

SUPPORTING INFORMATION

Photoresponsive Compound as a Visible Sensor for Organophosphorus Nerve Agents

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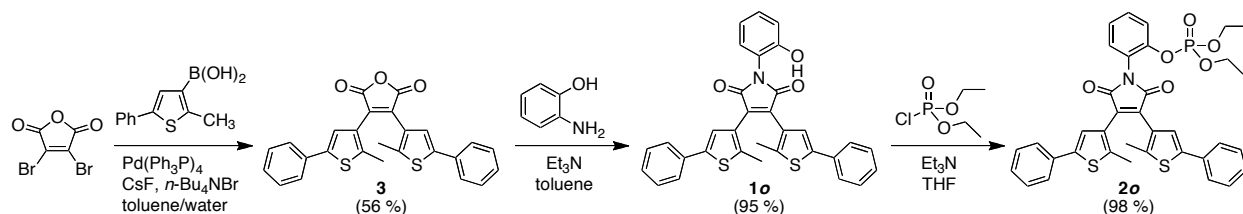
Materials and Methods

General. All solvents and reagents used for synthesis, chromatography and UV-vis spectroscopy were purchased from Aldrich and used as received, unless otherwise noted. Solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and used as received. Column chromatography was performed using silica gel 60 (230–400 mesh) from Silicycle Inc. All volumes for absorption studies and concentration measurements were measured out using an autopipette. The starting materials, 2-methyl-5-phenylthiophen-3-yl-boronic acid¹ and 3,4-dibromofuran-2,5-dione,² were prepared using published procedures.

Warning: Diethyl chlorophosphate (DCP) is highly toxic when in contact with skin, if swallowed or by inhalation. Extreme caution should be used while handling.

Instrumentation. ^1H NMR and ^{13}C NMR characterizations of all synthetic precursors to compound **1** were performed using a Bruker BioSpin 500 spectrometer with 32 scans per measurement. UV–vis absorption spectroscopy was performed using a Varian Cary 300 Bio spectrophotometer and a Varian Cary 100 Bio spectrophotometer. All chemical shifts are referenced to residual solvent signals, which were previously referenced to tetramethylsilane and splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). All solution-state studies of the photochemical ring-closing reactions of compounds **1o** and **2o** were carried out using the light source from a lamp used for visualizing TLC plates at 254 nm (Spectroline E-series, 470 W/cm²).

Synthetic Procedures



Synthesis of 3,4-bis(2-methyl-5-phenylthiophene-3-yl)furan-2,5-dione (3). A two-phase mixture of degassed toluene (20 mL) and degassed water (20 mL) was treated with 2-methyl-5-phenylthiophen-3-yl-boronic acid (654 mg, 3 mmol), CsF (608 mg, 4 mmol) and *n*-tetrabutylammonium bromide (100 mg, 0.3 mmol). This reaction was treated with 3,4-dibromofuran-2,5-dione (253 mg, 1 mmol) and Pd(PPh₃)₄ (115 mg, 0.1 mmol) and was stirred for 30 min under N₂. The reaction was heated to reflux, maintained there overnight, cooled to room temperature and poured in saturated aqueous NH₄Cl (100 mL). The mixture was extracted with ethylacetate (3 × 50 mL), the combined organic phases were dried with MgSO₄, filtered and

concentrated to dryness under vacuum. Purification by column chromatography using silica gel (10:1 hexanes:ethyl acetate) afforded 740 mg (56%) of the product as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.2$ Hz, 4H), 7.37 (dd, $J = 7.6, 7.2$ Hz, 4H), 7.31 (s, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 2.07 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 164.8, 143.0, 142.3, 133.6, 133.2, 129.0, 128.0, 126.5, 125.7, 123.6, 15.2.

HRMS (MH^+) expected: 442.0697; found: 442.0685.

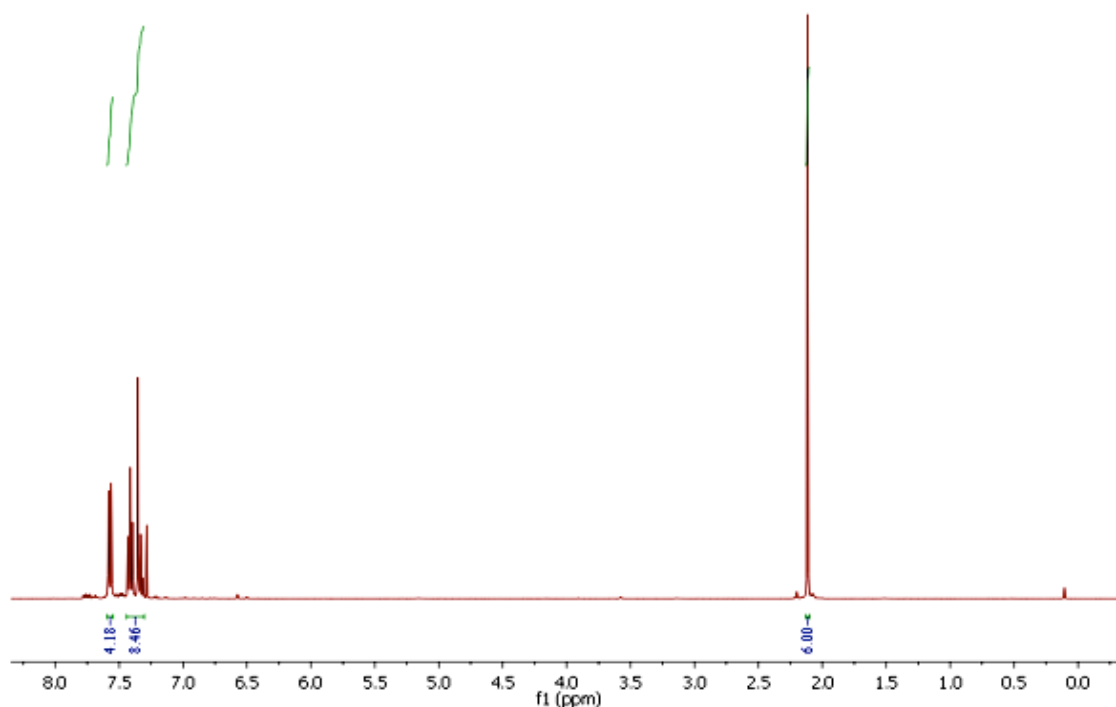


Figure S1. ^1H NMR spectrum of **3** in CDCl_3 .

Synthesis of 1-(2-hydroxyphenyl)-3,4-bis(2-methyl-5-phenylthiophen-3-yl)-1H-pyrrole-2,5-dione (1o). A solution of 3,4-bis(2-methyl-5-phenylthiophene-3-yl)furan-2,5-dione **3** (0.103 g, 0.232 mmol) in toluene (30 mL) was treated with *o*-aminophenol (0.028 g, 0.255 mmol) followed by triethylamine (0.1 mL). The reaction mixture was heated at reflux for 24 h using a Dean-Stark

condenser.³ The resulting solution was washed with brine, dried with MgSO₄, filtered and concentrated to dryness under vacuum to afford 124 mg (95 %) of the product as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.59-7.54 (m, 4H), 7.42-7.28 (m, 10H), 7.17-7.09 (m, 2H), 2.13 (s, 1H), 1.55 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 167.0, 150.8, 142.0, 133.6, 133.4, 130.0, 128.0, 127.8, 127.4, 125.6, 124.2, 121.7, 119.6, 76.7, 15.2.

HRMS (MH⁺) expected: 533.1119; found: 533.1109.

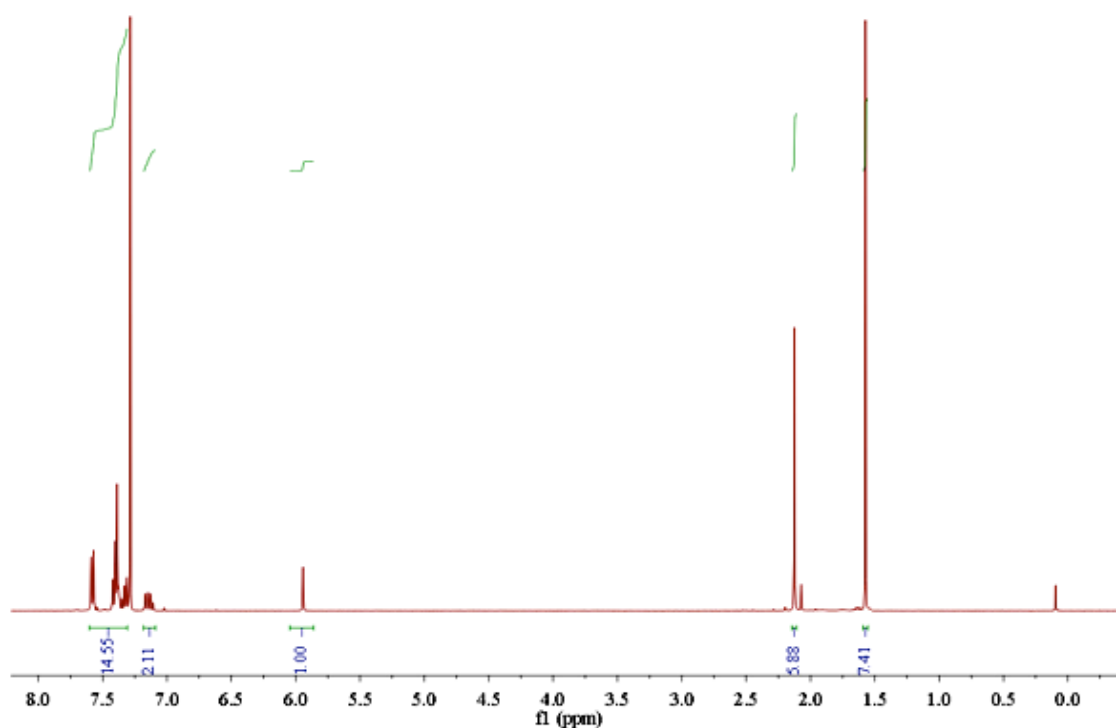


Figure S2. ¹H NMR spectrum of **1o** in CDCl₃.

Synthesis of diethyl (2-(3,4-bis(2-methyl-5-phenylthiophen-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-1yl)phenyl) phosphate (2o). A solution of 1-(2-hydroxyphenyl)-3,4-bis(2-methyl-5-phenylthiophen-3-yl)-1H-pyrrole-2,5-dione **1o** (23 mg, 0.04 mmol) and diethyl chlorophosphate

(0.01 mL, 2 mmol) in THF (10 mL) was treated with triethyl amine (0.01 mL, 0.08 mmol). The reaction mixture was stirred overnight⁴ at which time it was washed with 1M HCl. The aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL), the combined organic phases were washed with brine, dried with MgSO₄, filtered and concentrated to dryness under vacuum. Purification by column chromatography using silica gel (100:1 CH₂Cl₂:MeOH) afforded 26 mg (98%) of the product as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.68-7.66 (m, 2H), 7.60-7.55 (m, 2H), 7.48-7.25 (m, 12H), 4.25-4.10 (m, 4H), 2.18 (s, 6H), 1.30-1.24 (m, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 169.2, 141.5, 133.6, 133.2, 130.3, 130.3, 129.0, 127.7, 125.5, 125.5, 124.3, 121.0, 121.0, 77.2, 65.0, 64.9, 16.0, 16.0, 15.1.

HRMS (MH⁺) expected: 669.1409; found: 669.1401.

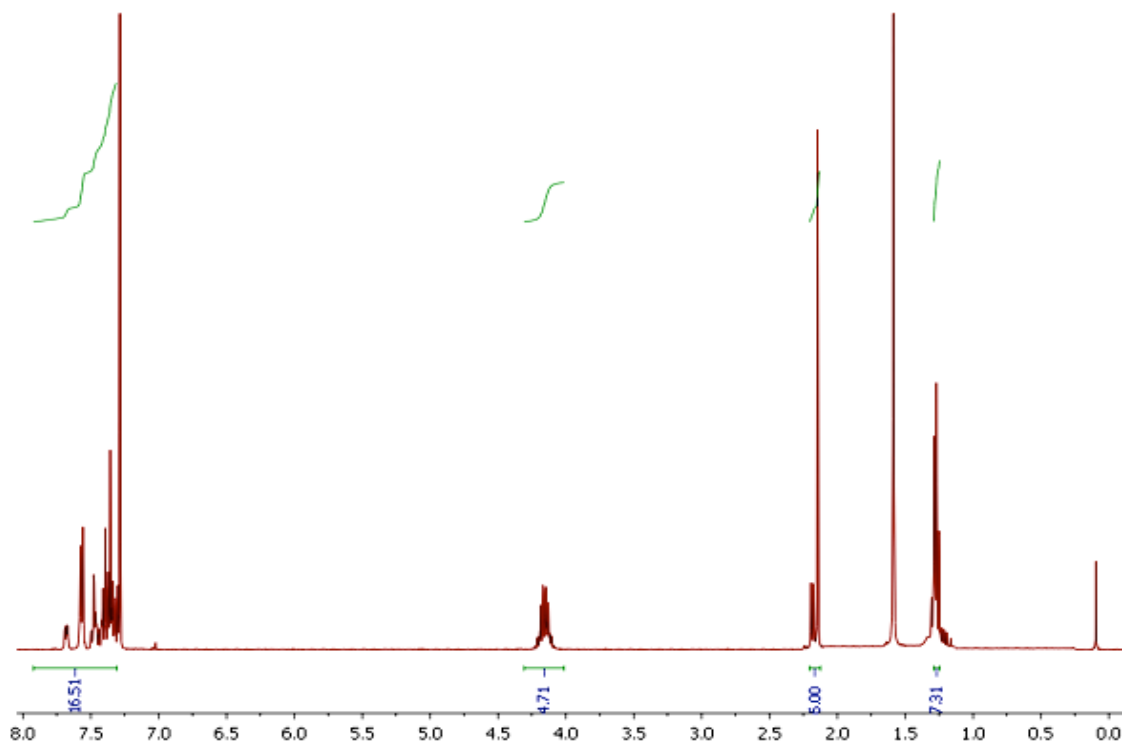


Figure S3. ¹H NMR spectrum of **2o** in CDCl₃.

Photochemical Ring-Closing of **1o** and **2o**.

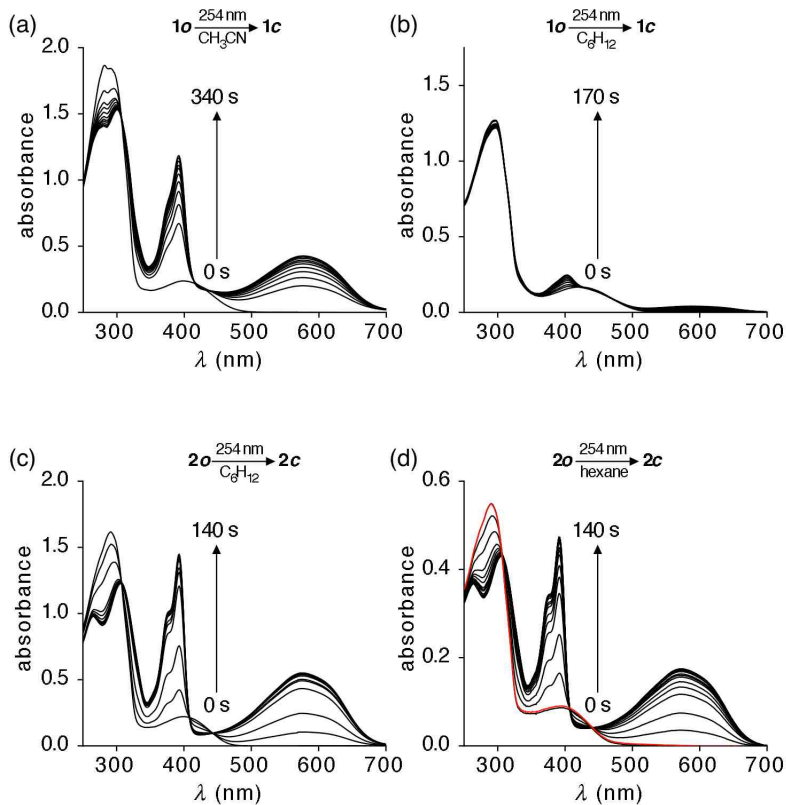
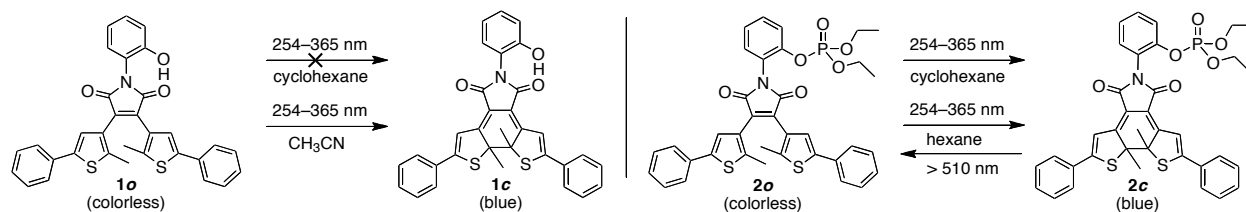


Figure S4. Changes in the absorption spectra of compounds (a) **1o** in CH₃CN (2.5×10^{-4} M), (b) **1o** in cyclohexane (1.5×10^{-4} M), (c) **2o** in cyclohexane (1.5×10^{-4} M) and (d) **2o** in hexane (5.4×10^{-5} M) when they are exposed to 254 nm light. The red line in (d) is the spectrum generated when the solution of **2c** is exposed to light at wavelengths greater than 510 nm.

¹ J. Kühni, V. Adamo, P. Belser, *Synthesis*, 2006, **12**, 1946-1948.

² S. V. Shorunov, F. M. Stoyanovich, M. M. Krayushkin. *Russ. Chem. Bull. Int. Ed.*, 2004, **53**, 2338-2339.

³ M. Ohsumi, T. Fukaminato, M. Irie, *Chem. Commun.*, 2005, 3921-3923.

⁴ T. J. Dale, J. Rebek, *J. Am. Chem. Soc.*, 2006, **128**, 4500-4501.