

# **Linked photoswitches where both photochromes open and close.**

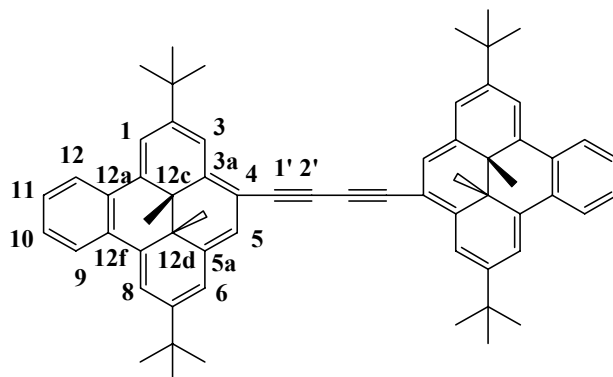
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**SUPPORTING INFORMATION**

## Synthesis of Photochrome 5



**5** (only one isomer shown)

Dichloro-*bis*-(triphenylphosphine)palladium (II) (14.1 mg, 0.02 mmol), CuI ( 4 mg, 0.02 mmol) and benzyl triethylammonium chloride (4 mg, 0.02 mmol) was added to a solution of the bromide **4**<sup>1</sup> (188mg, 0.40 mmol) and 2,7-dimethylocta-3,5-diyn-2,7-diol<sup>2</sup> (34 mg, 0.20 mmol) in dioxane (10 mL). The mixture was purged with argon for 20 min, and then aq. NaOH (5.5M, 4 mL) was added by syringe, and the reaction was heated under reflux for 2.5 h. After cooling to 20°C, excess of satd aq. NH<sub>4</sub>Cl was added, and stirring was continued for 30 min. The reaction mixture was then extracted with ether (3 x 50mL ), washed with water, dried over anhydrous sodium sulphate and evaporated to dryness. The dark brownish red residue was chromatographed over silica gel (60-200 mesh, deactivated with 3 wt, % NH<sub>4</sub>OH) using firstly hexane as eluant to elute unchanged bromide **4**, and then ether-hexane (1:1) to elute 102 mg (30%) of photochrome **5**. Recrystallization from cyclohexane yielded brownish-red crystals, mp 168-69 °C.

[NMR assignments were made by COSY, NOESY, HMQC and HSQC 2D expts]

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.74 – 8.70 (m, 4, H-9,12), 8.29 (d, *J* = 0.9 Hz, 2, H-1), 8.23 (d, *J* = 0.9 Hz, 2, H-8), 8.00 (d, *J* = 1.2 Hz, 2, H-3), 7.64 – 7.60 ( m, 4H, H-10, 11), 7.31 (s<sup>a</sup>, 2, H-6),

7.236 (note: CHCl<sub>3</sub> is at 7.240) (d,  $J = 0.7$  Hz, 2, H-5), 1.56 (s, 18, 2-C(CH<sub>3</sub>)<sub>3</sub>), 1.49 (s, 18, 7-C(CH<sub>3</sub>)<sub>3</sub>), -1.38 (s, 12c-CH<sub>3</sub>), -1.40 (s, 12d-CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.8 MHz)  $\delta$  148.38 (C-2), 145.66 (C-7), 144.77 (C-3a), 137.95 (C-12e), 137.55 (C-12b), 135.22 (C-5a), 129.75 (C-12f), 129.44 (C-12a), 126.56 and 126.33 (C-10,11), 124.85 and 124.75 (C-9,12), 122.68 (C-5), 119.55 (C-6), 118.63 (C-3), 117.72 (C-8), 117.52 (C-1), 112.32 (C-4), 83.90 (C-1'), 79.93 (C-2'), 37.11 (C-12c), 36.13 (2-C(CH<sub>3</sub>)<sub>3</sub>), 35.66 (7-C(CH<sub>3</sub>)<sub>3</sub>), 35.49 (C-12d), 30.88 (2-C(CH<sub>3</sub>)<sub>3</sub>), 30.76 (7-C(CH<sub>3</sub>)<sub>3</sub>), 18.25 (12c,d-CH<sub>3</sub>); UV (cyclohexane)  $\lambda_{\text{max}}$  nm ( $\epsilon_{\text{max}}$ ) 282 (19,300), 331 (15,000), 415 (23,500), 438 (16,400), 525 (6,830), tail to 700 nm; IR (KBr)  $\nu$  2214 cm<sup>-1</sup>; MS FAB  $m/z$  834.5 (M<sup>+</sup>); HRMS: Calcd for C<sub>64</sub>H<sub>32</sub>: 834.516. Found : 834.518. Attempted elemental analysis gave a carbon, 0.5% low, not uncommon with high C compounds.

<sup>1</sup> Sheepwash, M. A.; Ward, T. R.; Wang, Y.; Bandyopadhyay, S.; Mitchell, R. H.; Bohne, C. *Photochem. Photobiol. Sci.* **2003**, 2, 104-122.

<sup>2</sup> Sarkar, A.; Okada, S.; Nakanishi, H.; Matsuda, H. *Helv. Chim. Acta* **1999**, 82, 138-141.

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<sup>a</sup> Although H-6 appears as a singlet, COSY spectra indicate a small coupling to H-5 and H-8.

### Visible Opening to cyclophanediene form.

The dihydropyrene form, **C-C 5** (5 mg) in CDCl<sub>3</sub> (0.6 mL) in a quartz nmr tube (Wilmad, 535-PP-7QTZ), purged with argon and cooled by ice water was irradiated with a 500-W household tungsten-halogen lamp (Globe Electric, Montreal, Quebec, Canada, T-3, 8500 lumens) with an orange plastic filter (permits only light  $\lambda > 490$  nm to pass) between the lamp and the sample, until the color of the solution was pale yellow. The <sup>1</sup>H NMR spectrum was run at intervals, and showed no high field protons around  $\delta$  -1.5 when complete, about 20 mins.

The solution then contains essentially pure cyclophanediene form, **O-O 5**.  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.65-7.59 (m, 4), 7.41-7.34 (m, 4), 7.12 (s, 1), 7.11 (s, 1), 6.93 (s, 2), 6.90-6.84 (m, 4), 6.78 (2s, 2), 1.28 (s, 18), 1.24 (s, 18), 1.20 (s, 6), 1.17 (s, 6);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  151.45, 150.62, 143.96, 143.85, 142.37, 140.69, 140.23, 139.91, 138.91, 138.40, 135.99, 135.29, 129.61, 128.98, 128.92, 128.53, 124.47, 123.26, 123.00, 109.96, 86.91, 80.99, 34.51, 34.34, 32.16, 32.05, 31.53, 31.48, 29.92, 19.37, 18.69. This solution contains two diastereomers, however the internal  $\text{CH}_3$  and the external  $-\text{C}(\text{CH}_3)_3$  protons do not distinguish these. The spectra obtained at intermediate times showed mixtures of the O-O and C-C species to be present. The same spectra were observed when a red plastic filter (stops light  $\lambda < 590$  nm) was used. UV-vis spectra were obtained on  $3 \times 10^{-5}\text{M}$  solutions in cyclohexane - see text.

#### UV Closing to the dihydropyrene form

The above NMR sample was then irradiated with a low pressure Hg (Ar) pencil light (Oriel 6035) (254 nm) cooled with an electric fan, and the  $^1\text{H}$  NMR spectrum was recorded at intervals. The peaks of the **O-O** form were slowly replaced with those of the **C-C** form. No signals that could definitely be ascribed to an intermediate **O-C** form could be seen (even though it can be seen in UV-vis spectra, see text), but because two diastereomers are present, and because no large shift changes of either the closed or the open parts of **O-C** are expected from **O-O** or from **C-C** respectively, the increased broadness of the peaks due to the number of isomers, may prevent useful information from being obtained by NMR. We also attempted irradiation in  $\text{d}_6$ -benzene, but again no additional peaks could be seen. UV-vis spectra were obtained on  $3 \times 10^{-5}\text{M}$  solutions in cyclohexane - see text.