescence and Chemiluminescence emission of BTMIOA **6** doped polypropylene aged under O₂ at 150°C (260 nm excitation). Note the induction period for Chemiluminescence from undoped polypropylene is essentially zero over this timescale.

BTMIOA-Me **7** also has a much higher quantum yield than TMDBIO-Me (0.89 compared to 0.18), which indicates this probe is much more suitable for the imaging and mapping of free radical reactions in polymer degradation. Figure 2 shows images of doped polypropylene plaques excited between 254 and 290 nm using a short-range UV lamp. Like the undoped plaque (Figure 2a), the plaque doped with BTMIOA **6** (Figure 2b) displays low fluorescence due to quenching by the nitroxides. In comparison, the BTMIOA-Me **7** doped plaque (Figure 2d) is extremely fluorescent. Figure 2d gives an indication of the maximum fluorescence possible for dinitroxide **6** following radical trapping to form fluorescent diamagnetic alkoxyamine adducts. Furthermore, the sensitivity of BTMIOA **6** is demonstrated by comparing the images of the BTMIOA-Me **7** doped plaque (Figure 2d) with that of a TMDBIO-Me doped plaque (Figure 2c). Not only is the BTMIOA-Me **7** doped plaque considerably brighter, it also contains a significantly lower concentration of the adduct (0.17 mM compared to 1.1 mM for TMDBIO-Me).

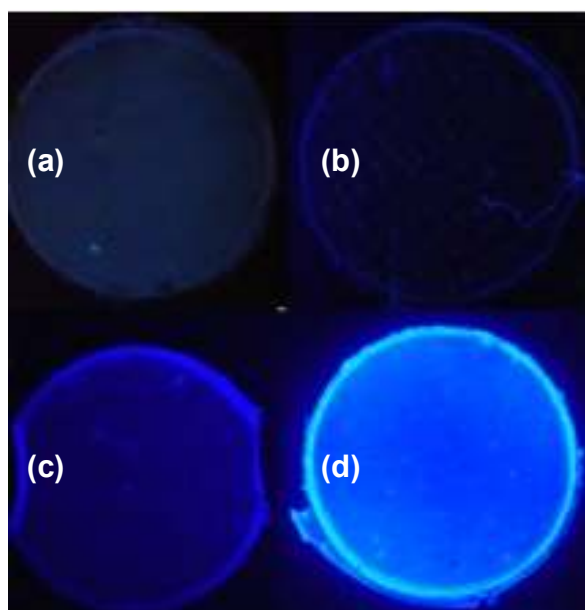


Figure 2. Polypropylene plaque images excited between 254-290 nm using short-range UV lamp (a) blank (b) doped with BTMIOA **6** at 0.17 mM (c) doped with TMDBIO-Me at 1.1 mM and (d) doped with BTMIOA-Me **7** at 0.17 mM.

Celina and coworkers¹² have shown infectious spreading of oxidation when polypropylene was spiked with benzoyl peroxide and degraded at 100°C in an O₂ environment. Using the new dinitroxide probe **6** allows a visual representation of this oxidation process, as can be observed in Figure 3. A polypropylene plaque doped with **6** (~0.17 mM) was spiked with benzoyl peroxide and degraded at 100°C in an O₂ environment to accelerate radical formation. After heating for 1 hour (Figure 3b and 3b'), an area of high fluorescence was observed in the centre of the plaque due to trapping by **6** of phenyl radicals and the initiated macro-radicals. With prolonged heating (Figure 3c-3f and 3c'-3f'), the fluorescence radiated outwards towards the edges of the plaque revealing the damage from propagating radicals. Thus, BTMIOA **6** is an ideal dual-functioning probe which allows polypropylene degradation to be mapped by imaging with fluorescence microscopy and also imparts stabilization to the polymer due to its effective radical scavenging ability.

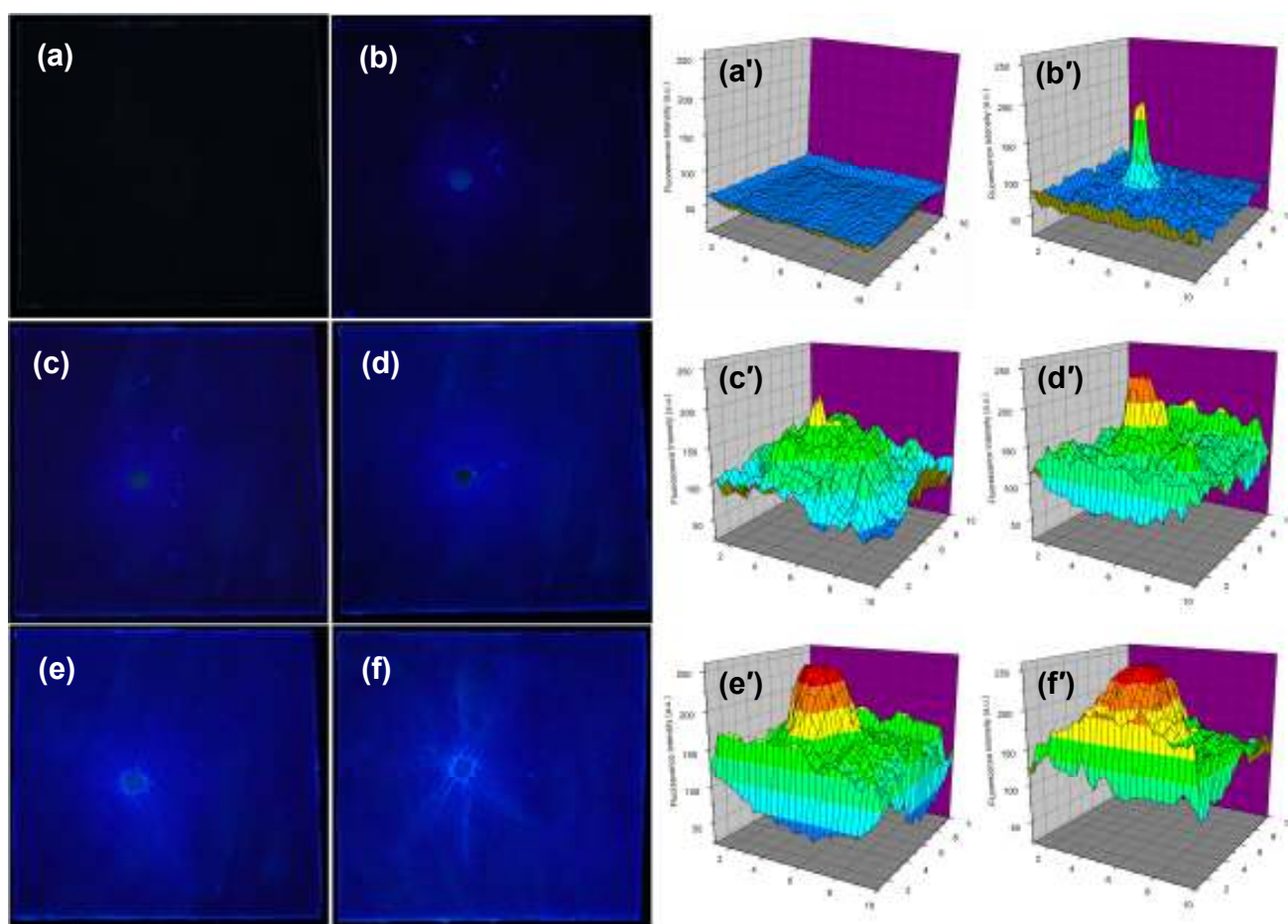


Figure 3. Fluorescent images of a BTMIOA **6** doped, 2.5 cm x 2.5 cm polypropylene plaque spiked with benzoyl peroxide initiator and heated at 100°C in O₂ for (a) 0 hr (b) 1 hr (c) 8 hr (d) 12 hr (e) 18 hr and (f) 24 hr. (a')-(f') are three-dimensional representations of fluorescence for images (a)-(f).

In conclusion, a novel dinitroxide probe **6**, based on a 9,10-diphenylanthracene core and incorporating nitroxides, has been developed and shown to image polypropylene degradation. This novel probe was synthesised by a Suzuki cross coupling reaction and switches on fluorescence as the nitroxides present spin-trap polymer alkyl radicals formed during the thermo-oxidative degradation of polypropylene. Compound **6** allows polymer breakdown during the induction period to be monitored by spectrofluorimetry and imaged using fluorescence microscopy. Furthermore, probe **6** displays enhanced stability towards further oxidation after trapping and subsequent loss of fluorescence. The ability to image radical damage in polypropylene using this probe indicates the potential for this sensitive technique to be used as a powerful analytical tool to study polypropylene, and other polymer, degradation. These results will be reported in due course.

ACKNOWLEDGMENT

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SUPPORTING INFORMATION PARAGRAPH

Supporting Information Available. Procedures for the doping of polypropylene plaques and synthesis and characterization of compounds **2**, **3**, **4**, **6** and **7**.

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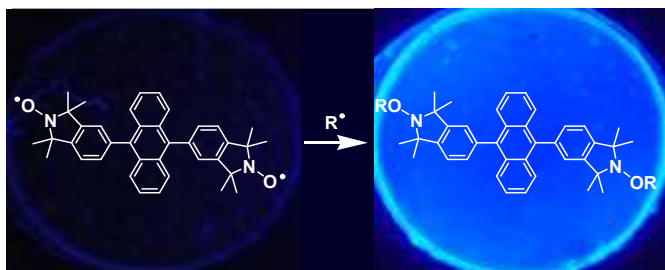
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SUPPORTING INFORMATION

General procedures

All air-sensitive reactions were carried out under an atmosphere of ultra-high purity argon. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketal and toluene dried over sodium wire. Tetrakis(triphenylphosphine)palladium(0) was prepared fresh before use using literature methods.¹ 5-Bromo-1,1,3,3-tetramethylisoindoline² **1** and anthracene-9,10-diboronic acid³ **5** were synthesised using established literature procedures. Unstabilised polypropylene was supplied by the Toho Catalyst Company Ltd and had M_n 86750 mol/g; M_w 318599 mol/g; M_w/M_n 3.7. The properties of this material and its oxidation characteristics have been described elsewhere.⁴ All other reagents were purchased from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer and referenced to the relevant solvent peak. Low and high resolution mass spectra were recorded at the Australian National University (ANU) using either a Micromass autospec double focusing magnetic sector mass spectrometer (EI+ spectra) or a Bruker Apex 3 fourier transform ion cyclotron resonance mass spectrometer with a 4.7 T magnet (ESI+ spectra). Formulations were calculated in the elemental analysis programs of Mass Lynx 4.0 or Micromass Opus 3.6. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 870 Nexus Fourier Transform Infrared Spectrometer equipped with a DTGS TEC detector and an ATR objective. Elemental analyses were carried out by the University of Queensland Microanalytical Service. Melting points were measured on a Gallenkamp Variable Temperature Apparatus by the capillary method and are uncorrected. Analytical and semi-preparative HPLC was performed on an Agilent Technologies

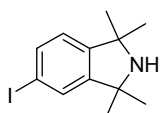
1200 series preparative HPLC system using C18 columns. Spectrofluorimetry was undertaken on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a standard multicell Peltier thermostatted sample holder. Plaques were loaded into a modified cuvette and excited at an angle of 45°C to the surface, with emission recorded from the back face of the sample, in order to minimise scattering effects. UV-vis spectroscopy was performed on a Varian Cary 50 spectrophotometer. Fluorescent images were captured with a Sony DSC-S75, CCD colour digital camera attached to a stereomicroscope while being excited by a short-range UV lamp at 254-290 nm. The three-dimensional representations of fluorescence (Figure 3a'-3f') were prepared by first converting the fluorescent images to a gray-scale using Scion Image for Windows (Scion Corporation, 2000-2001). The image pixel intensity was then converted into an XY matrix using ORIGIN 6.1 (OriginLab Corporation, 1991-2000). Data was then compressed to 10 000 data points (100 x 100 matrix) and plotted.

Doping of polypropylene plaques

Melt-pressed polypropylene plaques (40 x 40 x 0.4 mm) were prepared at 180 °C with an applied pressure of 10 ton over 5 minutes. The polymer granules were loaded between polyacetate sheets on a steel die and were quenched in air after pressing. The expected formation of some alkyl radicals during melt-processing of the polypropylene⁵ precluded the introduction of the nitroxide dopant prior to the plaque formation. Radical trapping by the nitroxide during the melt-processing would generate fluorescent alkoxyamines and undesirable background emission. Consequently, the polypropylene plaques were doped by immersion in toluene solutions (5 mM) of 9,10-bis(1,1,3,3-tetramethylisindolin-2-yloxy-5-yl)anthracene **6** and 9,10-bis(2-methoxy-1,1,3,3-tetramethylisindolin-5-yl)anthracene **7** in the dark, for 7 days. Upon removal from the swelling solutions, the plaques were rinsed with a minimum amount of ethanol and placed under high vacuum for 24 hours. From these plaques, a disk (5 mm diameter) was removed using a hole-punch. These were then placed in an aluminum pan and thermally degraded at 150 °C in a 100% O₂ environment. Samples were removed

from the oven periodically and their fluorescence spectra recorded (excitation - 260 nm). The nitroxide content of the doped plaques was determined using UV-vis spectroscopy (assuming that for a set absorbance, the concentration in solution is comparable to that in a solid plaque). The plaques were held in the instrument beam path and a baseline obtained using the undoped control plaque. Quantification was obtained using the 395 nm vibronic band (ϵ 12178, in a cyclohexane solution), which is in a region with low background from the polymer. This band displayed an absorbance of <1 absorbance unit in the doped plaques. The maximum concentration of BTMIOA **6** and BTMIOA-Me **7** in a doped plaques was both found to be ~ 0.17 mM, corresponding to ~ 0.009 wt% (assuming a polypropylene density of 0.9 g cm^{-3}).

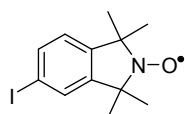
Synthesis of 5-iodo-1,1,3,3-tetramethylisoindoline **2**.



5-Bromo-1,1,3,3-tetramethylisoindoline **1** (4.00 g, 15.7 mmol) was dissolved in dry THF (45 mL) and cooled to -78°C under an atmosphere of argon. *n*-Butyllithium (1.6 M in hexanes, 25.7 mL, 41.1 mmol) was added slowly and the resulting solution stirred for 15 minutes. Iodine (12.0 g, 47.3 mmol) in dry THF (100 mL) was then added, the cold bath was removed and the mixture was allowed to warm to room temperature. The solution was poured into an ice/water slurry (300 mL), basified to pH 14 with 5 M NaOH and stirred vigorously for 30 minutes. The aqueous mixture was extracted with DCM (3×150 mL) and the combined DCM layers washed with brine (2×200 mL). The organic layers were dried (anhydrous Na_2SO_4) and concentrated *in vacuo* to give a yellow oil. The resulting oil was taken up in methanol (100 mL) and DCM (5 mL) and sodium hydrogen carbonate (0.50 g, 5.95 mmol) added. The solution was treated slowly with hydrogen peroxide solution (30 wt % in water, 10 mL) and then acidified to pH 1 with 2 M H_2SO_4 . The mixture was extracted with DCM (3×300 mL) and the combined DCM layers washed with 2 M H_2SO_4 (2×400 mL). The combined acidic phases were

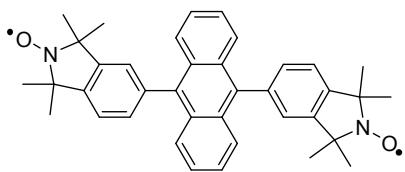
washed with DCM (2 × 300 mL) and then basified to pH 14 using 5 M NaOH. The aqueous layers were extracted with DCM (5 × 200 mL), washed with brine (2 × 400 mL), dried (anhydrous Na₂SO₄) and concentrated at reduced pressure to give the desired iodoamine **2** as a golden oil which rapidly crystallised (3.30 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ 1.43 (s, 6H, 2 × CH₃), 1.44 (s, 6H, 2 × CH₃), 1.99 (br, 1H, NH), 6.89 (d, *J* = 7.9 Hz, 1H, H7), 7.45 (d, *J* = 1.3 Hz, 1H, H4), 7.56 (dd, *J* = 7.9, 1.5 Hz, 1H, H6). ¹³C NMR (100 MHz, CDCl₃) δ 31.69 (2 × CH₃), 31.75 (2 × CH₃), 62.6 (C), 62.7 (C), 92.2 (C), 123.5 (CH), 130.8 (CH), 136.0 (CH), 138.6 (CH), 151.4 (CH). EIMS (+ve mode) 301 (M⁺, 1%), 286 (100%), 271 (30%). HRMS (Found: 301.03182. C₁₂H₁₆IN requires 301.03274). *v*_{max} (ATR) 3333 (NH), 3033 (aryl C-H), 2957 and 2916 (alkyl CH), 1439 and 1393 cm⁻¹ (aryl C-C). The resulting 5-iodo-1,1,3,3-tetramethylisoindoline **2** was used in the next step without further purification.

Synthesis of 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxyl **3**.



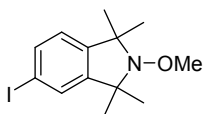
5-Iodo-1,1,3,3-tetramethylisoindoline **2** (3.00 g, 9.96 mmol) was dissolved in methanol (45 mL). Sodium hydrogen carbonate (1.00 g, 11.9 mmol), sodium tungstate dihydrate (0.44 g, 1.33 mmol) and hydrogen peroxide solution (30 wt % in water, 11 mL) were added. The reaction mixture was allowed to stir at room temperature for 3 days and then diluted with water (200 mL). The solution was extracted with DCM (3 × 150 mL), washed with 2 M HCl (2 × 150 mL) and brine (2 × 200 mL), dried (anhydrous Na₂SO₄) and concentrated *in vacuo* to give a yellow solid. Purification by column chromatography (eluent 30/70 ethyl acetate/hexane, sample loaded in DCM) yielded the desired compound **3** as a yellow solid (1.80 g, 57%). Mp 132-135°C. EIMS (+ve mode) 316 (M⁺, 75%), 301 (35%), 286 (100%). HRMS (Found: 316.01959. C₁₂H₁₅INO requires 316.01983). *v*_{max} (ATR) 3040 (aryl C-H), 2975 and 2926 (alkyl CH), 1465 and 1429 (aryl C-C), 1373 and 1357 cm⁻¹ (N-O).

Synthesis of 9,10-bis(1,1,3,3-tetramethylisoindolin-2-yloxy-5-yl)anthracene **6**.



A solution of dry THF (4 mL) containing anthracene-9,10-diboronic acid **5** (0.10 g, 0.38 mmol), 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxy **3** (0.29 g, 0.94 mmol), anhydrous sodium carbonate (0.08 g, 0.75 mmol) and water (2 mL) was degassed by subjecting to three freeze-pump-thaw cycles. Tetrakis(triphenylphosphine)palladium(0) (35.0 mg, 0.03 mmol) was added and the reaction mixture was heated at 80°C under an atmosphere of argon for 3 days. The solution was cooled, water (20 mL) added and extracted with diethyl ether (3 × 30 mL). The ether layers were washed with brine (2 × 20 mL), dried (anhydrous Na₂SO₄) and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent 100% chloroform) to give the desired compound **6** as a cream coloured solid (0.06g, 29%). Mp 312-315°C (dec). ESMS (+ve mode) 555 (MH⁺, 15%). EIMS (+ve mode) 554 (M⁺, 10%). HRMS (Found: 554.2936. C₃₈H₃₈N₂O₂ requires 554.2933). ν_{\max} (ATR) 2970 and 2924 (alkyl CH), 1494 and 1437 (aryl C-C), 1373 and 1358 cm⁻¹ (N-O). Anal. calcd for C₃₈H₃₈N₂O₂.H₂O: C, 79.69; H, 7.04; N, 4.89. Found: C, 79.84; H, 6.99; N, 4.83.

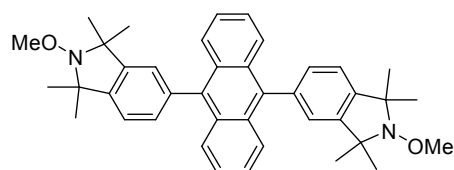
Synthesis of 5-iodo-2-methoxy-1,1,3,3-tetramethylisoindoline **4**.



Hydrogen peroxide solution (30 wt % in water, 0.36 mL) was added dropwise to a solution of 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxy **3** (0.50 g, 1.58 mmol) and iron (II) sulphate heptahydrate (0.88 g, 3.16 mmol) in DMSO (10 mL). The resulting solution was stirred at room temperature for 30 minutes, then poured into 1 M NaOH (50 mL). The mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic layers washed with brine (2 × 100 mL), dried (anhydrous Na₂SO₄) and concentrated *in vacuo*. Purification by column chromatography (eluent 10% ethyl acetate/90% hexane) gave the desired methyl adduct **4** as a colourless oil (0.40 g, 76%). ¹H NMR (400 MHz, CDCl₃) δ 1.43 (br s, 12H,

4 × CH₃), 3.79 (s, 3H, CH₃), 6.87 (d, *J* = 8.0 Hz, 1H, H7), 7.43 (d, *J* = 1.5 Hz, 1H, H4), 7.56 (dd, *J* = 7.9, 1.6 Hz, 1H, H6). ¹³C NMR (100 MHz, CDCl₃) δ 25.3 (br, CH₃), 30.1 (br, CH₃), 65.6 (CH₃), 66.87 (C), 66.94 (C), 92.1 (C), 123.6 (C), 130.7 (C), 136.1 (C), 144.9 (C), 147.7 (C). EIMS (+ve mode) 331 (M⁺, 10%). HRMS (Found: 331.0444. C₁₃H₁₈INO requires 331.0433). *v*_{max} (ATR) 2972 and 2931 (alkyl CH), 1475 and 1460 (aryl C-C), 1372 and 1359 cm⁻¹ (N-O), 1048 cm⁻¹ (C-O).

Synthesis of 9,10-bis(2-methoxy-1,1,3,3-tetramethylisoindolin-5-yl)anthracene 7.



A solution of dry THF (4 mL) containing anthracene-9,10-diboronic acid **5** (0.06 g, 0.24 mmol), 5-iodo-2-methoxy-1,1,3,3-tetramethylisoindoline **4** (0.20 g, 0.60 mmol), anhydrous sodium carbonate (0.05 g, 0.50 mmol) and water (2 mL) was degassed by subjecting to three freeze-pump-thaw cycles. Tetrakis(triphenylphosphine)palladium(0) (35.0 mg, 0.03 mmol) was added and the reaction mixture was heated at 80°C under an atmosphere of argon for 3 days. The solution was cooled, water (20 mL) added and extracted with diethyl ether (3 × 30 mL). The ether layers were washed with brine (2 × 20 mL), dried (anhydrous Na₂SO₄) and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent 30% DCM/70% hexane) to give the desired compound **7** as a white solid (0.06 g, 43%). Mp >300°C (dec). ¹H NMR (400 MHz, CDCl₃) δ 1.51 (br s, 12H, 4 × CH₃), 1.61 (br s, 12 H, 4 × CH₃), 3.89 (s, 6H, 2 × CH₃), 7.21 (d, *J* = 10.1 Hz, 2H, Ar-H), 7.32-7.38 (m, 8H, Ar-H), 7.72 (dd, *J* = 6.8, 3.2 Hz, 4H, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ 25.0 (br, CH₃), 30.0 (br, CH₃), 65.6 (CH₃), 67.2 (C), 121.4 (CH), 124.4 (CH), 124.9 (CH), 127.0 (CH), 130.0 (CH), 130.2 (C), 137.9 (C), 144.3, (C), 145.4 (C). EIMS (+ve mode) 584 (M⁺, 35%). HRMS (Found: 584.3405. C₄₀H₄₄N₂O₂ requires 584.3403). *v*_{max} (ATR) 2971 and 2930 (alkyl CH), 1461 and 1438 (aryl C-C), 1052 cm⁻¹ (C-O).

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