## Supporting Information

## Halochromism and Protonation-Induced Assembly of a Benzo[g]indolo[2,3b]quinoxaline Derivative

Hayden T. Black, Ian Pelse, Rylan M. W. Wolfe, and J. R. Reynolds\*

School of Chemistry and Biochemistry, School of Materials Science and Engineering, Center for Organic Photonics and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, GA, USA

\* Corresponding author: reynolds@chemistry.gatech.edu

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Materials and Instrumentation:

All materials were used as received unless otherwise stated. Reactions were carried out in dry glassware under a nitrogen environment. TBPAF<sub>6</sub> (Acros Organics, 98%) was recrystallized from ethanol prior to electrochemical experiments. UV-vis absorption measurements were acquired on a Varian Cary 5E UV-Vis-NIR spectrophotometer. The acid-dependent halochromism solution UV-vis measurements were carried out by adding an excess of concentrated acid (50  $\mu$ L) to a 1 x 10<sup>-5</sup> M solution of BIQ or BBIQ-T in either DCM. Titrations of BBIQ-T were carried out by step-wise addition of concentrated acid solutions to a 1 x 10<sup>-5</sup> M solution in DCM. Solution fluorescence measurements were acquired on a HORIBA Jobin Yvon Fluorolog coupled to an iHR320 Imaging Spectrometer using an excitation wavelength of 450 nm.

Thin films for UV-vis and fluorescence measurements were cast on clean 1" square glass slides, cleaned sequentially in an ultrasonicator with a water/SDS solution (followed by a water rinse), acetone, then isopropanol for 10 minutes each. Drop-cast films were prepared by dropping a 1 x  $10^{-5}$  M solution in DCM (with or without addition of TFMSA) onto a clean glass slide and allowing the film to dry in air. Blade coated films were made from 70 µL of a 20 mg/mL solution in 1,2-dichlorobenzene, coated at 8 mm/s with a 150 µm blade gap. Glass substrates were kept warm during deposition (~35°C). For thin film fluorescence, excitation/emission slits were set so the peak intensity was ~1 million counts, using an excitation wavelength of 430 nm for BBIQ-T.

In situ UV/vis: To a cuvette equipped with a stir bar was added 3.5 mL of  $10^{-5}$  M solution of BBIQ-T in DCM. UV/vis spectra was taken on an Ocean Optics fiber optic spectrometer, with a scan rate set to 100 milliseconds. After ~10 seconds, 50 µL of concentrated TFMSA, H<sub>2</sub>SO<sub>4</sub>, or HCl was added to the cuvette and spectra were continuously acquired for ~ 15 min.

CV: Electrochemistry was performed in a three-electrode cell with a platinum flag as the counter electrode, an Ag/Ag+ reference electrode, and a platinum button as the working electrode. An EG&G PAR 273 potentiostat was used under the control of CorrWare software. The electrolyte used was 0.5 M TBAPF<sub>6</sub> in propylene carbonate. A film was dropcast onto a clean, polished platinum button from a  $10^{-5}$  M solution of BBIQ-T. Measurements were taken at a scan rate of 50 mV/s.

Optical Microscopy: Silicon substrates were scrubbed with isopropanol and sonicated with the same for 10 minutes. Substrates were then blown dry with Argon. Precipitate suspensions were made from ~4 mL solutions of  $10^{-5}$  M BBIQ-T in DCM with 50 uL of concentrated TFMSA, H<sub>2</sub>SO<sub>4</sub>, or HCl, which were sealed in vials and shaken vigorously. Suspensions were allowed to equilibrate and precipitate for ~1 hour. The homogeneous solution was decanted with a pipette, leaving behind the precipitate, and DCM was added to further dilute the solution relative to the insoluble precipitates. 100 µL of the precipitate/DCM suspension was dropcast on the cleaned silicon substrates, left to dry overnight, then further dried in a 160 °C vacuum oven for ~3 hours.

Theoretical Calculations: Density functional theory calculations were carried out at the B3LYP/6-31G+(d,p) level for BIQ species and B3LYP/6-31G(d,p) level for BBIQ-T species. Optimized structures were determined for each protonation state and used to generate frontier molecular orbitals plots. These structures were used as inputs for time dependent calculations at the same level of theory using 15 singlet states. Simulated UV-Vis spectra were generated using GaussView with 0.333 eV half-width at halfheight broadening.



**6-bromo-1-dodecylindoline-2,3-dione:** Following a general procedure, to a dry round bottom flask was added K<sub>2</sub>CO<sub>3</sub> (1.15 g, 8.3 mmol), 6-bromoisatin (1.50 g, 6.6 mmol) and 50 mL anhydrous DMF. Tetrabutylammonium bromide (0.26 g, 0.81 mmol) and 1-bromododecane (1.65 g, 6.6 mmol) were then added and the reaction was warmed to 50 °C and allowed to stir overnight. The reaction was then cooled to room temperature and added to a separatory funnel along with 200 mL of H<sub>2</sub>O. The product was then extracted with diethyl ether (3 x 50 mL) and washed with H<sub>2</sub>O (4 x 75 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The product was purified via flash chromatography on silica gel using 10:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes as eluent to afford a yellow solid (1.54 g, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.45 (1H, d, *J* = 8 Hz), 7.27 (1H, dd, *J* = 8, 2 Hz), 7.05 (1H, d, *J* = 2 Hz), 3.68 (2H, t, *J* = 7 Hz), 1.68 (2H, p, *J* = 7 Hz), 1.34-1.38 (4H, m), 1.25 (14H, m, b), 0.87 (3H, t, *J* = 7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 182.2, 157.9, 151.8, 133.4, 126.7, 126.3, 116.2, 113.7, 40.4, 31.8, 29.5, 29.4, 29.3, 29.2, 29.0, 27.1, 26.8. HRMS-EI<sup>+</sup> (m/z) calculated for C<sub>20</sub>H<sub>28</sub>BrNO<sub>2</sub>: 393.1303, found: 393.1307 (M<sup>+</sup>).



Figure S1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 6-bromo-1-dodecylindoline-2,3-dione.



Figure S2. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 6-bromo-1-dodecylindoline-2,3-dione.



**3-bromo-5-dodecyl-5H-benzo[g]indolo[2,3-b]quinoxaline:** To a 30 mL microwave reaction tube was added 6-bromo-1-dodecylindoline-2,3-dione (0.50 g, 1,3 mmol), naphthalene-2,3-diamine (0.20 g, 1.3 mmol) and 5 mL glacial acetic acid. The reaction was warmed to 150 °C in a microwave reactor and stirred for 20 min. The reaction was then cooled to room temperature and allowed to sit for 1 hr before filtering the reaction mixture over a Buchner funnel to collect the product as a dark yellow solid. The solid was washed with 50 mL of H<sub>2</sub>O and dried under vacuum to afford the pure product (0.56 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.85 (1H, s), 8.65 (1H, s), 8.30 (1H, d, *J* = 8 Hz), 8.14 (1H, d, *J* = 8 Hz), 8.10 (1H, d, *J* = 8 Hz), 7.51-7.59 (3H, m), 7.48 (1H, dd, *J* = 8, 2 Hz), 4.40 (2H, t, *J* = 7 Hz), 1.95 (2H, p, *J* = 7 Hz), 1.42 (4H, m), 1.23-1.27 (14H, m, b), 0.86 (3H, t, *J* = 7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 145.9, 145.7, 141.4, 137.4, 136.9, 133.2, 131.2, 128.2, 127.5, 127.3, 126.1, 125.9, 125.0, 124.6, 123.9, 123.8, 118.1, 112.4, 41.3, 31.8, 29.6, 29.5, 29.3, 29.2, 28.1, 26.9, 22.6, 14.1. HRMS-EI<sup>+</sup> (m/z) calculated for C<sub>30</sub>H<sub>34</sub>BrN<sub>3</sub>: 515.1936, found: 515.1935 (M<sup>+</sup>).



**Figure S3.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 3-bromo-5-dodecyl-5H-benzo[g]indolo[2,3-b]quinoxaline (BIQ).



**Figure S4.** <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) of 3-bromo-5-dodecyl-5H-benzo[g]indolo[2,3-b]quinoxaline (BIQ).



**2,5-bis(5-dodecyl-5H-benzo[g]indolo[2,3-b]quinoxalin-3-yl)thiophene:** To a dry 25 ml 3-neck round bottom flask was added 3-bromo-5-dodecyl-5H-benzo[g]indolo[2,3-b]quinoxaline (0.1 g, 0.19 mmol), 2,5-bis(trimethylstannyl)thiophene (0.037 g, 0.09 mmol), and 6 mL anhydrous DMF. The mixture was purged with argon for ten minutes, followed by addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (7 mg, 6 µmol). The reaction mixture was then purged with argon for an additional 15 min and then warmed to 90 °C and stirred overnight. After cooling to room temperature the orange precipitate was collected by filtration on a Buchner funnel and then washed with MeOH (60 ml). The solid was then recrystallized from CHCl<sub>3</sub> to afford the pure product as an orange solid (65 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 50 °C):  $\delta$  (ppm) 8.81 (2H, s), 8.60 (2H, s), 8.43 (2H, d, *J* = 8 Hz), 8.10 (2H, d, *J* = 8 Hz), 8.04 (2H, d, *J* = 8 Hz), 7.63 (2H, d, *J* = 8 Hz), 7.56 (2H, s, b), 7.52 (2H, s), 7.46-7.49 (4H, m), 4.49 (4H, t, *J* = 7 Hz), 2.04 (4H, p, *J* = 7 Hz), 1.43-1.56 (8H, m), 1.23-1.35 (28H, m), 0.85 (6H, t, *J* = 7 Hz). HRMS-MALDI, dithranol matrix, (m/z) calculated for C<sub>64</sub>H<sub>71</sub>N<sub>6</sub>S: 955.5461, found: 955.5485 ([M+H]<sup>+</sup>).



**Figure S5.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 50 °C) of 2,5-bis(5-dodecyl-5H-benzo[g]indolo[2,3-b]quinoxalin-3-yl)thiophene (BBIQ-T).



Figure S6. Solvatochromism of BBIQ-T.



**Figure S7.** Zoomed in view of UV/Vis spectra of BIQ in CHCl<sub>3</sub> (1 x  $10^{-5}$  M) after addition of different acids.



**Figure S8.** UV/Vis spectra of BBIQ-T in DCM  $(1.7 \times 10^{-5} \text{ M})$  before addition of trifluoromethanesulfonic acid (TFMSA) (yellow), after addition of 10 equivalents TFMSA (orange), and after addition of 700 equivalents TFMSA (red).



**Figure S9.** Conversion of BBIQ-T ( $1.0 \times 10^{-5}$ M in CHCl<sub>3</sub>) to the diprotonated state via sequential addition of trifluoroacetic acid (TFA).



Figure S10. UV/Vis spectra of BBIQ-T in DCM (1 x  $10^{-5}$ M) after addition of 50 µL concentrated TFA, HCl, and H<sub>3</sub>PO<sub>4</sub>.



**Figure S11.** DFT calculated HOMO/LUMO orbital topologies and HOMO-LUMO energy gaps for BBIQ-T, BBIQ-T-H<sup>+</sup>, BBIQ-T-H<sup>2+</sup>, BBIQ-T-H<sup>3+</sup>, and BBIQ-T-H<sup>4+</sup>.



**Figure S12.** TD-DFT Calculated UV-Vis spectra of neutral and protonated derivatives of (a) BIQ and (b) BBIQ-T.



Figure S13. Time-lapsed in-situ UV/Vis scans of BBIQ-T solutions in DCM (1.0 x 10<sup>-5</sup>M in  $CH_2Cl_2$ ) after addition of 50 µL of HCl (top) and  $H_2SO_4$  (bottom). Concentrated acid was added after  $\sim 10$  seconds. These experiments aided the visualization of spectral changes in the short time before precipitation. The addition of excess HCl or H<sub>2</sub>SO<sub>4</sub> led to the rapid transformation of neutral to diprotonated state (BBIQ-T-2H<sup>+</sup>  $\lambda_{max} \sim 560$  nm), followed by slower transitions to the unique states induced by the two acids. The second transition for the HCl treated solution possessed a clear isosbestic point and afforded a partially stable solution with limited precipitation over the course of  $\sim 20$  min. We speculate that this second transition may be due to a discrete dimer formation of the diprotonated BBIQ-T-2H<sup>+</sup>. On the other hand, the H<sub>2</sub>SO<sub>4</sub> treated solution undergoes a more complex evolution of peaks with continuous red-shift of the absorption and an eventual loss of intensity due to significant precipitation. This observation suggests the formation of BBIQ-T-4H<sup>+</sup> which then assembles into larger structures with delocalized electronic states. Unfortunately the TFMSA treated solution could not be studied via in-situ absorption experiments due to excessive scattering; however, we point out that the final spectrum acquired during titration of BBIQ-T with TFMSA is distinctive from the final states observed for HCl and H<sub>2</sub>SO<sub>4</sub> treated solutions.

## TFMSA



**Figure S14.** Optical microscope images of the precipitates of BBIQ-T after addition of TFMSA (top),  $H_2SO_4$  (bottom left), and HCl (bottom right).



**Figure S15.** Cyclic voltammogram of drop-cast BBIQ-T thin-film in propylene carbonate /  $TBAPF_6$  (0.5 M), showing one quasi reversible oxidation peak at + 0.47 V and one irreversible oxidation peak at + 0.79 V.



Figure S16. Images of BBIQ-T in DCM after addition of various acids.



**Figure S17.** Fluorescence spectra of BBIQ-T in  $CHCl_3$  before addition of acid, after addition of trifluoroacetic acid, and after recovery of the acidified solution by addition of triethylamine. The inlaid spectrum of the zoomed residual fluorescence of BBIQ-T after addition of trifluoroacetic acid shows the red-shift in fluorescence upon protonation.



**Figure S18**. On/off fluorescence switching characteristics of the BBIQ-T film in the presence of HCl vapour (cycles 1,3,5,7,9) and TEA vapour (cycles 2, 4, 6, 8, 10).