Electronic Supplementary Information

Effect of anion binding on charge stabilization in a bis-fullerene-oxoporphyrinogen conjugate

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General
Solvents and reagents were obtained from Aldrich Chemical Co., Fischer Chemical Co., Wako Chemical Co., Tokyo Kasei Chemical Co. or Kanto Chemical Co. Buckminsterfullerene, C$_{60}$ (+99.95%) was from SES Research, (Houston, TX). The tetra-$n$-butylammonium anion salts ($n$-Bu$_4$N)ClO$_4$ used in electrochemical and anion binding studies were from Fluka Chemicals. $^1$H and $^{13}$C NMR spectra were measured at 298 K from CDCl$_3$ or CDCl$_3$/d$_6$-DMSO solutions of the samples using a JEOL model AL300BX spectrometer with tetramethylsilane as internal standard. Electronic absorption spectra were measured from dichloromethane solutions of the samples using a Shimadzu model UV-3600 UV/Vis/NIR spectrophotometer. FTIR spectra were measured from samples cast on a barium fluoride disc using a Nicolet model 760X FTIR spectrometer. Matrix–assisted laser desorption/ionization time–of–flight mass spectrometry (MALDI–TOF–MS) was measured using a Shimadzu-Kratos model Axima CFR+ mass spectrometer with dithranol as matrix. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. DPVs were recorded on an EG&G PARSTAT electrochemical analyzer using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas.

Time-resolved Transient Absorption Measurements. Femtosecond laser flash photolysis was conducted using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (Helios). The source for the pump and probe pulses were derived from the...
fundamental output of Clark laser system (775 nm, 1 mJ/pulse and fwhm = 150 fs) at a repetition rate of 1 kHz. A second harmonic generator introduced in the path of the laser beam provided 410 nm laser pulses for excitation. A 95% of the fundamental output of the laser was used to generate the second harmonic, while 5% of the deflected output was used for white light generation. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provided an experimental time window of 1.6 ns with a maximum step resolution of 7 fs. The pump beam was attenuated at 5 μJ/pulse with a spot size of 2 mm diameter at the sample cell where it was merged with the white probe pulse in a close angle (<10°). The probe beam after passing through the 2 mm sample cell was focused on a 200 μm fiber optic cable which was connected to a CCD spectrograph (Ocean Optics, S2000-UV-vis for visible region and Horiba, CP-140 for NIR region) for recording the time-resolved spectra (450-800 and 800-1400 nm). Typically, 5000 excitation pulses were averaged to obtain the transient spectrum at a set delay time. The kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data.

Nanosecond time-resolved transient absorption measurements were carried out using the laser system provided by UNISOKU Co., Ltd. Measurements of nanosecond transient absorption spectrum were performed according to the following procedure. A deaerated solution containing a dyad was excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at λ = 430 nm. The photodynamics was monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. Transient spectra were recorded using fresh solutions in each laser excitation. The solution was deoxygenated by argon purging for 15 min prior to measurements.

**Synthesis of bis-fullerene-oxoporphyrinogen conjugate, 1**

$N_{21},N_{23}$-**Bis(4-bromobenzyl)-5,10,15,20-tetrakis(3,5-di-t-butyl-4-oxocyclohexa-2,5-dienyl)-porphyrinogen** [(4BrBz)$_2$OxP] was prepared by a literature method.$^{51}$

$N_{21},N_{23}$-**Bis[4-(4-formylphenyl)benzyl]-5,10,15,20-tetrakis(3,5-di-t-butyl-4-oxocyclohexa-2,5-dienyl)porphyrinogen.**

[1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) dichloromethane complex (15 mg, ~10 mol%) was added to a degassed mixture of (4BrBz)$_2$OxP (137 mg, 9.35 × 10$^{-5}$ mol), 4-formylphenylboronic acid (45 mg, 3 × 10$^{-4}$ mol) and K$_2$CO$_3$ (0.1 g dissolved in H$_2$O (1 mL)) in a mixture of toluene (10 mL) and ethanol (2 mL). The resulting mixture was stirred at 60 °C for 48 h under an atmosphere of dry nitrogen. The mixture was
allowed to cool to room temperature and poured into water. The mixture was extracted with dichloromethane (2 × 40 mL) and the combined organic fractions were dried over anhydrous Na₂SO₄. Solvents were subsequently evaporated under reduced pressure and the residue chromatographed on silica gel eluting with dichloromethane. Product containing fractions were combined and the solvents removed under reduced pressure yielding the desired product as a dark green solid, which was used without further purification. Yield: 104 mg, 74 %. UV/Vis (CH₂Cl₂): λ<sub>max</sub> = 508.5 nm. ¹H-NMR (CDCl₃, 25 °C, 300 MHz): δ = 1.18 (s, 36H, ¹Bu-H), 1.36 (s, 36H, ¹Bu-H), 4.59 (s, 4H, benzyl –CH₂–), 6.58 (s, 4H, β-pyrrole-H), 6.92 (d, ³J = 8.06 Hz, 4H, biphenyl(H), 6.97 (s, 4H, cyclohexa-2,5-dienyl-H), 7.06 (s, 4H, β-pyrrole-H), 7.41 (d, ³J = 8.25 Hz, biphenyl-H), 7.56 (d, ³J = 8.07 Hz, 4H, biphenyl-H), 7.63 (s, 4H, cyclohexa-2,5-dienyl-H), 7.90 (d, ³J = 8.07 Hz, 4H, biphenyl-H), 9.87 (br. s, 2H, pyrrole-NH), 10.02 (s, 2H, formyl-H) ppm. ¹³C-NMR [CDCl₃: d₆-DMSO (50:50 v/v), 25 °C, 300 MHz]: δ = 29.31, 29.41, 35.10, 35.41, 120.59, 121.51, 127.26, 127.78, 130.07, 131.26, 131.55, 132.37, 135.31, 135.99, 137.69, 145.65, 146.15, 147.12, 185.55 (formyl-C) ppm. FT-IR: ν = 2997.8 (w, C-H str.), 2955.2 (m, C-H str.), 2864.1 (m, C-H str.), 1702.9 (m, C=O str.), 1594.8 (s, C=C str.), 1563.0 (m), 1264.0 (m), 1228.5 (w), 1169.4 (w), 1088.4 (m), 1040.2 (w), 1028.4 (m), 1005.4 (w), 949.0 (m), 929.6 (w), 886.6 (w), 840.5 (w), 818.7 (w), 801.2 (m), 757.7 (m), 743.7 (m) cm⁻¹. MALDI-TOF-MS (dithranol): [M + 2H]⁺ (C₁₀₄H₁₁₄N₄O₆): calcd. 1516.88; found 1516.99.

**Bis-C₆₀-adduct, 1:** N₂₁,N₂₃-Bis[4-(4-formylphenyl)benzyl]-5,10,15,20-tetrakis (3,5-di-t-butyl-4-oxocyclohexa-2,5-dienyl) porphyrinogen (51 mg, 3.37 × 10⁻⁵ mol) C₆₀ (50 mg, 6.94 × 10⁻⁵ mol) and N-methylglycine (62 mg, 6.97 × 10⁻⁴ mol) were added to dry toluene (50 mL) and heated at reflux with stirring under an atmosphere of dry nitrogen for 20 hrs. The reaction mixture was allowed to cool to room temperature then solvents were removed under reduced pressure. The residue was first chromatographed on silica gel eluting with chloroform. Product containing fractions were combined and the solvents removed under reduced pressure. The residue was subsequently further purified by gel permeation chromatography on BioBeads SX-1 eluting with tetrahydrofuran giving the product as a dark green solid after removal of solvents. Yield: 28 mg, 28 %. UV/Vis (CH₂Cl₂): λ<sub>max</sub> = 525.5, 258.0 nm. ¹H-NMR (CDCl₃, 55 °C, 300
MHz): δ = 1.13, 1.15 (overlapping s, 36H, tBu-H), 1.33 (s, 36H, tBu-H), 2.79 (s, 6H, N-CH₃), 4.25 (d, J = 9.37 Hz, 2H, pyrrolidine-H), 4.53 (s, 4H, benzyl –CH₂–), 4.93 (s, 2H, pyrrolidine-H), 4.97 (d, J = 9.54 Hz, 2H, pyrrolidine-H), 6.54 (s, 4H, β-pyrrole-H), 6.84 (d, J = 7.89 Hz, 4H, biphenyl-H), 6.91 (s, 4H cyclohexa-2,5-dienyl-H), 7.03 (d, J = 4.40 Hz, 4H, β-pyrrole-H), 7.35 (d, J = 8.07 Hz, 4H, biphenyl-H), 7.46 (d, J = 7.87 Hz, 4H, biphenyl-H), 7.59 (s, 4H cyclohexa-2,5-dienyl-H), 7.81 (d, J = 7.70 Hz, 4H, biphenyl-H), 9.21 (br. s, 2H, pyrrole NH) ppm. The bis-C₆₀-adduct is too insoluble to obtain ¹³C-NMR data. FT-IR: ν = 2951.1 (m, C-H str.), 2920.6 (m, C-H str.), 2860.4 (m, C-H str.), 2779.8 (w, C-H str.), 1637.3 (w, C=C str.), 1597.5 (s, C=C str.), 1538.9 (w), 1492.6 and 1485.4 (s, tBu, asym. def.), 1461.2 and 1453.1 (s, tBu, sym. bend.), 1419.4 (w), 1404.9 (w), 1387.5 (m), 1360.2 (s, tBu, sym. bend.), 1333.0 (m), 1307.8 (m), 1257.4 (m), 1230.5 (w), 1204.6 (w), 1178.5 (m), 1106.9 (w), 1087.7 (m), 1027.9 (s), 1006.2 (m), 946.9 (m), 930.1 (w), 885.9 (m), 865.6 (w), 840.2 (m), 816.8 (m) cm⁻¹. MALDI-TOF-MS positive ion mode (dithranol): [M + 2H]⁺ (C₂₂₈H₁₂₄N₆O₄): calcd. 3011.97; found 3012.14. MALDI-TOF-MS negative ion mode (dithranol/TnBAF): [M + F]⁻ (C₂₂₈H₁₂₂N₆O₄F): calcd. 3028.96; found 3029.47.

References
Figure S1. (a) Nanosecond transient absorption spectra obtained by 430 nm laser light of 1 in deaerated DCB. (b) Time profile of $C_{60}^{-}$ band at 1000 nm.