Electronic Supplementary Information (ESI)

A novel BF_2-chelated azadipyrromethene-fullerene dyad: Synthesis, electrochemistry and photodynamics

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Chemicals. Buckminsterfullerene, C_{60} (+99.95%) was obtained from SES Research, (Houston, TX). All the reagents were from Aldrich Chemicals (Milwaukee, WI) while the bulk solvents utilized in the syntheses were from Fischer Chemicals. The tetra-*n*-butylammonium anion salts (n-$Bu_4N)ClO_4$ used in electrochemical studies were from Fluka Chemicals.

Instrumentation. ^{1}H NMR spectra were obtained using chloroform-d_1 solutions using a Varian 300 MHz NMR spectrometer with tetramethylsilane as an internal standard. The UV-visible spectral measurements were carried out with a Shimadzu Model 1600 UV-visible spectrophotometer. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. CFs 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. 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 *m*J/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 *m*m 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.

Syntheses

1,3-Diphenyl-propenone. Benzaldehyde (5.25 g, 0.049 mol), acetophenone (5.94 g, 0.049 mol) and potassium hydroxide (0.083 g, 0.0015 mol) were dissolved in ethanol/water (85:15 v/v, 100 mL) and stirred at rt for a period of 24 h. The reaction mixture was allowed to cool in ice-water bath during which the product precipitated. Filtration of the reaction mixture yielded pale yellow solid product: Yield 8.76g (85%); ^{1}H NMR ($CDCl_3$) δ: 7.40-7.46 (m, 3H), 7.48-7.55 (m, 2H), 7.56-7.61 (m, 1H), 7.62-7.86 (m, 4H), 8.0-8.06 (m, 2H).

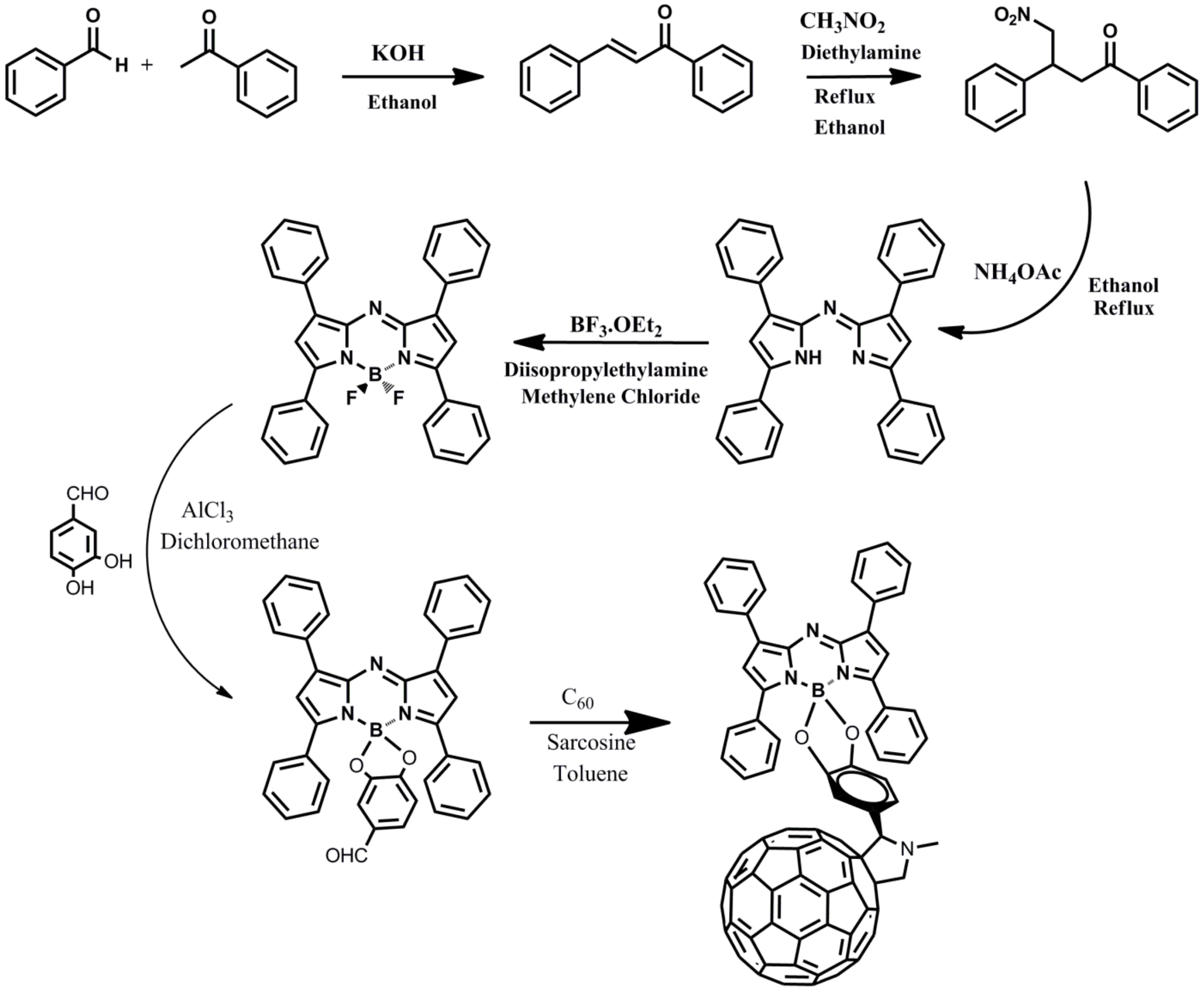
4-Nitro-1,3-diphenyl-butan-1-one. 1,3-Diphenyl-propenone (5.0 g, 0.024 mol), nitromethane (7.33 g, 0.12 mol) and diethylamine (8.78 g, 0.12 mol) were dissolved in dry methanol (65 mL) and heated under reflux for 24 h. The solution was cooled, acidified with 1M HCl to precipitate the product: Yield 5.49g (85%); ^{1}H NMR ($CDCl_3$) δ: 7.9-7.94 (m, 2H), 7.55-7.61 (m, 1H), 7.43-7.49 (m, 2H), 7.26-7.36 (m, 5H), 4.65-4.86 (m, 2H), 4.18-4.30 (m, 1H), 3.42-3.50 (m, 2H).

(3,5-Diphenyl-1H-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine. 4-Nitro-1,3-diphenyl-butan-1-one (0.5 g, 1.86 mmol) and ammonium acetate (5.01 g, 0.065 mol) and ethanol (20 mL) was heated under reflux for 24 h. During the course of the reaction, the product precipitated as a blue-black solid. The reaction was allowed to cool to room temperature and solid was filtered and washed with ethanol to yield the product: Yield 0.15g (35%) ^{1}H NMR ($CDCl_3$) δ: 8.04-8.09 (m, 4H), 7.94-7.99 (m, 4H), 7.33-7.57(m, 12H), 7.21(s, 2H). λ_{max} ($CHCl_3$) nm: 598.

BF_2 chelate of (3, 5-diphenyl-1H-pyrrol-2-yl)(3, 5-diphenylpyrrol-2-ylidene)amine. (3, 5-Diphenyl-1H-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine (0.10 g, 0.22 mmol) was dissolved in dry CH_2Cl_2 (40 mL). Diisopropylethylamine (0.40 mL, 2.3 mmol) and boron trifluoride diethyl etherate (0.50 mL, 4.02 mmol) were added and the mixture was stirred at room temperature under N_2 for 24 h. The mixture was washed with water and the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica) with CH_2Cl_2/hexane 1:1 to give the product as a metallic brown solid: Yield 0.095g (86%). ^{1}H NMR ($CDCl_3$) δ: 8.02-8.08(m, 8H), 7.40-7.55(m, 12H), 7.04(s, 2H). λ_{max} ($CHCl_3$) nm: 650. Maldi mass, calcd. 497.35, found 497.32.

ADP-aldehyde. BF_2 chelate of (3,5-diphenyl-1H-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine (0.1g, 0.20mmol), 3,4-dihydroxybenzaldehyde (0.138 g, 1.01 mmol) and $AlCl_3$ (0.134 g, 1.01 mmol) in 20 mL dry CH_2Cl_2 were stirred at rt for a period of 24 h. The mixture was evaporated to dryness and the residue was purified by column chromatography (silica) with CH_2Cl_2/hexane 3:1 to give the product: Yield 0.077g (64%) ^{1}H NMR δ: 6.12 (d, 1H), 6.56 (s, 1H), 6.8(s, 2H), 6.86-7.02(m, 8H), 7.24-7.30(m, 2H), 7.42-7.52(m, 7H) 8.05-8.1(m, 4H), 9.6(s, 1H). λ_{max} (benzonitrile) nm: 633.

ADP-C_{60} dyad. To a solution of C_{60} (0.012 g, 0.017 mmol), in dry toluene (100 mL), sarcosine (0.0030 g, 0.033 mmol) and ADP-aldehyde (0.015 g, 0.025 mmol) were added. The solution mixture was refluxed for 24 h and the solvent was removed under vacuum. The residue was purified by column chromatography (silica) with 3:7 ethyl acetate and toluene as eluent to give the product: Yield 0.014g (56%) ^{1}H NMR δ: 8.02-8.1 (m, 4H), 7.3-7.5 (m, 9H), 7.15-7.22 (m, 2H), 6.85-7.1 (m, 6H), 6.78-6.84 (m, 3H) 6.1(m, 1H), 4.9(d, 1H), 4.55(s, 1H), 4.1(d, 1H), 2.55(s, 3H). λ_{max} (benzonitrile) nm: 640, MALDI-Mass, calcd. 1343.17, found 1343.41 and 1338.47.



Scheme 1. Synthetic scheme employed to prepare ADP-C$_{60}$ dyad in the present study.

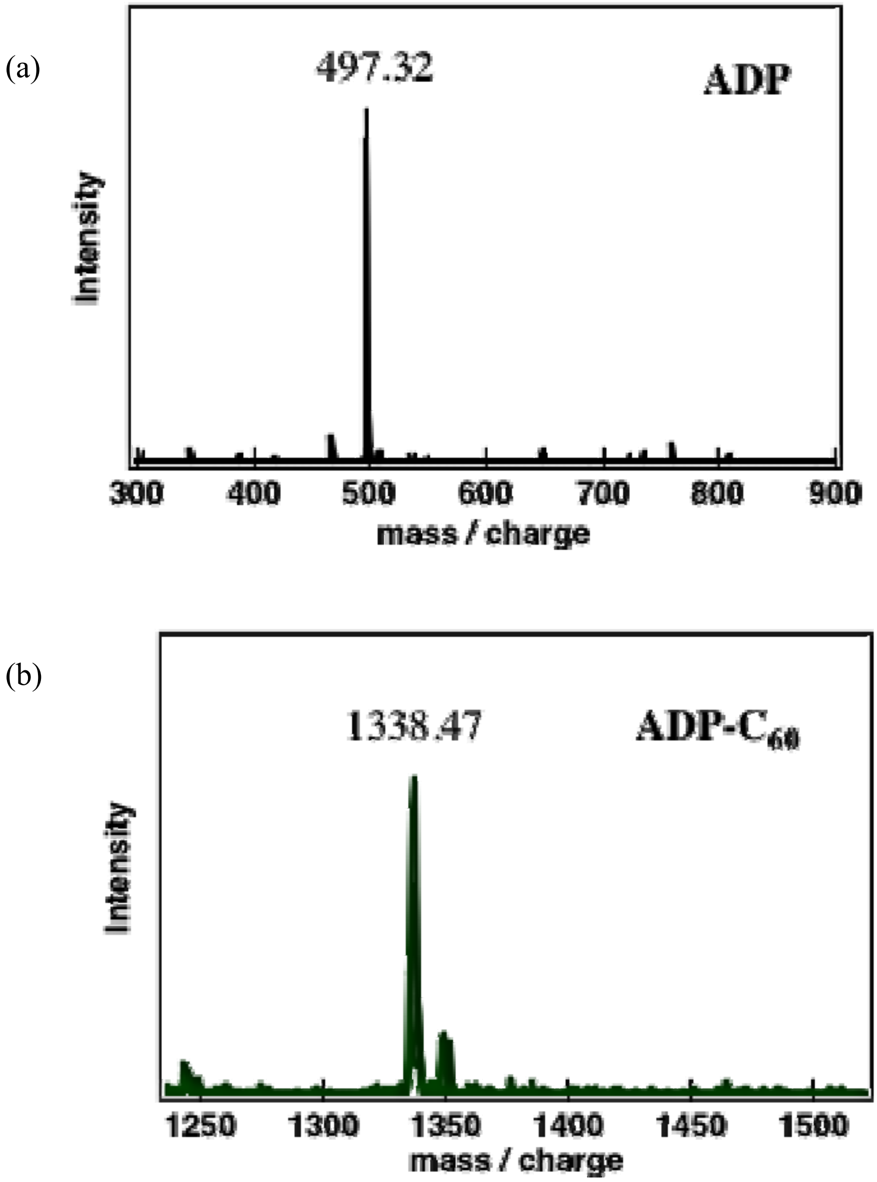


Fig. S1. MALDI-Mass spectra of (a) BF_2-chelated azadipyrromethene and (b) BF_2-chelated azadipyrromethene-fullerene dyad.

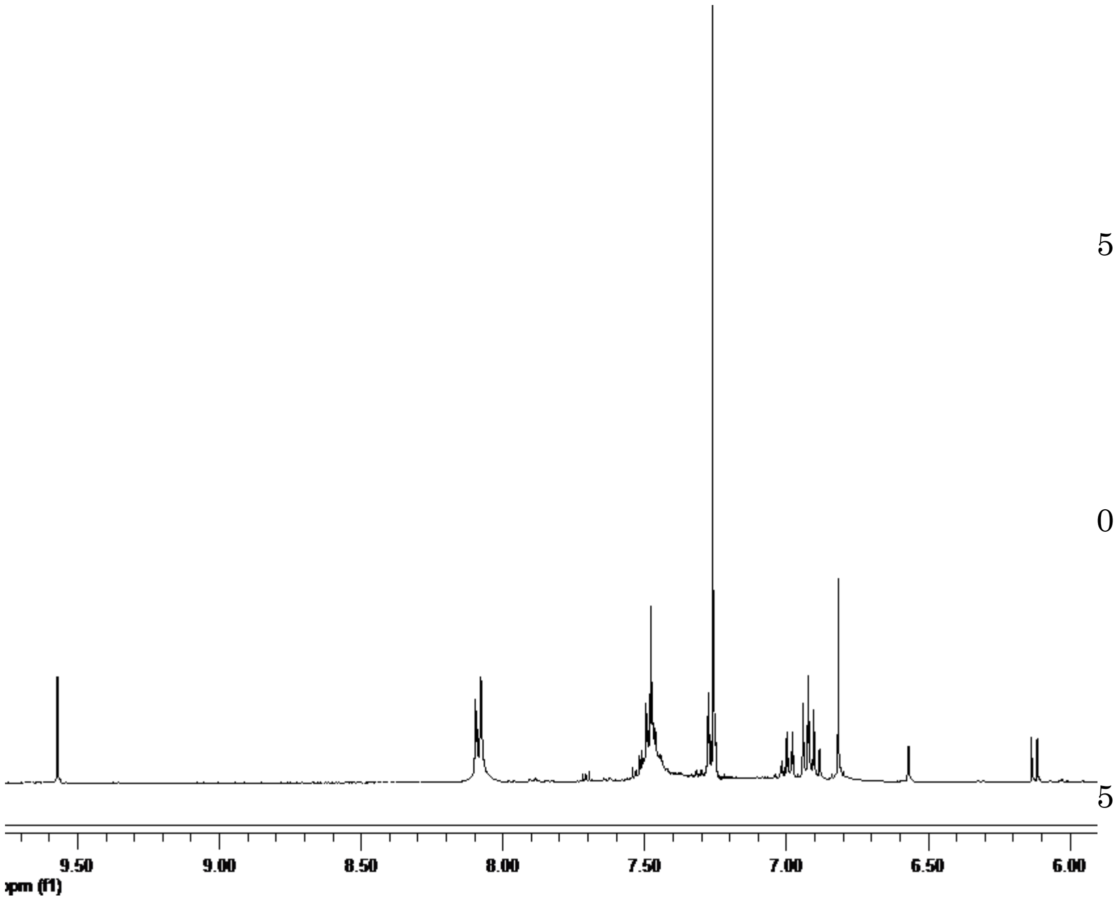


Fig. S2. ^{1}H NMR spectrum of ADP-aldehyde in $CDCl_3$.

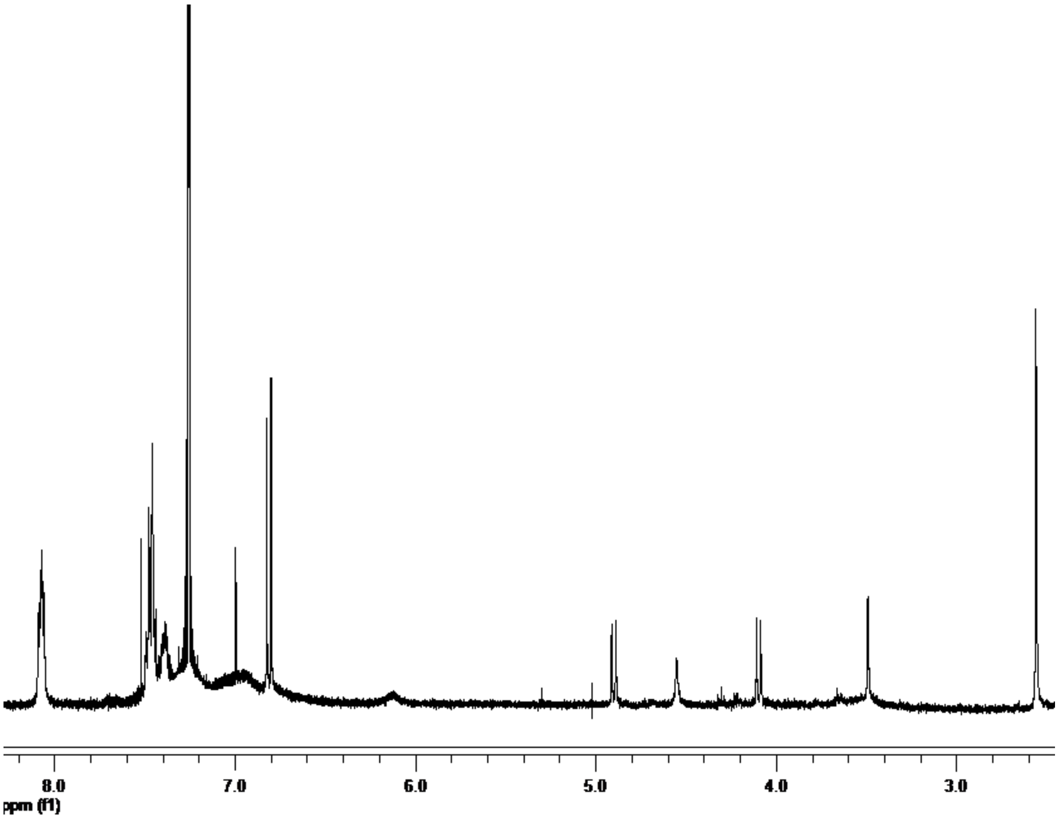


Fig. S3. ^{1}H NMR spectrum of ADP-C_{60} dyad in $CHCl_3$.

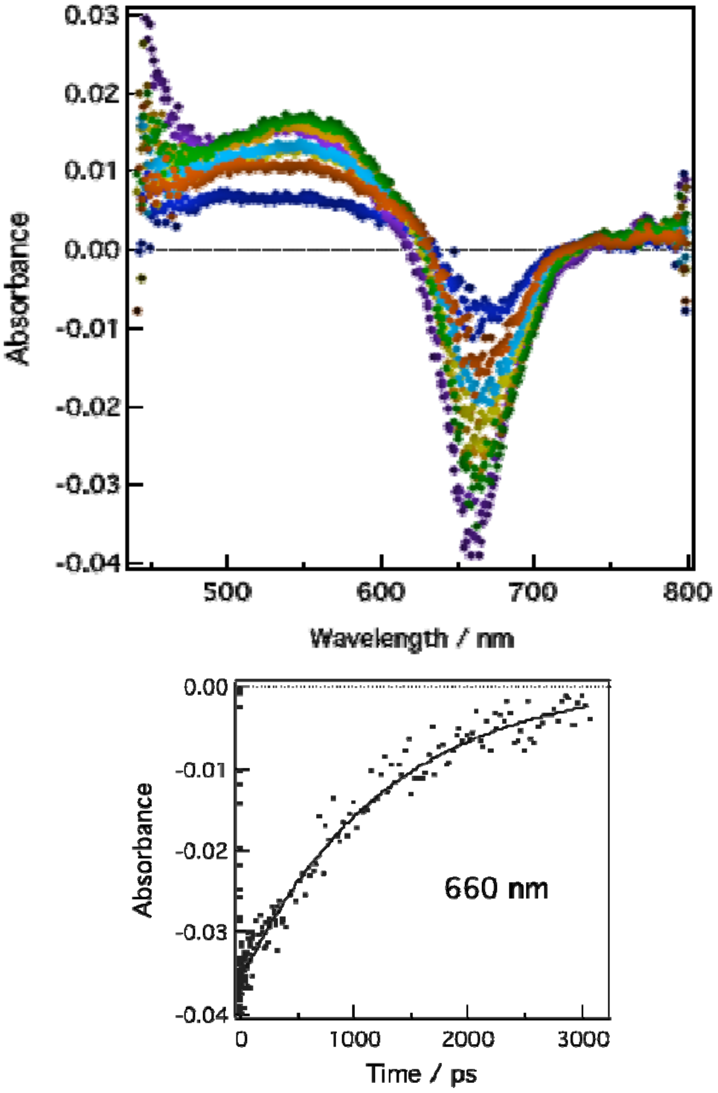


Fig. S4. (Upper) Femtosecond transient absorption spectra of ADP-BF_2 (BDP control) in deaerated benzonitrile. λ_{ex} = 480 nm. (Lower) Decay time profile at 660 nm.