

Accessory Information

Photoswitchable Sensitization of Porphyrin Excited States

Stephen D. Straight,^A Yuichi Terazono,^A Gerdenis Kodis,^A Thomas A. Moore,^{A,B}

Ana L. Moore^{A,B} and Devens Gust^{A,B}

^A Department of Chemistry and Biochemistry, Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, AZ 85287-1604, USA

^B Corresponding authors. Email: gust@asu.edu, tom.moore@asu.edu, amoore@asu.edu

Instrumental Techniques.

The ¹H NMR spectra were recorded on Varian Unity spectrometers at 300 MHz. Samples were dissolved in deuteriochloroform with tetramethylsilane as an internal reference. Mass spectra were obtained on a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). The solvent for all spectroscopic measurements was freshly distilled 2-methyltetrahydrofuran, unless otherwise stated. All samples were deoxygenated by bubbling with argon for 15 min unless otherwise stated. Ground-state absorption spectra were measured on a Shimadzu UV-3101PC UV-vis-NIR spectrometer. Steady-state fluorescence emission spectra were measured using a Photon Technology International MP-1 fluorimeter and corrected. Excitation was produced by a 75 W xenon lamp and a single grating monochromator. Fluorescence was detected at 90° to the excitation beam via a single grating monochromator and an R928 photomultiplier tube having S-20 spectral response and operating in the single-photon-counting mode.

Fluorescence decay measurements were performed on $\sim 1 \times 10^{-5}$ M solutions by the time-correlated single-photon-counting method. The excitation source was a cavity-dumped Coherent 700 dye laser pumped by a frequency-doubled Coherent Antares 76s Nd:YAG laser or directly by the Nd:YAG laser as specified. Fluorescence emission was detected at a magic angle using a double grating monochromator and microchannel plate photomultiplier (Hamamatsu R2809U-11). The instrument response time was ca. 35-120 ps, as verified by scattering from Ludox AS-40 at the excitation wavelength.

The femtosecond transient absorption apparatus consisted of a kilohertz pulsed laser source and a pump-probe optical setup. Laser pulses of 100 fs at 800 nm were

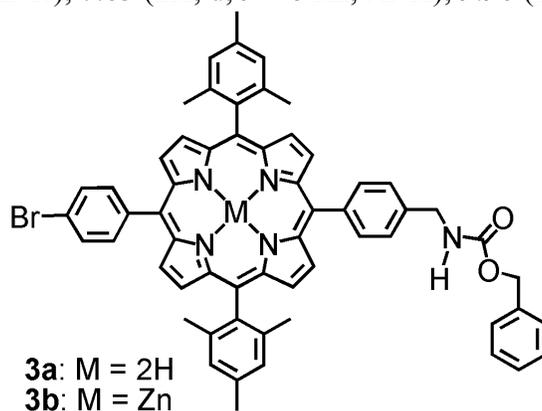
generated by an amplified, mode-locked titanium sapphire kilohertz laser system (Millennia/Tsunami/Spitfire, Spectra Physics). Part of the laser pulse energy was sent through an optical delay line and focused on a 2 mm sapphire plate to generate a white light continuum for the probe beam. The remainder of the pulse energy was used to pump an optical parametric amplifier (Spectra Physics) to generate excitation pulses, which were modulated using a mechanical chopper. The excitation intensity was adjusted using a continuously variable neutral density filter. The probe beam was sent through a monochromator (SP150, Action Res. Corp.) and recorded by a diode detector (Model 2032, New Focus Inc.) and box car integrator (SR250, Stanford Research Systems).

The photoisomerizations of the fulgimides were performed using a UVP hand-held UV lamp model UVGL-25 (366 nm, 1.5 mW/cm² at the sample) or with an ORIEL Corp. model 66028 Xe/HgXe lamp. Illumination from the Xe/HgXe lamp was passed through water cooled double IR filters ($A = 1.8$ and 2.3 at 900 and 970 nm, respectively), and in addition appropriate filters were used to obtain the desired wavelength region. Broad spectrum visible light ($450 \text{ nm} < \lambda < 650$) was obtained using an Ednalite G medium green filter; the power density of the resulting light at the sample was $\sim 10.5 \text{ mW/cm}^2$.

Synthesis.

Preparation of [(4-cyanophenyl)methyl]-carbamic acid phenylmethyl ester has been described previously.^{1,2}

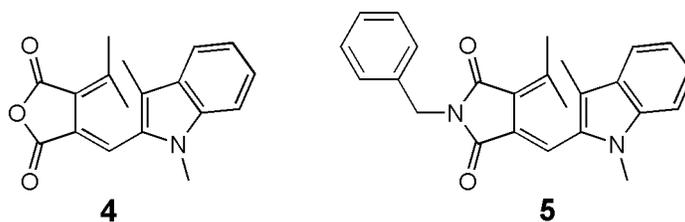
[(4-Formylphenyl)methyl]-carbamic acid phenylmethyl ester (7). A 266 mg (1 mmol) sample of [(4-cyanophenyl)methyl]-carbamic acid phenylmethyl ester was dissolved in 15 mL of tetrahydrofuran under nitrogen and cooled to 0° C. Diisobutylaluminum hydride (3 mmol, 3 mL of a 1 M solution in hexanes) and 10 mL of 1.5 M HCl was added and the mixture was stirred for 30 min. The mixture was then diluted with dichloromethane, washed repeatedly with water and dried, and the solvent was evaporated at reduced pressure to give 194 mg (0.72 mmol, 72 % yield) of **7**. ¹H NMR, δ 4.46 (2H, d, $J = 6$ Hz, -CH₂-N), 5.14 (2H, s, -CH₂-O), 7.25-7.40 (5H, m, Ar-H), 7.43 (2H, d, $J = 8$ Hz, Ar-H), 7.83 (2H, d, $J = 8$ Hz, Ar-H), 9.98 (1H, s, -CHO).



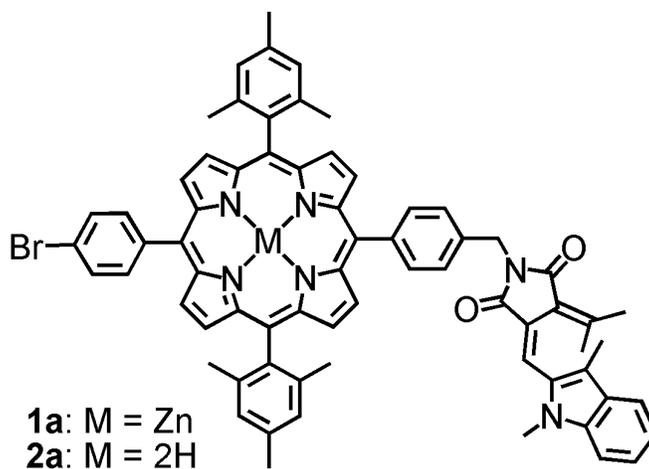
{4-[15-(4-Bromophenyl)-10,20-bis(2,4,6-trimethylphenyl)-porphyrin-5-yl]-benzyl} carbamic acid phenylmethyl ester (3a). A 200 mg (0.75 mmol) sample of **7**, 394 mg (1.5 mmol) of 5-(2,4,6-trimethylphenyl)dipyrromethane, and 137 mg (0.74 mmol) of 4-bromobenzaldehyde were dissolved in 150 mL of dichloromethane and

bubbled with nitrogen for 15 min. Sodium chloride (560 mg) was added, followed by 18.6 μL (0.15 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and the reaction mixture was stirred for 2.5 h before the addition of 575 mg (2.53 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The reaction mixture was stirred overnight and filtered through a short silica gel column to remove excess DDQ. Fractions containing porphyrin were mixed and the solvent was removed by evaporation at reduced pressure. The residue was chromatographed on silica gel eluted with dichloromethane to give 80 mg (0.085 mmol, 11 % yield) of **3a**. $^1\text{H NMR}$, δ -2.64 (2H, s, N-H), 1.83 (12H, s, mesityl CH_3), 2.62 (6H, s, mesityl CH_3), 4.74 (2H, d, $J = 6$ Hz, $-\text{CH}_2\text{-NH-}$), 5.26 (2H, s, $-\text{CH}_2\text{-O-}$), 5.39 (1H, br s, carbamate NH), 7.28 (4H, s, mesityl Ar-H), 7.32-7.49 (5H, m, Ar-H), 7.64 (2H, d, $J = 8$ Hz, Ar-H), 7.87 (2H, d, $J = 9$ Hz, Ar-H), 8.08 (2H, d, $J = 9$ Hz, Ar-H), 8.17 (2H, d, $J = 8$ Hz, Ar-H), 8.67-8.78 (8H, m, β -pyrrole H); MALDI-TOF m/z calcd for $\text{C}_{59}\text{H}_{50}\text{N}_5\text{O}_2\text{Br}$, 941.314, obsd 941.329; UV-vis (dichloromethane) 645, 590, 549, 514, 481, 418, 371 nm.

Zinc-{4-[15-(4-bromophenyl)-10,20-bis(2,4,6-trimethylphenyl)-porphyrin-5-yl]-benzyl} carbamic acid phenylmethyl ester. (3b) A small portion of **3a** was quantitatively metalated by dissolving in a small amount of dichloromethane and adding an excess of zinc acetate in methanol solution. After stirring overnight, the product was isolated by washing the reaction mixture with water and evaporating the solvent at reduced pressure. $^1\text{H NMR}$, δ 1.82 (12H, s, mesityl CH_3), 2.63 (6H, s, mesityl CH_3), 4.74 (2H, m, $-\text{CH}_2\text{-NH-}$), 5.24 (2H, s, $-\text{CH}_2\text{-O-}$), 5.39 (1H, br s, carbamate NH), 7.28 (4H, s, mesityl Ar-H), 7.3-7.5 (5H, m, Ar-H), 7.6-7.7 (2H, m, Ar-H), 7.87 (2H, d, $J = 8$ Hz, Ar-H), 8.10 (2H, d, $J = 8$ Hz, Ar-H), 8.2 (2H, m, Ar-H), 8.65-8.95 (8H, m, β -pyrrole H); MALDI-TOF m/z calcd for $\text{C}_{59}\text{H}_{48}\text{N}_5\text{O}_2\text{BrZn}$, 1003.226, obsd 1003.229; UV-vis (2-methyltetrahydrofuran) 595, 556, 424 nm.



2-Indolyfulgide 4 and model **fulgimide 5** were prepared by the methods of Rentzepis.³⁻⁵



Dyad (1) was synthesized by a modification of the procedure described by Rentzepis for the preparation of fulgimides.^{4,5} Deprotection of **3a** was achieved by dissolving 110 mg (0.12 mmol) in 20 mL of trifluoroacetic acid and 25 mL of concentrated hydrochloric acid and stirring the resulting mixture under nitrogen for 2.5 h at 70° C. The reaction mixture was then diluted with dichloromethane and washed with water until the wash water was neutral. Toluene (30 mL) was added and the dichloromethane was evaporated at reduced pressure. Freshly distilled dichloromethane (20 mL) and 34 mg (0.12 mmol) of **4** were then added. After 3 h at ambient temperature, all of the dichloromethane was evaporated, leaving only toluene as the solvent. The resulting solution was stirred overnight, after which time TLC indicated that fulgimide **4** had been consumed. The reaction mixture was then heated at 80°C and 3 mL of saturated zinc acetate in methanol was added. The reaction mixture was stirred for 2 h, cooled to room temperature, diluted with dichloromethane and washed with water to remove excess zinc acetate. The dichloromethane was then evaporated, leaving a toluene solution, and an additional 20 mL of toluene were added and the mixture distilled at reduced pressure in order to remove any remaining water as the azeotrope. The resulting toluene solution was heated at 80° C, 20 mg of ZnCl₂ and 40 μL of hexamethyldisilazane (HMDS) were added, and the mixture was stirred under nitrogen. TLC in dichloromethane was used to monitor the reaction progress. After 2 h an additional 50 mg of ZnCl₂ and 600 μL of HMDS were added, and the reaction mixture was stirred overnight. The following morning another 25 mg of ZnCl₂ and 200 μL of HMDS were added, and stirring was continued for 5 h. Chromatography (silica gel eluted with dichloromethane) gave 79 mg of **1** (0.069 mmol, 59 % yield). ¹H NMR, δ 1.32 (3H, s, -CH₃), 1.82 (12H, s, mesityl-CH₃), 2.01 (3H, s, -CH₃), 2.53 (3H, s, -CH₃), 2.62 (6H, s, mesityl-CH₃), 3.74 (3H, s, N-CH₃), 5.02 (2H, m, -CH₂-), 7.1-7.2 (1H, m, Ar-H), 7.28 (4H, s, mesityl Ar-H), 7.30 (1H, s, Ar-H), 7.5-7.64 (3H, m, Ar-H), 7.69 (2H, d, *J* = 8 Hz, Ar-H), 7.84 (2H, d, *J* = 8 Hz, Ar-H), 8.08 (2H, d, *J* = 8 Hz, Ar-H), 8.16 (2H, d, *J* = 8 Hz, Ar-H) 8.75-8.90 (8H, m, β-pyrrole); MALDI-TOF *m/z* calcd for C₆₉H₅₇N₆O₂BrZn, 1146.300, obsd 1146.301; UV-vis (2-methyltetrahydrofuran) 648, 591, 547, 513, 489, 418, 372, 287 nm.

Dyad 2. Dyad **1** (20 mg, 0.0174 mmol) was dissolved in 10 mL of dichloromethane and then acidified with 0.5 mL of trifluoroacetic acid. The reaction mixture was stirred for 5 min and then washed with water until neutral, and the solvent was evaporated at reduced pressure to give 18 mg (0.017 mmol, 95% yield) of **2**. ¹H

NMR, δ -2.65 (2H, s, N-H), 1.35 (3H, s, -CH₃), 1.83 (12H, s, mesityl -CH₃), 2.04 (3H, s, -CH₃), 2.59 (3H, s, -CH₃), 2.62 (6H, s, mesityl -CH₃), 3.77 (3H, s, N-CH₃), 5.19 (2H, s, -CH₂-), 7.1-7.31 (7H, m, Ar-H, mesityl Ar-H), 7.60 (1H, m, Ar-H) 7.7-7.9 (5H, m, Ar-H), 8.07 (2H, d, $J = 9$ Hz, Ar-H), 8.19 (2H, d, $J = 8$ Hz, Ar-H), 8.6-8.9 (8H, m, β -pyrrole H); MALDI-TOF calcd for C₆₉H₅₉N₆O₂Br, 1084.388, obsd 1084.387; UV-vis (2-methyltetrahydrofuran) 648, 591, 547, 513, 489, 418, 372, 287 nm.

References.

1. Maligres, P.E.; Waters, M.S.; Wiessman, S.A.; McWilliams, J.C.; Lewis, S.; Cowen, J.; Reamer, R.P.; Rieder, P.J.; Askin, D. *J. Heterocyclic Chem.* **2003**, *40*, 229-241.
2. Dener, J.M.; Rice, K.D.; Newcomb, W.S.; Wang, V.R.; Young, W.B.; Gangloff, A.R.; Kuo, E.Y.-L.; Cregar, L.; Putnam, D.; Wong, M. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1629-1633.
3. Liang, Y.; Dvornikov, A.S.; Rentzepis, P.M. *J. Photochem. Photobio. A.* **1999**, *125*, 70-84.
4. Liang, Y.; Dvornikov, A.S.; Rentzepis, P.M. *J. Mater. Chem.* **2000**, *10*, 2466-2482.
5. Reddy, P.Y.; Kondo, S.; Toru, T.; Ueno, Y. *J. Org. Chem.* **1997**, *62*, 2652-2654.