

Electronic supporting Information

Modulating the generation of long-lived charge separated states exclusively from the triplet excited states in palladium porphyrin–fullerene conjugates

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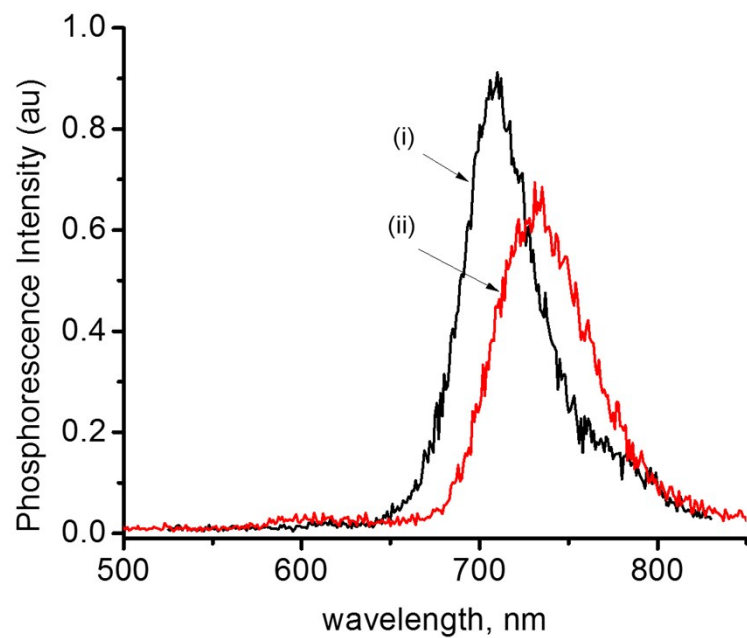


Fig. S1. Phosphorescence spectrum of (i) *meso*-tetra(toluy)porphyrinato palladium(II) ($\lambda_{\text{ex}} = 420$ nm), and (b) *meso*-tetra(triphenylamino)porphyrinato palladium(II) ($\lambda_{\text{ex}} = 432$ nm) in benzonitrile at room temperature.

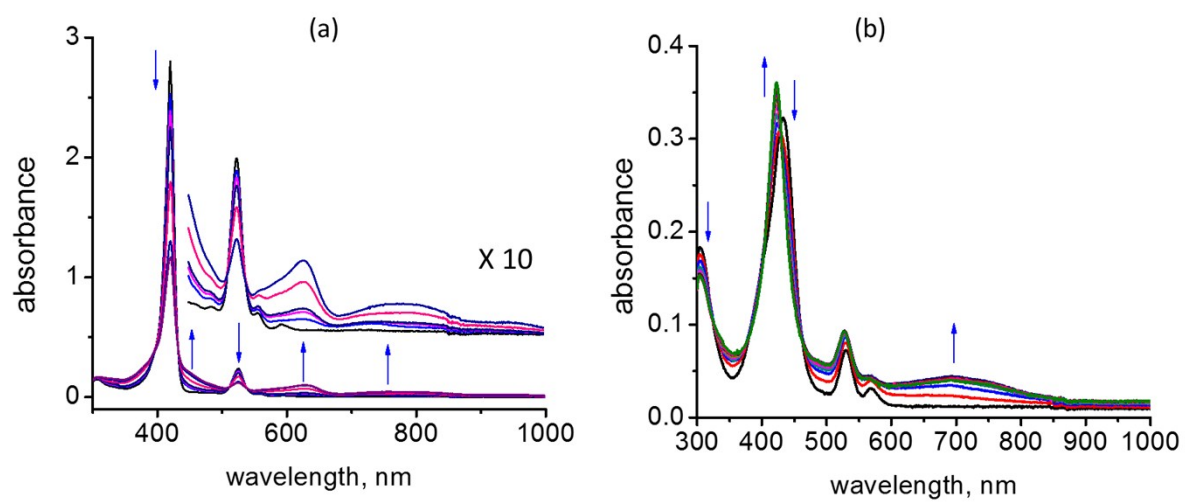


Figure S2. Spectral changes observed during first oxidation of (a) (TTP)Pd, and (b) (TPA)₄PPd in benzonitrile containing 0.1 M (TBA)ClO₄.

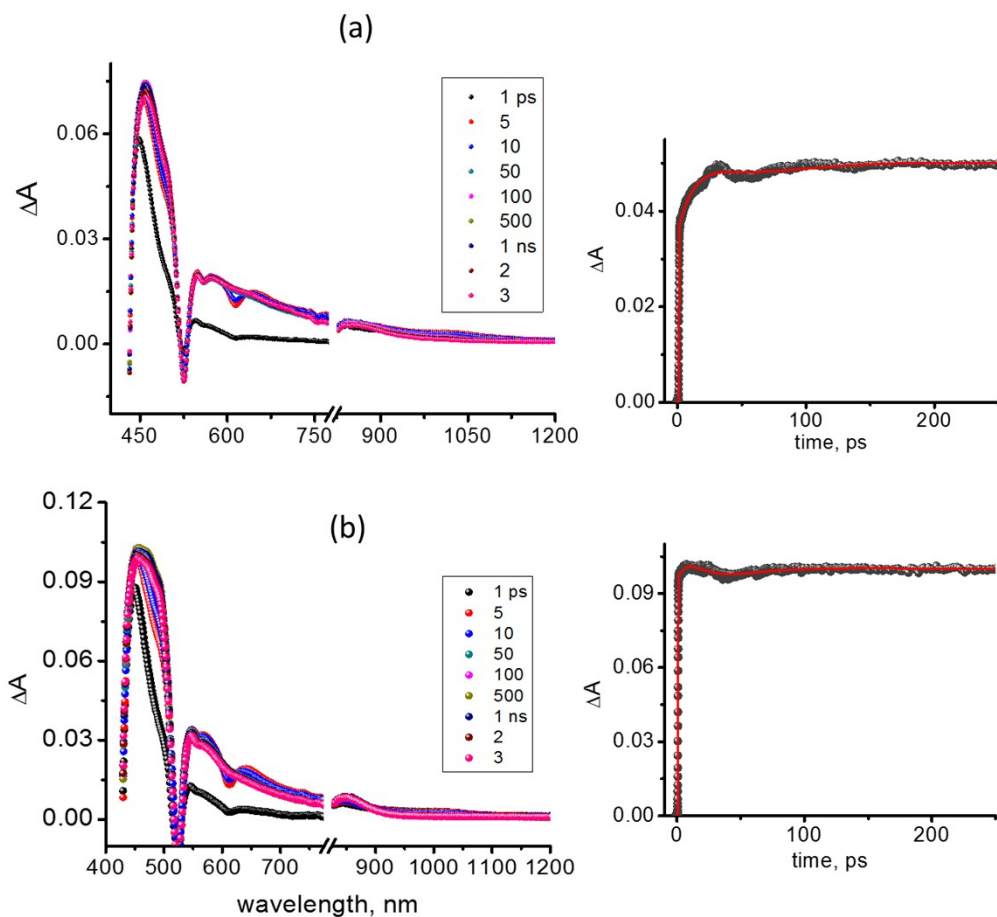


Fig. S3. Femtosecond transient absorption spectra of (TTP)Pd in (a) Ar-saturated benzonitrile and (b) Ar-saturated toluene (100 fs laser pulses of 400 nm wavelength). The time profile of the 460 peak corresponding to $^3\text{PdP}^*$ formation is shown on the respective right hand side panel.

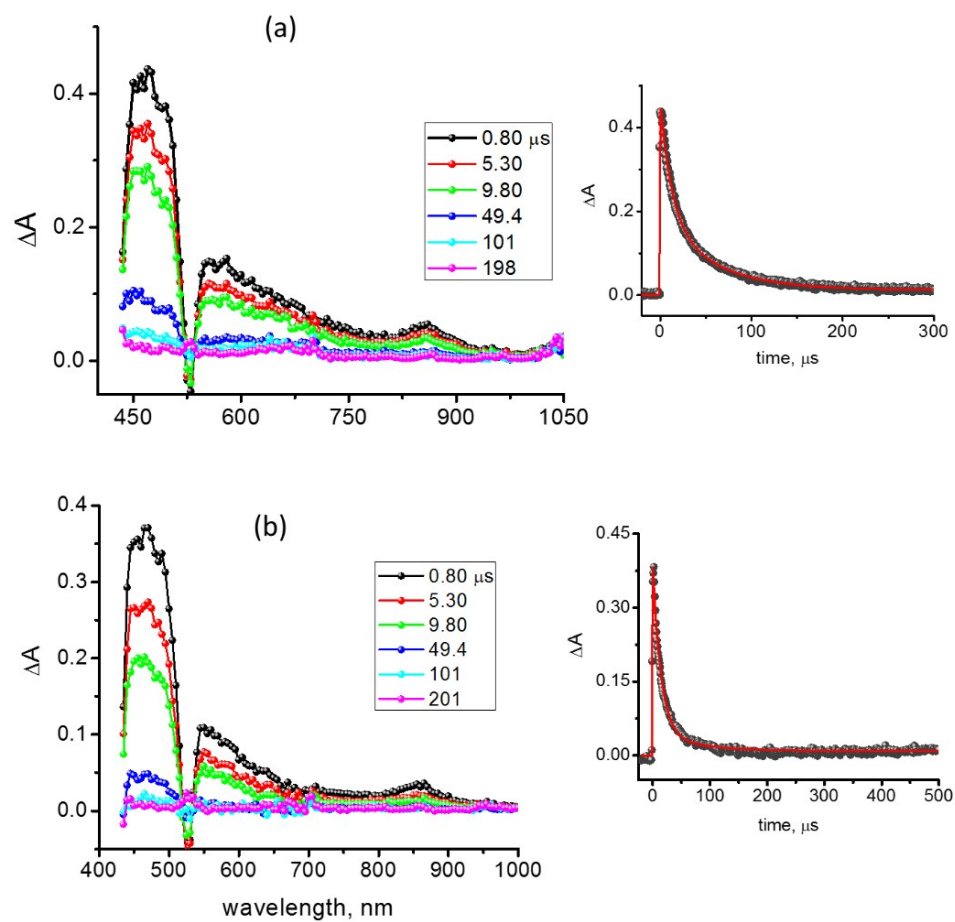


Fig. S4. Nanosecond transient absorption spectra of (TTP)Pd in (a) Ar-saturated benzonitrile and (b) Ar-saturated toluene (7 ns laser pulses of 525 nm wavelength). The time profile of the 460 nm peak corresponding to decay of 3PdP is shown on the respective right hand side panel.

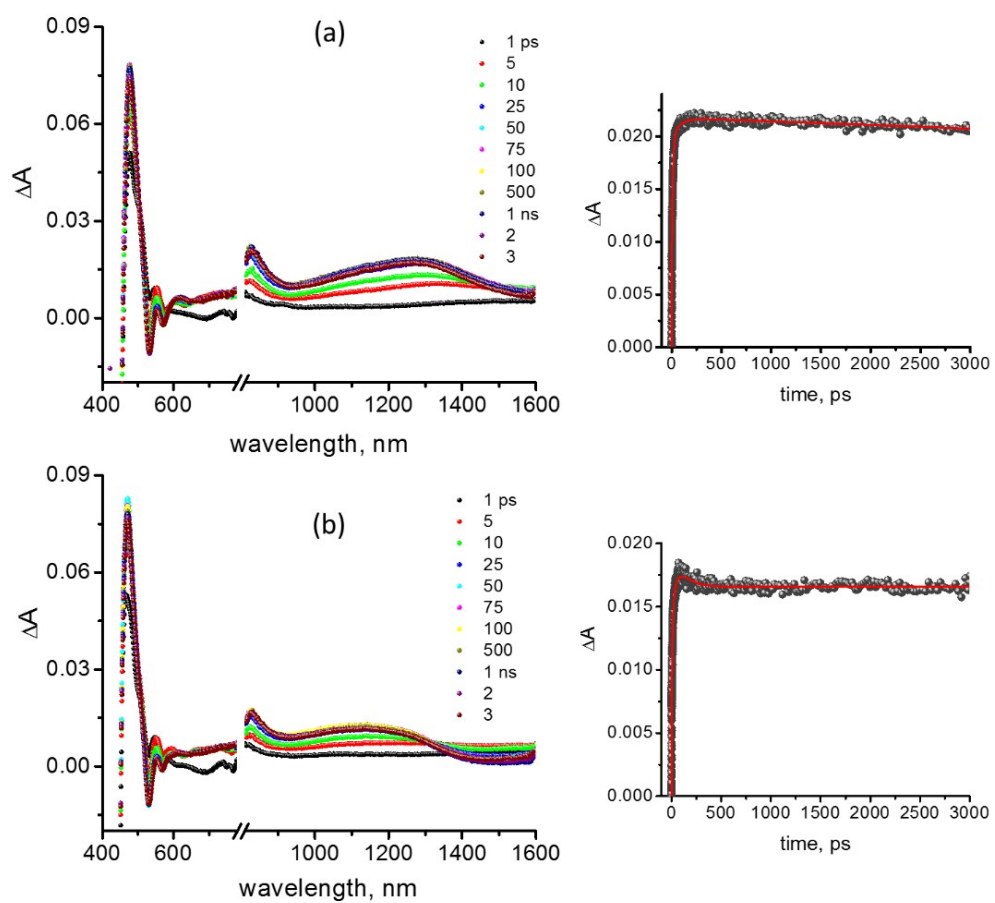


Fig. S5. Femtosecond transient absorption spectra of (TPA)₄PPd in (a) Ar-saturated benzonitrile and (b) Ar-saturated toluene (100 fs laser pulses of 400 nm wavelength). The time profile of the 830 nm peak corresponding to ³PdP* formation is shown on the respective right hand side panel.

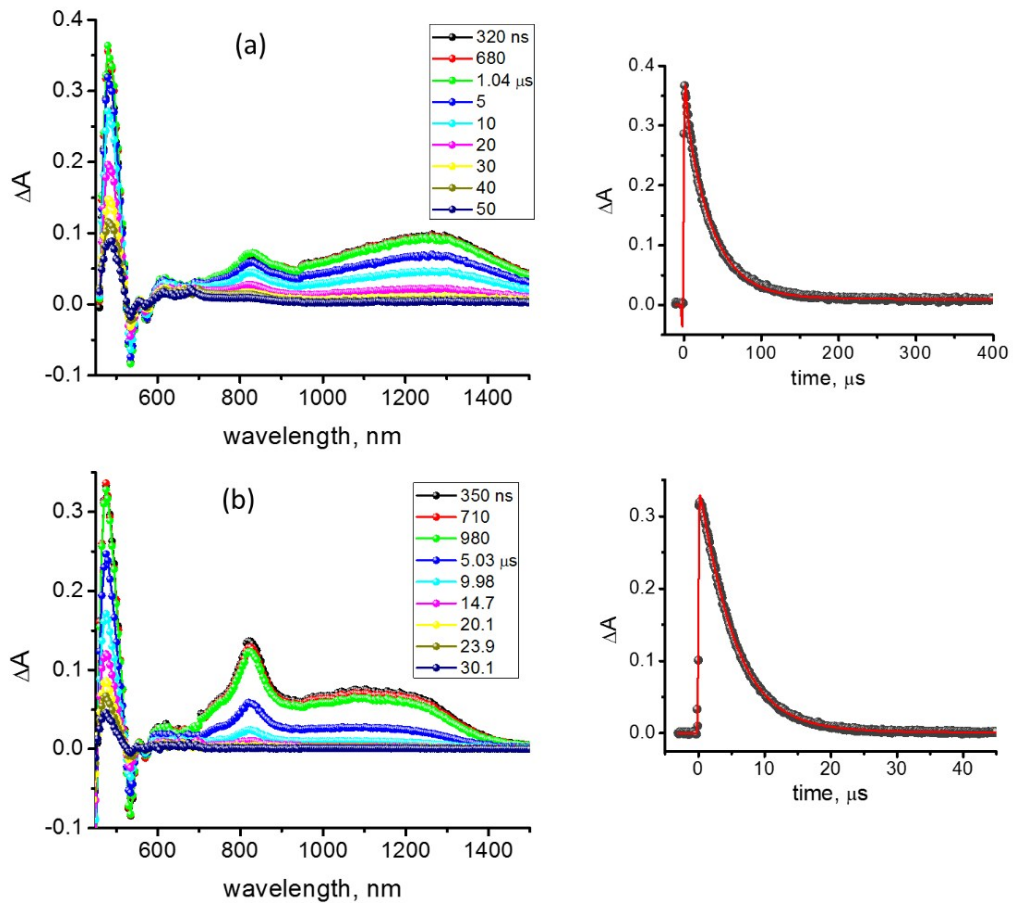


Fig. S6. Nanosecond transient absorption spectra of $(\text{TPA})_4\text{PPd}$ in (a) Ar-saturated benzonitrile and (b) Ar-saturated toluene (7 ns laser pulses of 525 nm wavelength). The corresponding time profiles of the 460 nm peak due to ^3P are shown on the respective right hand side panel.

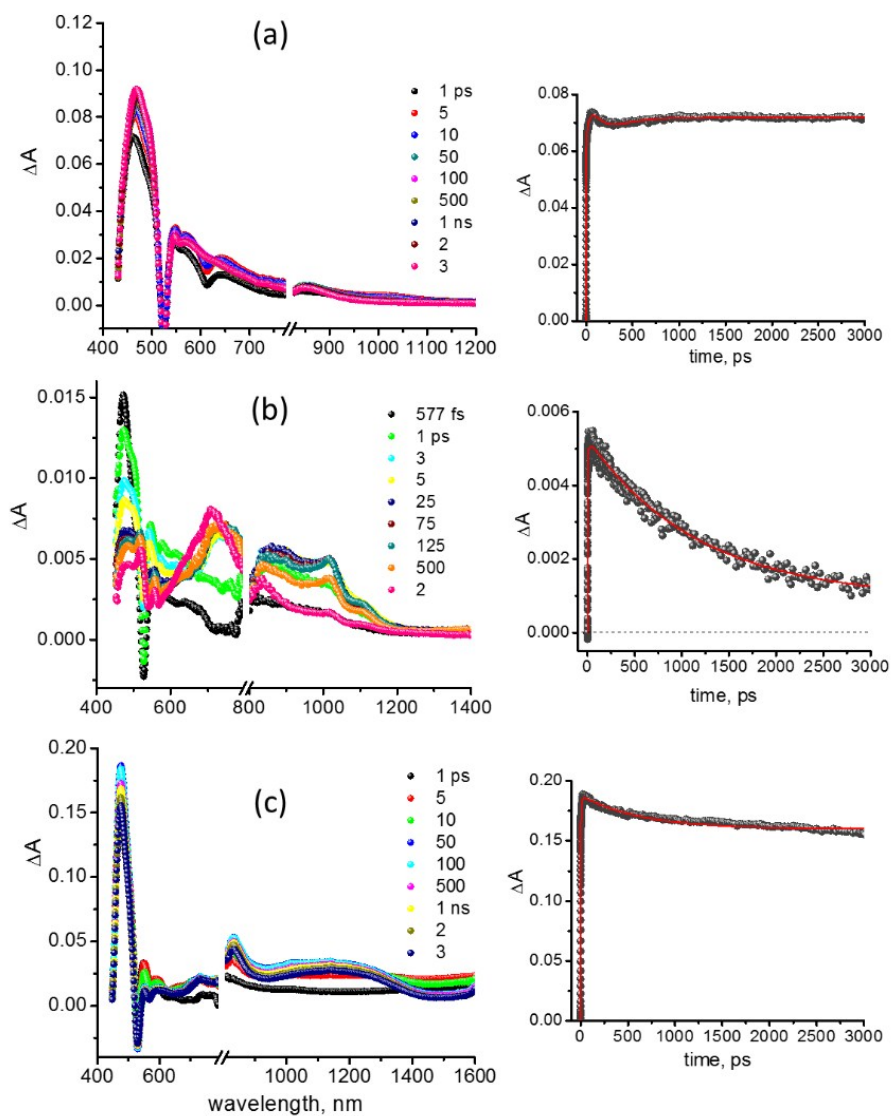


Fig. S7. Femtosecond transient absorption spectra of (a) **1**, (b) **2**, and (c) **3** in Ar-saturated toluene (100 fs laser pulses of 400 nm wavelength). The time profile of the 496 nm peak of **1** corresponding to ${}^3\text{PdP}^*$ formation, 1010 nm peak of **2** corresponding to $\text{C}_{60}^{\bullet-}$, and 475 nm peak of **3** corresponding to ${}^3(\text{TPA})_3\text{PPd}^*$, are shown on the respective right hand side panel.

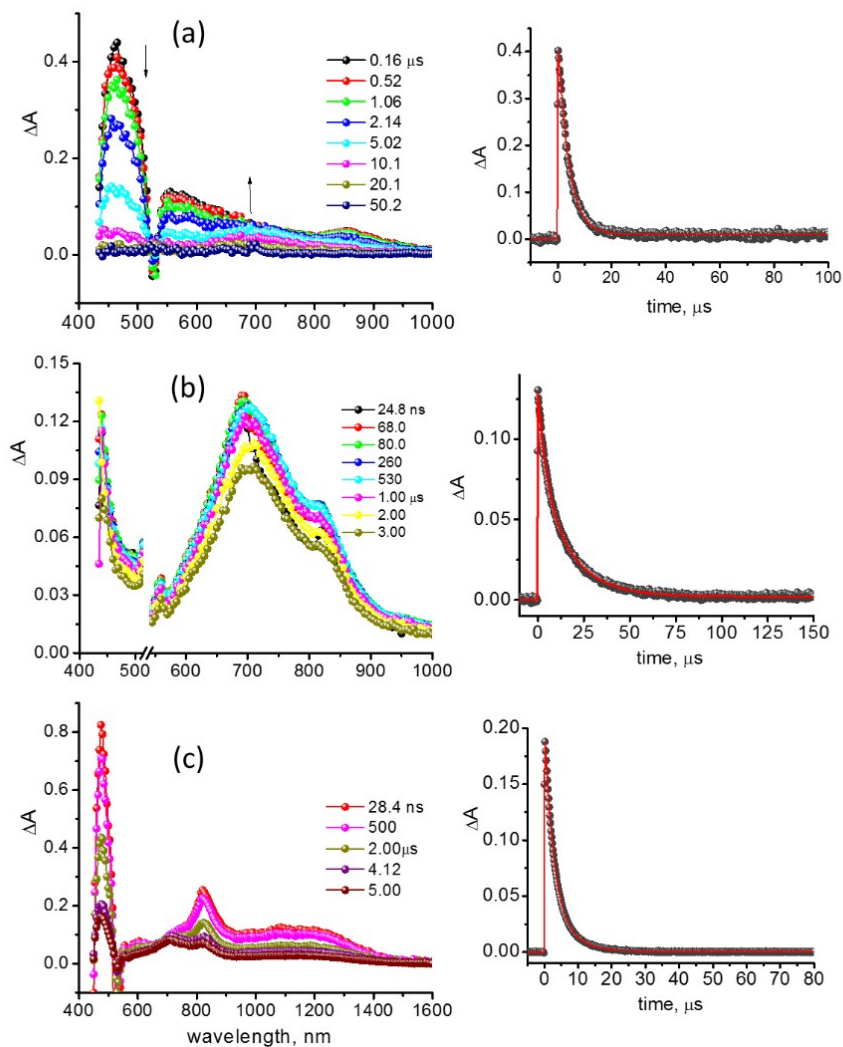
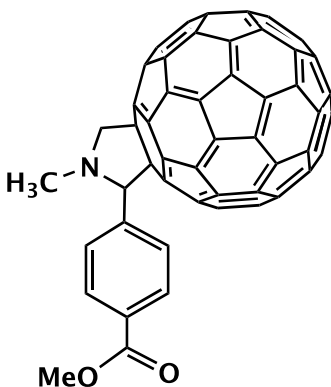


Fig. S8. Nanosecond transient absorption spectra of (a) **1**, (b) **2**, and (c) **3** in Ar-saturated toluene (7 ns laser pulses of 525 nm wavelength). The time profile of the 470 nm peak of **1** corresponding to decay of $^3\text{PdP}^*$, 710 nm peak of **2** corresponding to $^3\text{C}_{60}^*$ decay, and 820 nm peak of **3** revealing decay of $^3(\text{TPA})_3\text{PPd}^*$, are shown on the respective right hand side panel.

EXPERIMENTAL SECTION

Chemicals. Buckminsterfullerene, C₆₀ (99.95% purity), was obtained from SES Research (Houston, TX). Synthesis of C₆₀-Ph-COOMe has been previously reported.¹ Tetra-*n*-butyl ammonium perchlorate, (n-C₄H₉)₄NClO₄, was obtained from Sigma Chemicals. All chromatographic materials and solvents were procured from Fisher Scientific and were used as receive. Synthesis of dyad **1** is given elsewhere.²



C₆₀-Ph-COOMe

Synthesis of free base tetratolylporphyrin, (TTP)H₂

To propionic acid (100 ml) in a round-bottomed flask, pyrrole (0.138g, 2.05mmoles) and *p*-tolualdehyde (0.25 g, 2.05 mmoles) were added and the mixture was refluxed for 4.5 hours. The solvent was removed under vacuum. The crude extract was purified by chromatography over silica gel using hexanes/chloroform (70:30) system. Yield 25 %. ¹H NMR in CDCl₃, δ (ppm) 8.80 (s, 8H, β-pyrrole-H), 8.0 (d, 8H, phenyl-H), 7.45 (d, 8H, phenyl-H), 2.62 (s, 12H, tolyl;-CH₃), -2.81 (s, 2H, imino-H).

Synthesis of (TTP)Pd

Tetratolylporphyrin (TTP)H₂, 80.0 mg, 0.0190 mmoles) and palladium(II) acetate (40.1 mg 0.0179 mmoles) were added into a dry toluene (20 mL) in a round bottomed flask. The mixture was refluxed for 12 hours under inert conditions. The solvent was removed under vacuum and the crude was purified by column chromatography on silica gel using CHCl₃:Hexane system (60:40 v/v). Yield 70.1 %. ¹H NMR in CDCl₃, δ (ppm) 8.79 (s, 8H, β-pyrrole-H), 8.0 (d, 8H, phenyl-H), 7.45 (8H, d-, phenyl-H), 2.61 (s, 12H, tolyl;-CH₃).

2-Formyl-5, 10, 15, 20-tetratolyporphyrinato palladium(II), 2b

(TTP)Pd (0.096 g, 0.124 mmoles) and the Vilsmeier complex (dry DMF (1.2 mL) and phosphorous oxychloride (0.95 mL) were dissolved in 1, 2-dichloroethane (10 mL) in a round bottomed flask. The mixture was heated at reflux for 7 hours and then left overnight standing at room temperature. Next the mixture was vigorously mixed and concentrated sulfuric acid (2 mL) was added. Continuously the mixture was stirred for 6 minutes and then was poured into an ice – cold solution of 0.3 M sodium hydroxide solution (300 mL). The mixture was extracted using chloroform (100 mL) and washed with a saturated solution of sodium bicarbonate (2 x100 mL). The organic layer was dried over anhydrous sodium sulfate and excess solvent removed by vacuum. The crude product was purified on silica using hexane/ dichloromethane (3:2 v/v) as eluent.

¹H NMR in CDCl₃, δ (ppm), 9.38 (1H, s, CHO), 9.20 (1H, s), 8.79 and 8.70(s, 6H, β-pyrrole-H), 8.0 (d, 8H, phenyl-H), 7.45 (8H, d-, phenyl-H), 2.61 (s, 12H, tolyl;-CH₃).

Synthesis of (TTP)Pd-β-C₆₀, 2

To 20 ml of toluene in a round-bottomed flask, 2-formyl-5, 10, 15, 20, tetratolyporphyrin palladium(II), **2b** (0.068 g, 0.086 mmoles), 3 equivalents of fullerene C₆₀ (0.185g, 0.257 mmoles) and 5 equivalents of sarcosine (0.038, 0.423 mmoles) were added. The mixture was refluxed overnight under nitrogen. The solvent was removed by vacuum and the residue was chromatographed over silica using Toluene and hexane (70:30, v/v). ¹H NMR in CDCl₃, δ (ppm), 9.20 (1H, s), 8.76 and 8.70(s, 6H, β-pyrrole-H), 8.0 (d, 8H, phenyl-H), 7.45 (8H, d-, phenyl-H), 5.39 (s, 1H, pyrrolidine), 4.65 (d, 1H, pyrrolidine) 4.15 (s, 1H, pyrrolidine), 2.75 (s, 3H, N-CH₃). ¹³C NMR (400 MHz, CS₂/CDCl₃) δ 156.0-119.9, 69.7, 69.2, 40.0, 29.8 MS (MALDI): Calcd. 1550.97[M⁺]; found 1582.4, 1570.7, 1565.4, 1555.8, 1554.8, 1553.8, 1552.8, 1550.8, 1549.8, 1548.8, 15 [M⁺].

5-(4'-Hydroxyphenyl)-10, 15, 20-tri(N, N-diphenylaminophenyl)porphyrin, 3a

Pyrrole (0.491 g, 7.32 mmol), diphenylaminobenzaldehyde (1.50 g, 5.49 mmol), and 4-hydroxybenzaldehyde (0.223 g, 1.83 mmol) were added to propionic acid (100 ml) in a round-bottom flask and the mixture was refluxed for 4.5 hours. The solvent was removed under vacuum, and the crude product was purified by column chromatography on silica gel with

chloroform/methanol solvent system (90:10 v/v) as eluent. Yield 24.9 %. ¹H NMR in CDCl₃: δ (ppm) 9.0 (m, 8H, β-pyrrole-H), 8.1 (m, 6H, ortho-phenyl-H), 7.42 (m, 6H, metaphenyl-H), 8.9, 8.1 (d, d, 4H, substituted phenyl-H), 7.0-7.16 (m, m, 30 H, N-phenyl), 5.35 (s (br), 1H, hydroxy-H), -2.79 (s, 2H, imino-H).

5-{4''-Formyl benzoic acid-4'-phenyl ester}-10, 15, 20-tri(N, N-diphenylaminophenyl) porphyrin, 3b

Porphyrin **3a** (0.252 g, 0.22 mmol), 4-carboxybenzaldehyde (0.167g, 1.11mmol), and of 4-di(methylamino)pyridine (DMAP, 0.136 g 1.11 mmol) were dissolved in 50 mL of dry dichloromethane in a round bottomed flask. The reaction mixture was cooled to 0 °C, and N, N'-dicyclohexylcarbodiimide (DCC, 0.229 g, 1.11 mmol) was added and the reaction mixture was stirred for 8 h at room temperature. The solvent was removed in vacuum and the crude compound was extracted with CHCl₃. The compound was then purified on a silica gel column using toluene and chloroform (95:5 v/v) as eluent. Yield 29.5 %. ¹H NMR in CDCl₃, δ (ppm) 10.21 (1H, -CHO), 9.05 (m, 8H, β-pyrrole-H), 8.1 (m, 6H, ortho-phenyl-H), 7.45 (m, 6H, metaphenyl-H), 8.9, 8.3 (d, d, 4H, substituted phenyl-H), 8.55, 7.65 (d, d, 4H, phenyl-CHO), 7.1-7.2 (m, 30 H, N-phenyl), -2.75 (s, 2H, imino-H).

5-{4''-Formyl benzoic acid-4'-phenyl ester}-10, 15, 20-tri (N, N-diphenylaminophenyl) porphyrinato palladium(II), 3c

To 20 ml of dry toluene, 5-{4''-formyl benzoic acid-4'-phenyl ester}-10,15,20-tri(N,N-diphenylaminophenyl), **3b** (102.1 mg, 0.081 mmoles) and palladium acetate (0.036 g, 0.16 mmoles) were added and refluxed under nitrogen for 5 hours monitoring the reaction with UV. Upon disappearance of Q-bands, the reaction was stopped and the solvent removed under vacuum. The crude metallated product was the purified on silica gel, with hexanes/toluene solvent system (10/90 v/v) yield 14.7 % 9.05 (m, 8H, pyrrole-H), 8.1 (m, 6H, ortho-phenyl-H), 7.47 (m, 6H, metaphenyl-H), 8.9, 8.3 (d, d, 4H, substituted phenyl-H), 8.55, 7.65 (d, d, 4H, phenyl-CHO), 7.1-7.2 (m, 30 H, N-phenyl).

5-[2-(4''-Benzoic acid-4'-phenyl ester)-N-methyl-3, 4-fulleropyrrolidine]-10, 15, 20-tri (N, N-diphenylaminophenyl)porphyrinato palladium(II), (TPA)₃PdP-C₆₀, 3

To 20 mL of dry toluene, compound **3c** (0.052g, 0.048 mmol), C₆₀ (0.104g, 0.144 mmol), and of sarcosine (0.167g 0.188 mmol) were added, and the mixture was refluxed for 12 h. Solvent was removed under vacuum, and the crude compound was adsorbed onto silica gel and was purified on a silica gel column using toluene and hexane (95:5 v/v) as eluent. Yield 37%. ¹H NMR in CDCl₃, δ (ppm) 8.97 (m, 8H, β-pyrrole-H), 8.1 (m, 6H, ortho-phenyl-H), 7.41 (m, 6H, meta-phenyl-H), 8.9, 8.25 (d, d, 4H, substituted phenyl-H), 8.42, 7.61 (d, d, 4H, phenyl-pyrrolidine), 7.1-7.2 (m, 30H, N-phenyl), 5.0 (s, 1H, pyrrolidine-H), 4.05, 4.35 (d, d, 2H, pyrrolidine-H) 2.84 (s, 3H, pyrrolidine N-CH₃). ¹³C NMR (400 MHz, CS₂/CDCl₃) δ 147.83, 147.56, 145.99, 145.20, 141.87, 141.75, 141.46, 135.06, 129.50, 129.02, 128.21, 124.92, 124.86, 123.30, 121.25, 29.69. MS (MALDI): Calcd, 2114.42 [M⁺]; found 2248.7, 2132.4, 1990.1, 1850.9, 1702.9, 1485.9, 1396.9, 1393.9, 1390.9, 1382.9, 1379.9, 1363.9, 1250.8, 1242.6, 1238.9, 1234.9 (M⁺ - C₆₀).

Spectral measurements. The UV-visible and near-IR spectral measurements were carried out with a Shimadzu 2550 UV-Vis spectrophotometer or Jasco V-670 spectrophotometer. The steady-state fluorescence emission was monitored by using a Varian (Cary Eclipse) Fluorescence Spectrophotometer or a Horiba Jobin Yvon Nanolog spectrofluorimeter equipped with PMT (for UV-visible) and InGaAs (for near-IR) detectors. A right angle detection method was used for fluorescence measurements at room temperature. All the solutions were purged prior to spectral measurements using argon gas. The ¹H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard.

Electrochemistry. Differential pulse voltammetry was recorded on a Princeton Applied Research potentiostat/galvanostat Model 263A using a three electrode system. A platinum button electrode was used as the working electrode, while a platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical measurements with nitrogen gas.

Femtosecond Laser Flash Photolysis: Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent

incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into harmonic generator which produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Explorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

Nanosecond Laser Flash Photolysis: The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with second and third harmonics OPO (tuning range 410-2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with the powers of 1.0 to 3 mJ *per* pulse. The transient absorption measurements were performed using a Proteus UV-Vis-NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic delivered white probe light and either a fast rise Si photodiode detector covering the 200-1000 nm range or a InGaAs photodiode detector covering 900-1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope. Data analysis was performed using Surface Explorer software supplied by Ultrafast Systems.

Transient EPR Spectroscopy: Transient EPR experiments were carried out using a modified Bruker EPR 200D-SRC X-band spectrometer described elsewhere.³⁻⁴ Light excitation at 532 nm was achieved using 10 ns pulses from a Nd:YAG laser at a repetition rate of 10 Hz. EPR samples were prepared by dissolving the solid compound of interest in benzonitrile (PhCN) to a nominal concentration of ~ 1 mM. The solution was then warmed to about 60°C and filtered to remove any undissolved compound, purged with N₂ and placed in a flat cell, which was sealed to prevent contact with oxygen.

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2. Obondi, C. O.; Lim, G. N.; D'Souza, F. *J. Phys. Chem. C.* **2015**, *119*, 176.
3. Xu, W.; Chitnis, P.; Valieva, A.; van der Est, A.; Pushkar, Y. N.; Krzystyniak, M.; Teutloff, C.; Zech, S. G.; Bittl, R.; Stehlik, D., *J. Biol. Chem.* **2003**, *278*, 27864.
4. Sakuragi, Y.; Zybailov, B.; Shen, G.; Jones, A. D.; Chitnis, P. R.; van der Est, A.; Bittl, R.; Zech, S.; Stehlik, D.; Golbeck, J. H., *Biochemistry* **2002**, *41*, 394.

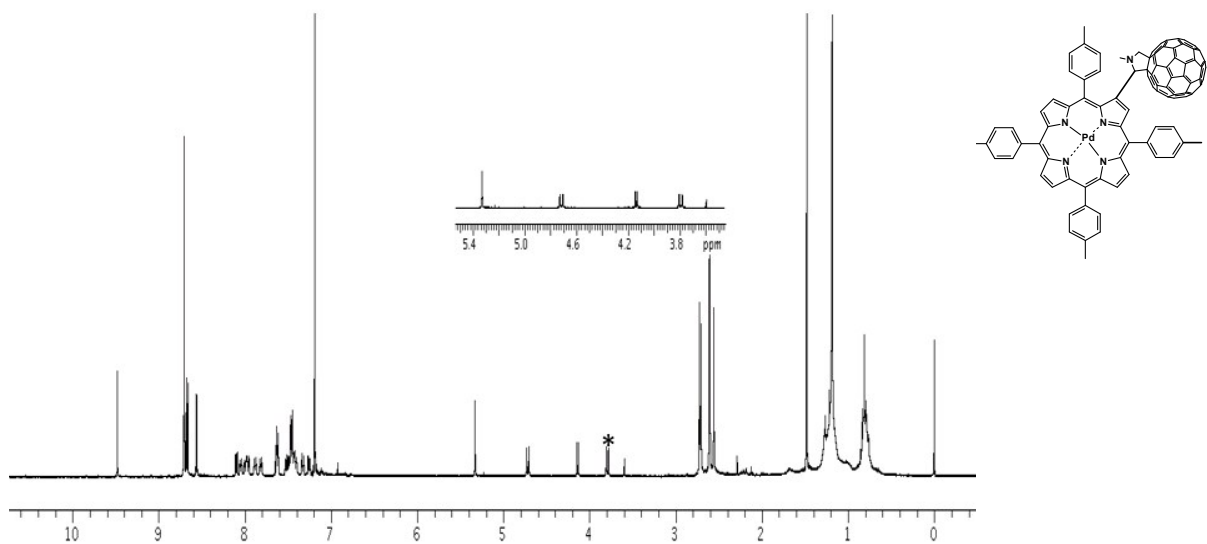


Figure S9: ^1H NMR of compound **2** in CDCl_3 . The * refers to solvent impurity.

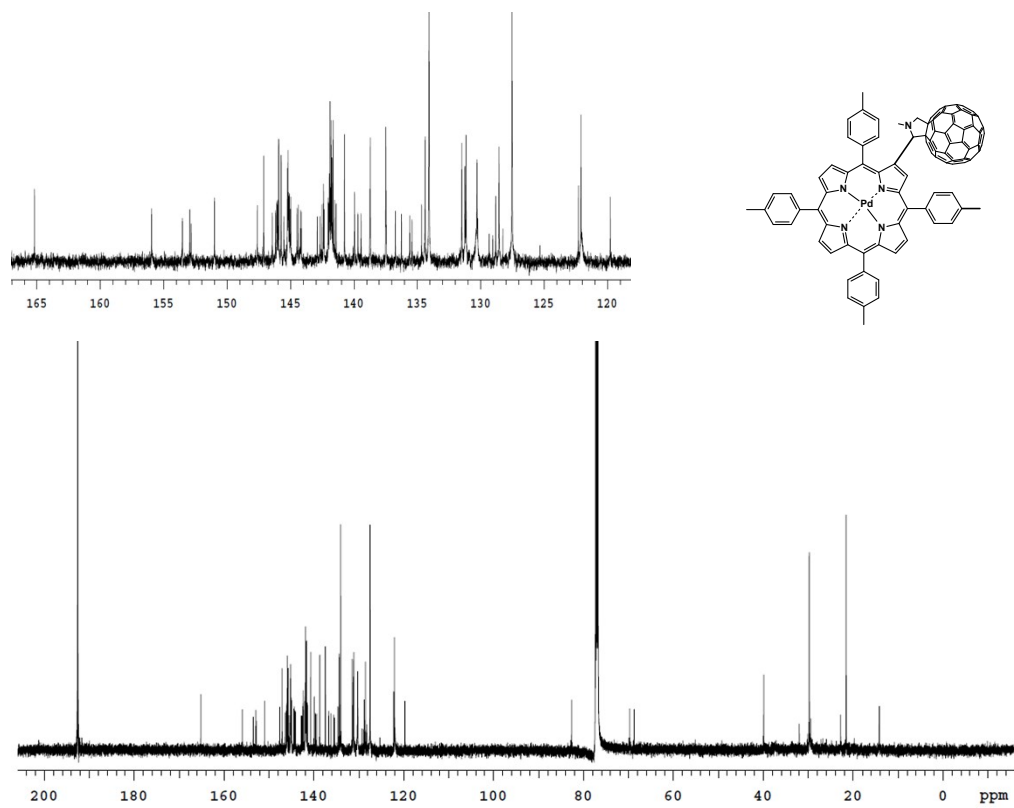


Figure S10: ^{13}C NMR of compound **2** in CDCl_3 .

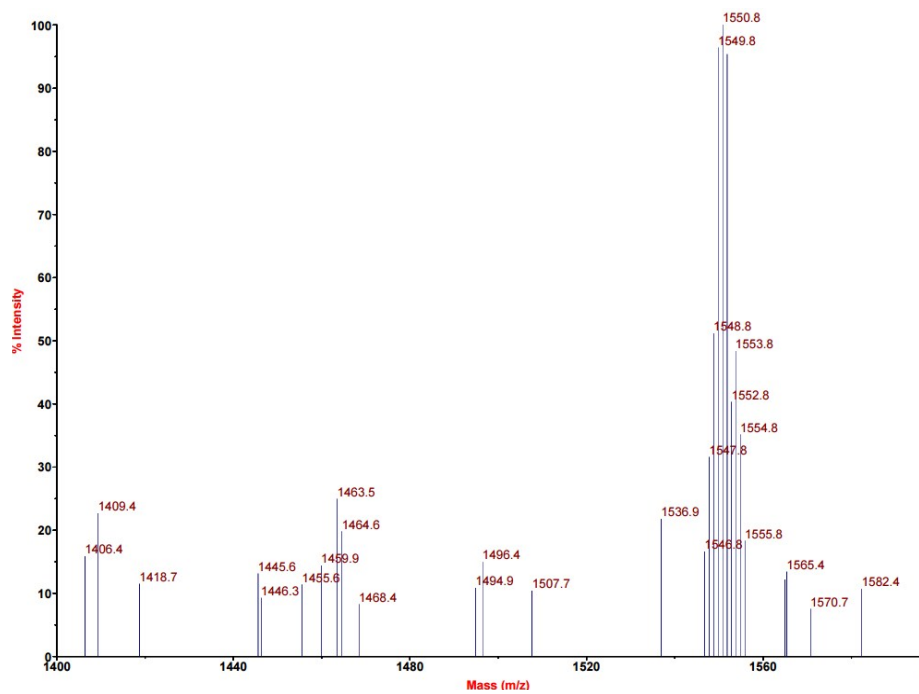


Figure S11. MALI-TOF Mass spectrum of compound **2**.

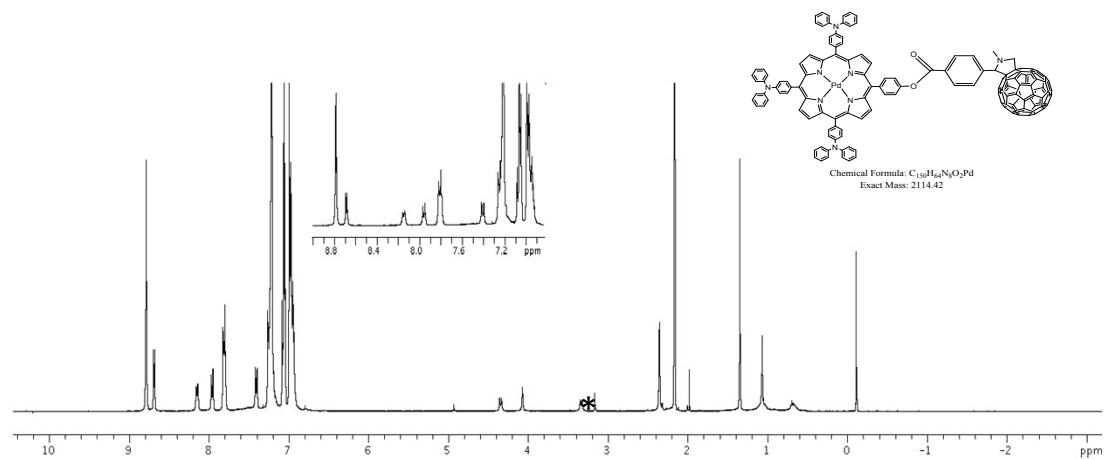


Figure S12: ¹H NMR of compound **3** in CDCl₃. The * refers to solvent impurity.

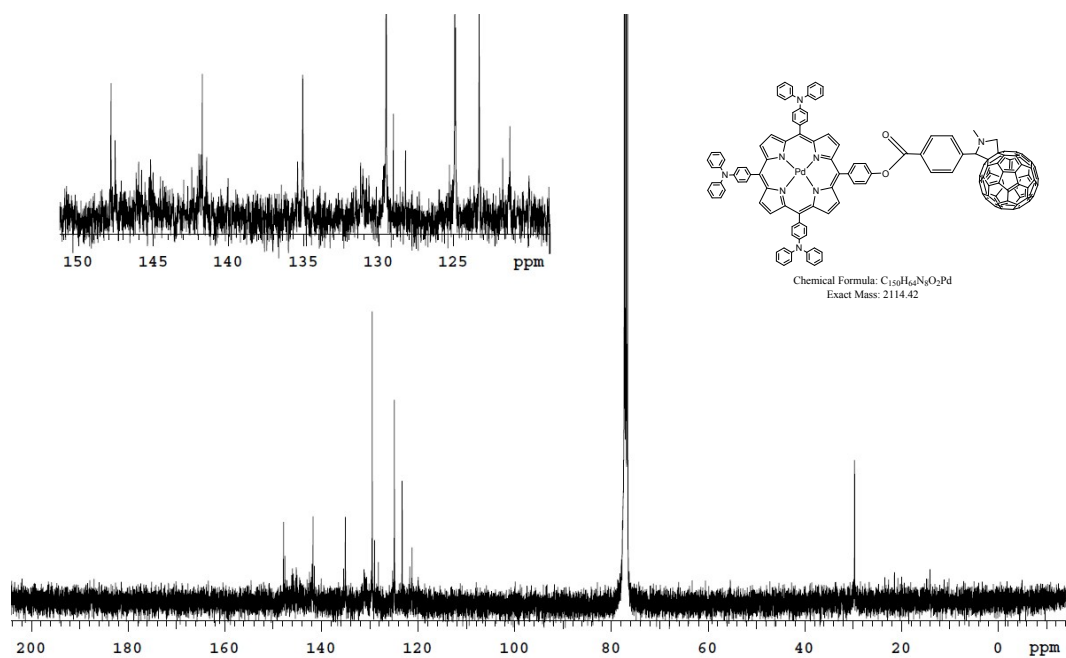


Figure S13: ¹³C NMR of compound **3** in CDCl₃.

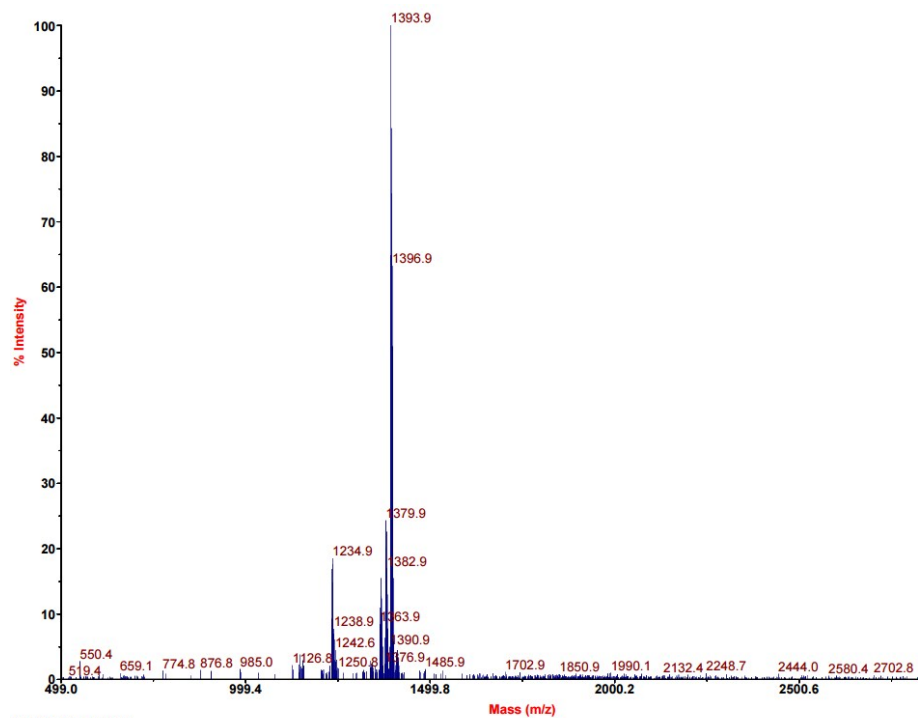


Figure S14. MALI-TOF Mass spectrum of compound 3.