

ADVANCED MATERIALS

Supporting Information

for

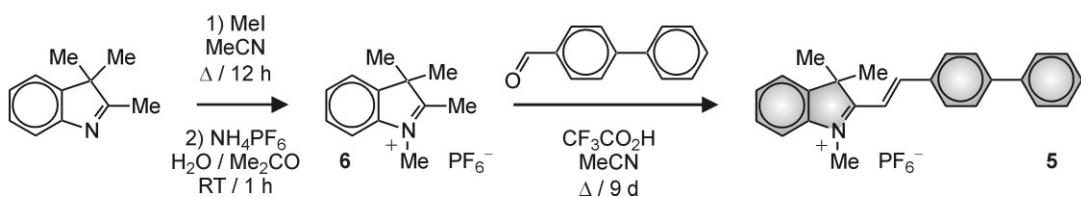
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Supporting Information

Amplification of the Coloration Efficiency of Photochromic Oxazines

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1,3,3-Trimethyl-2-(4-phenylphenylene)ethylene-3H-indolium (5) Hexafluorophosphate. A solution **6** (50 mg, 0.2 mmol), 4-biphenylcarboxaldehyde (41 mg, 0.2 mmol) and $\text{CF}_3\text{CO}_2\text{H}$ (24 μL , 0.03 mmol) in MeCN (20 mL) was heated under reflux and Ar for 9 d. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The solid residue was purified by column chromatography (SiO_2 : hexane / MeCO_2Et (2:1, v/v) \rightarrow MeCO_2Et / MeOH (3:1, v/v) to afford **5** (52%, 40 mg) as a yellow solid. FABMS: m/z = 338 [$\text{M} - \text{PF}_6^-$] $^+$; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 1.85 (6H, s), 4.39 (3H, s), 7.42–7.45 (1H, m), 7.50 (2H, t, 8 Hz), 7.56–7.65 (4H, m), 7.68 (2H, d, 8 Hz), 7.80 (2H, d, 8 Hz), 7.94 (1H, d, 16 Hz), 8.11 (2H, d, 8 Hz), 8.21 (1H, d, 16 Hz); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ = 27.1, 35.1, 52.9, 112.4, 115.0, 122.9, 127.7, 128.5, 129.5, 130.2, 130.3, 131.8, 133.6, 139.8, 141.7, 143.3, 146.9, 154.9, 182.7.

1,2,3,3-Tetramethyl-3H-indolium (6) Hexafluorophosphate. A solution of 2,3,3-trimethyl-3H-indole (200 μL , 1.3 mmol) and MeI (100 μL , 1.6 mmol) in PhMe (20 mL) was heated at 80°C for 12 h under N_2 . After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in hexane (20 mL), sonicated for 30 min and filtered off to afford the iodide salt of **6** (84%, 0.33 g) as a purple solid. FABMS: m/z = 174 [$\text{M} - \text{I}$] $^+$; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 1.69 (6H, s), 3.13 (3H, s), 4.30 (3H, s), 7.55–7.58 (2H, m), 7.59–7.62 (2H, m), 7.66–7.67 (1H, m); $^{13}\text{C-NMR}$ (100 MHz, CD_3CN): δ = 14.5, 21.9, 35.3, 54.8, 115.4, 123.7, 129.6, 130.3, 142.1. A solution of NH_4PF_6 (0.75 g, 5 mmol) in H_2O (5 mL) was added to a solution of the iodide salt of **6** (1.38 g, 5 mmol) in Me_2CO (30 mL). The mixture stirred for 1 h, concentrated to ca. 10 mL under reduced pressure and cooled down to 5°C. The resulting precipitate was filtered to give the hexafluorophosphate salt of **6** (95%, 1.40 g) as a pink solid.