

## Supporting Information

### Simultaneous fluorescence and redox modulation in an irreversible photochrome based on a strained dibenzo-acridinium cation

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#### Experimental

All chemicals were purchased from commercial sources and were used as received. Solvents for synthesis were dried by standard literature methods before being distilled and stored under nitrogen over 4Å molecular sieves. High quality spectroscopic grade and dry acetonitrile and Me-THF were purchased in Sure Seal® bottles and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a JEOL Lambda 500 MHz or Bruker AVANCE 300 MHz spectrometers. Deuterated acetonitrile (CD<sub>3</sub>CN) as always showed a resonance corresponding to water. The solvent was distilled from P<sub>2</sub>O<sub>5</sub> before use. Routine mass spectra and elemental analyses were obtained using in-house facilities.

Cyclic voltammetry experiments were performed using a fully automated HCH Instruments Electrochemical Analyzer, and a three electrode set-up consisting of a glassy carbon working electrode, a platinum wire counter electrode and a Ag wire reference electrode. All experiments were performed in dry CH<sub>3</sub>CN containing *N*-tetrabutylammonium hexafluorophosphate (0.2 M) as background electrolyte. Ferrocene was used as the redox standard and potentials were rescaled to SCE using the conversion factor Fc/Fc<sup>+</sup> = +0.45 V vs SCE.

Absorption spectra were recorded with an Hitachi U3310 spectrometer while corrected fluorescence spectra were recorded with an Hitachi F4500 spectrophotometer. All fluorescence measurements were made using optically dilute solutions and were corrected for spectral imperfections of the instrument by reference to a standard lamp. Time-resolved fluorescence measurements were made with a Spex Fluorolog tau-3 spectrophotometer.

Spectroscopic kinetic measurements were made in a 1cm quartz cuvette equipped with a gas bubbler. In a typical experiment a solution of **Ph-RO-Acr**<sup>+</sup> in dry acetonitrile was purged with either N<sub>2</sub>, O<sub>2</sub> or air, and irradiated for fixed time periods with white light using a glass filter to remove UV radiation. Sample concentrations were typically in the order of 10<sup>-6</sup> M.

#### Preparation of 7,14-diphenyl-7,14-dihydrodibenzo[a,j]acridine (1)

To a 500 ml flask was added *N*-phenyl-2-naphthylamine (14g, 64 mmol), 2-naphthol (9.4g, 65 mmol), benzaldehyde (6.8g, 64 mmol) and glacial acetic acid (250 ml). The mixture was stirred vigorously and refluxed overnight. Upon cooling an orange precipitate formed which was filtered off, dried and recrystallised from toluene to afford a white solid which was dried under vacuum (6.1g, 22% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 6.69-6.73 (d, 2H, *J* = 9 Hz), 6.89 (s, 1H), 6.91-6.94 (t, 1H, *J* = 6

Hz), 7.03-7.08 (t, 2H,  $J = 6$  Hz), 7.23-7.28 (t, 2H,  $J = 9$  Hz), 7.36-7.54 (m, 9H), 7.59-7.62 (d, 2H,  $J = 6$  Hz), 7.64-7.67 (d, 2H,  $J = 9$  Hz), 8.43-8.46 (d, 2H,  $J = 9$  Hz). EI-MS  $m/z$  calc. (fnd.) for  $C_{33}H_{23}N$  433.1831 (433.1813).

#### Preparation of 7,14-diphenyl-7,14-dihydrodibenzo[a,j]acridin-14-ol (**2**)

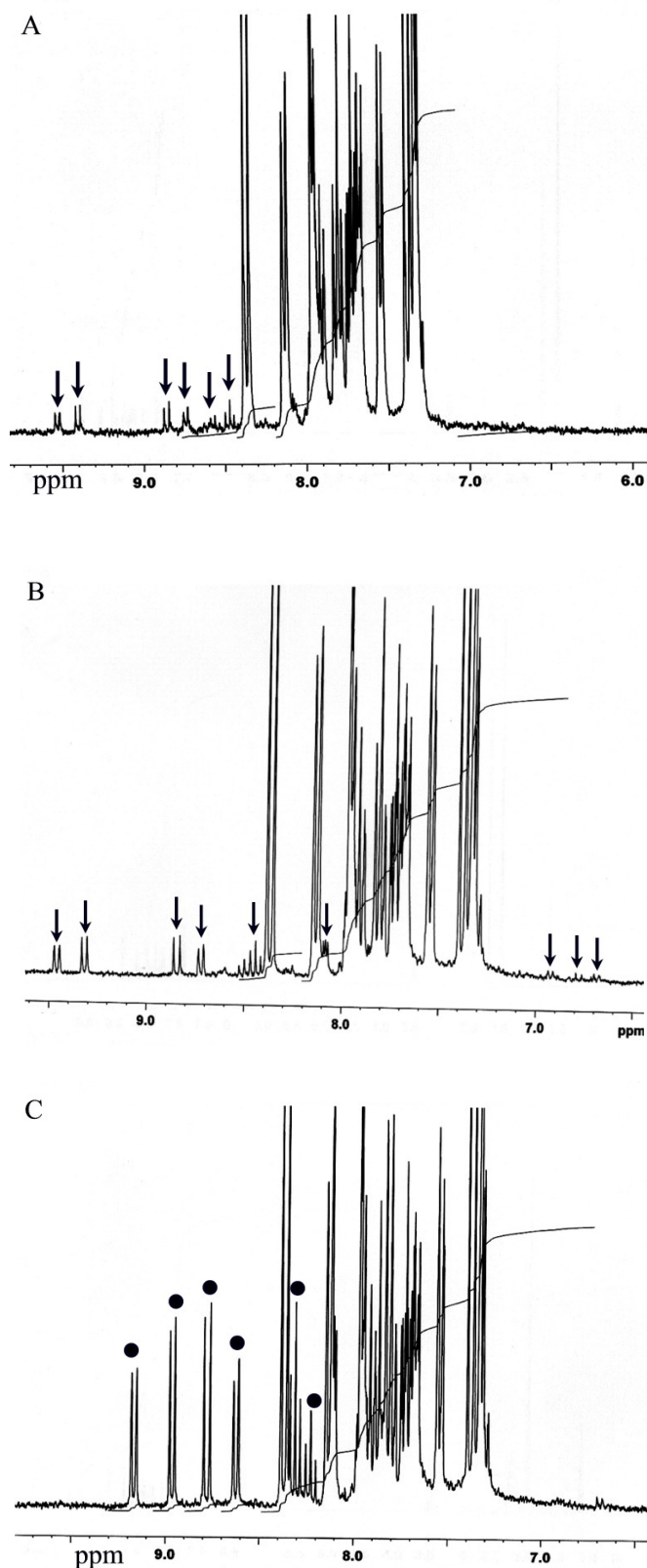
To a solution of compound **1** (5g, 11.5 mmol) dissolved in glacial acetic anhydride (250 ml) was added  $MnO_2$  (2g, 23 mmol). The reaction flask was protected from light and the mixture bubbled with HCl gas and refluxed for 1hr. Whilst the solution was still hot the  $MnO_2$  was filtered off and the reaction mixture cooled to room temperature. Addition of  $Et_2O$  precipitated a solid which was filtered off, dried under vacuum and recrystallised from acetone to afford a white solid of the desired compound (1.0g, 20% yield). The remaining  $Et_2O$ /acetic anhydride solution was removed on a rotary evaporator and the crude product could also be used in the next step.

#### Preparation of 7,14-diphenyldibenzo[a,j]acridinium hexafluorophosphate (**Ph-ROAc**<sup>+</sup> $PF_6^-$ )

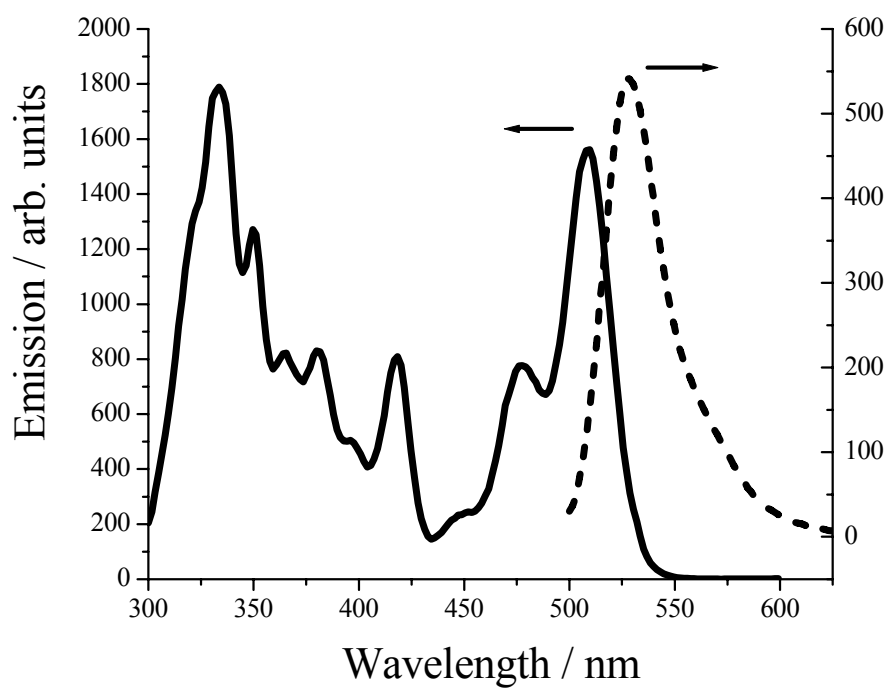
To a solution of **2** (0.5g, 1.1 mmol) in glacial acetic acid (20 ml) was added a few drops of conc HCl. The mixture was stirred for 5 mins. and  $Et_2O$  added slowly to afford a yellow/green solid which was filtered off and dried. The yellow product was dissolved in hot water (50 ml), filtered to remove black insoluble material, and a saturated solution of  $KPF_6$  (aq) added. The resultant bright yellow precipitate was filtered off, dried and recrystallised from  $CH_3CN/ Et_2O$  to afford golden yellow needles (287mg, 45% yield).  $^1H$  NMR (500MHz,  $CD_3CN$ )  $\delta = 7.27-7.34$  (m, 4H), 7.34-7.36 (d, 2H,  $J = 9.5$  Hz), 7.51-7.53 (d,d 2H,  $J = 8.2$  Hz,  $J' = 1.2$  Hz), 7.63-7.765 (m, 2H), 7.68-7.71 (t,d, 2H,  $J = 7.2$  Hz,  $J' = 1.5$  Hz) 7.76-7.79 (t, 2H,  $J = 7$  Hz), 7.86-7.94 (m, 4H), 8.09-8.11 (d, 2H,  $J = 8.6$  Hz), 8.33-8.35 (d, 2H,  $J = 9.5$  Hz).  $^{13}C$  NMR ( $CD_3CN$ ). 125.1, 127.9, 128.2, 128.9, 129.0, 129.2, 129.3, 130.0, 130.9, 131.5, 131.6, 131.9, 132.6, 138.7, 140.2, 140.8, 143.0. (Note : some resonances are missing because of overlap). ES-MS ( $CH_3CN/MeOH$ )  $m/z$  calc. (fnd.) 432.2 (432.2)  $[M-PF_6]^+$ . CHN analysis calc. (fnd) for  $C_{33}H_{22}NPF_6 \cdot 0.75H_2O$  C, 67.07(67.59); H, 4.00(4.44); N, 2.37(2.76)%.

#### Preparation of **Ph-RCAc**<sup>+</sup>

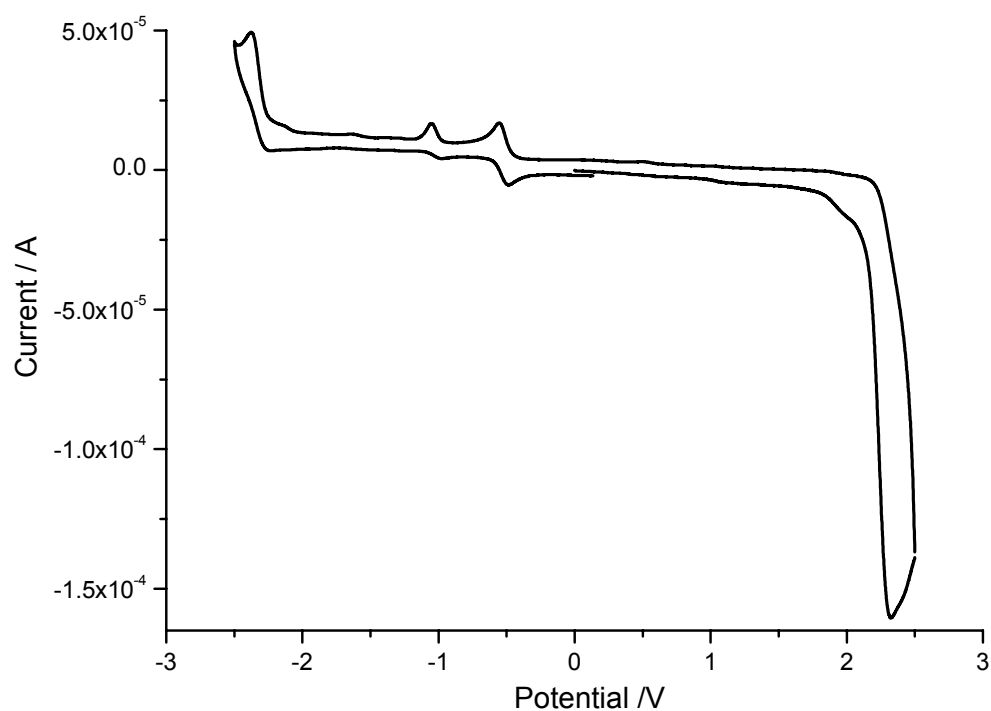
A solution of **Ph-ROAc**<sup>+</sup> (10mg, 0.017 mmol) in MeCN (1 ml) was bubbled with air and left exposed to sunlight for several hours. The product was precipitated out by slow vapour diffusion of dry  $Et_2O$  to afford dark red crystals (9.6mg, 98% yield).  $^1H$  NMR (500 MHz,  $CD_3CN$ )  $\delta = 7.79-7.82$  (m, 4H), 8.08-8.09 (m, 3H), 8.12-8.15 (t, 1H,  $J = 8$  Hz), 8.24-8.27 (t, 2H,  $J = 7.6$  Hz), 8.57-8.61 (d, 2H,  $J = 7.6$  Hz), 8.73-8.74 (d, 2H,  $J = 9.2$  Hz), 8.85-8.87 (d, 2H,  $J = 8$  Hz), 9.07-9.08 (d, 2H,  $J = 7.6$  Hz). ES-MS ( $CH_3CN/MeOH$ )  $m/z$  calc. (fnd.) 428.1 (428.3)  $[M-PF_6]^+$ . CHN analysis calc. (fnd) for  $C_{33}H_{18}NPF_6$  C, 69.12(68.80); H, 3.16(3.40); N, 2.44(2.80)%.



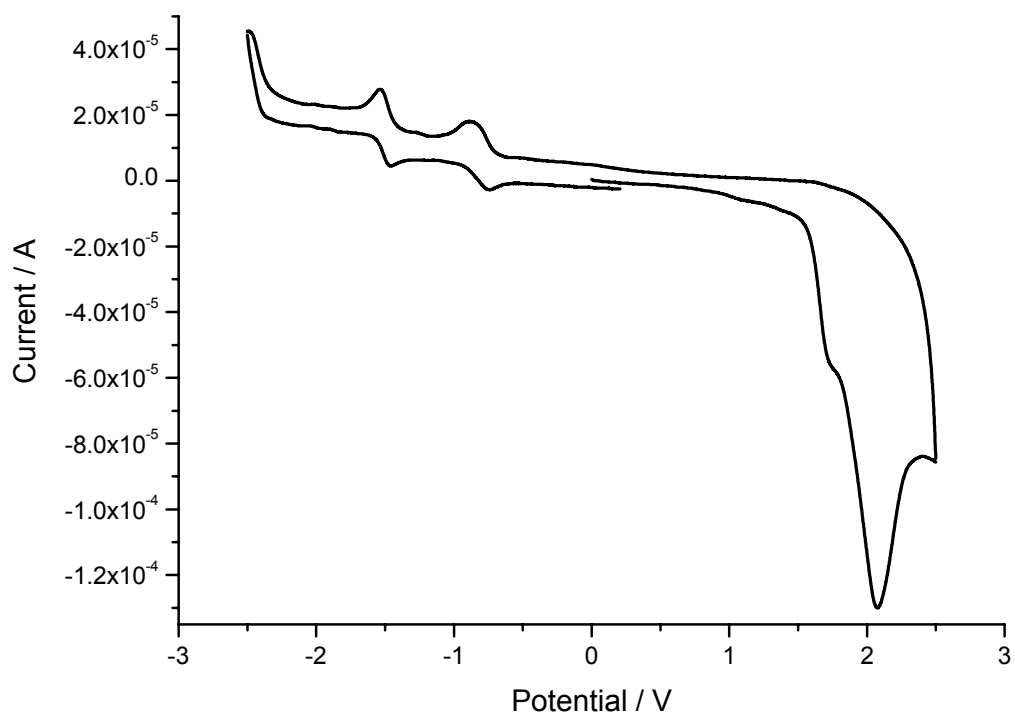
**S1.** Selected 300MHz  $^1\text{H}$  NMR spectra of  $\text{Ph-ROAc}^+$  in air-equilibrated  $\text{CD}_3\text{CN}$  following irradiation at time differences  $t = 30$  mins (**A**),  $t = 1$  h (**B**) and  $t = 7$ h (**C**). Arrows in panel **A** and **B** mark new resonances. In panel **C**,  $\bullet$  represent resonances associated with the final product.



**S2.** Excitation (-) and fluorescence (---) spectra recorded for **Ph-RCr<sup>+</sup>** in N<sub>2</sub>-purged dry acetonitrile at 25 °C.



**S3.** Cyclic voltammogram for **Ph-ROAc<sup>+</sup>** in dry CH<sub>3</sub>CN containing 0.2 M TBAHFP background electrolyte. Glassy carbon working electrode and 100 mV s<sup>-1</sup> scan rate.



**S4.** Cyclic voltammogram obtained after irradiating **Ph-ROAc<sup>+</sup>** with white light in dry CH<sub>3</sub>CN containing 0.2 M TBAHFP background electrolyte. Glassy carbon working electrode and 100 mV s<sup>-1</sup> scan rate.

