Supplementary Information for:

Photophysical properties and electronic structure of retinylidene–chlorin–chalcones and analogues

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Experimental methods

Synthesis procedures and characterization

13-[(*2E*,*4E*,*6E*,*8E*,*10E*)-5,9-dimethyl-1-phenyl-11-(2,6,6-trimethylcyclohex-1-enyl)undeca-2,4,6,8,10-pentaen-1-one (I). The synthesis was carried out via traditional heating as well as via microwave heating. In both cases, an excess of all-*trans*-retinal (1.5 equiv) was found to be desirable to completely consume acetophenone given the similar polarity of acetophenone and title compound upon chromatographic purification.

Traditional thermal route: Following a procedure for aldol condensation of retinal,[20] a solution of acetophenone (60 mg, 0.50 mmol), all-*trans*-retinal (213 mg, 0.75 mmol), and potassium *tert*-butoxide (112 mg, 1.00 mmol) in anhydrous ethanol (20 mL) was refluxed under argon. After 3 h, the solution was concentrated to dryness under reduced pressure. The resulting crude product was dissolved in CH_2Cl_2 (30 mL) and washed with a saturated aqueous solution of NH_4Cl (30 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. Two column chromatography procedures [silica, hexane/diethyl ether (1:0) → (10:1)] afforded a light-sensitive, red, oily liquid (38.5 mg, 20%).

Microwave route: The synthesis was carried out under microwave irradiation using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC), which was equipped with an infrared sensor for temperature monitoring. The reaction vessel was an 80-mL crimp-sealed thick-wall glass tube equipped with magnetic stir bar and a pressure sensor. Following a procedure for formation of hydroporphyrin–chalcones,[16] samples of acetophenone (120 mg, 1.00 mmol), all-*trans*-retinal (425 mg, 1.50 mmol), NaOH (800 mg, 2.00 mmol) and absolute ethanol (60 mL) were added to the reaction vessel. The vessel was sealed with a septum, stirred magnetically, and subjected to microwave irradiation at 40 W with the following protocol: (1) heat from room temperature to 80 °C (irradiate for 2 min), (2) hold at 80 °C (irradiate for 18 min), (3) allow to cool to room temperature (~2 min), (4) check the reaction mixture by TLC analysis, and (5) repeat once. The total time for irradiation was 40 min. The reaction mixture was concentrated under reduced pressure. The resulting crude product was dissolved in CH_2Cl_2 and washed with a saturated aqueous solution of NH_4Cl. The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatography [silica, hexanes/diethyl ether (1:0) → (9:1)] afforded a light-sensitive, red, oily liquid (286 mg, 74%).

Data for the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 6H, 1-CH_3), 1.44–1.50 (m, 2H, 2-CH_2), 1.58–1.64 (m, 2H, 3-CH_2), 1.73 (s, 3H, 5-CH_3), 1.98–2.06 (m, 2H, 4-CH_2), 2.01 (s, 3H, 9-CH_3), 2.13 (s, 3H, 13-CH_3), 6.16 (d, J = 16.1 Hz, 1H, 8-H), 6.18 (d, J = 11.7 Hz, 1H, 10-H), 6.27 (d, J = 16.1 Hz, 1H, 7-H), 6.38 (d, J = 12.1 Hz, 1H, 14-H), 6.41 (d, J = 15.0 Hz, 1H, 12-H), 6.89 (dd, J = 15.0, 11.7 Hz, 1H, 11-H), 7.01 (d, J = 14.7 Hz, 1H, 16-H), 7.44–7.51 (m, 2H, Ar-H), 7.52–7.58 (m, 1H, Ar-H), 7.91 (dd, J = 14.7, 12.1 Hz, 1H, 15-H),

7.95–7.99 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 13.6, 19.5, 22.0, 29.2, 33.4, 34.5, 39.8, 128.3, 128.5, 128.8, 129.3, 129.7, 129.9, 130.2, 130.4, 132.7, 136.3, 137.7, 138.0, 138.8, 139.1, 140.9, 146.7, 190.6; ESI-MS obsd 387.2686, calcd 387.2682 [$(M + H)^+$, M = $C_{28}H_{34}O$]; λ_{abs} (toluene) = 423 nm (ε = 37,400 $M^{-1}cm^{-1}$).

13-Acetyl-17,18-dihydro-10-mesityl-18,18-dimethylporphyrin (FbC-A). A solution of **ZnC-A** (3.5 mg, 6.2 μmol) in anhydrous CH_2Cl_2 (3.1 mL) was treated with TFA (25 μL). The mixture was stirred for 1 h at room temperature. The reaction mixture was quenched by addition of 10% aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic extract was washed with water, dried (Na_2SO_4), and filtered. The filtrate was concentrated. Purification on a short column [silica, CH_2Cl_2/hexanes (3:1)] afforded a brown purple solid (2.8 mg, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ –1.50 to –1.32 (br, 1H), –1.18 to –1.02 (br, 1H), 1.86 (s, 6H), 2.02 (s, 6H), 2.63 (s, 3H). 4.59 (s, 2H), 7.26 (s, 2H, overlap with resonance from $CHCl_3$), 8.37 (d, *J* = 4.3 Hz, 1H), 8.74 (s, 1H), 8.75 (d, *J* = 4.3 Hz, 1H), 8.85 (d, *J* = 4.7 Hz, 1H), 8.90 (s, 1H), 9.10 (d, *J* = 4.7 Hz, 1H), 9.56 (s, 1H), 10.07 (s, 1H); LD-MS obsd 500.13, calcd 500.26 ($C_{33}H_{32}N_4O$); λ_{abs} (CH_2Cl_2) 414, 657 nm; λ_{em} (CH_2Cl_2) 660 nm. The data are in accord with those for the title compound derived from acidic demetalation of 13-bromo-17,18-dihydro-10-mesityl-18,18-dimethylporphinatozinc(II), Pd-mediated coupling of the resulting free base chlorin with tributyl(1-ethoxyvinyl)tin, and subsequent acid hydrolysis of the ethoxyvinyl substituent.[16]