Supplementary Information

Exclusive triplet electron transfer leading to long-lived radical ion-pair formation in an electron rich platinum porphyrin covalently linked to fullerene dyad

Diliraj Subedi,[a] Habtom B. Gobeze,[a] Yuri E. Kandrashkin,[b] Prashanth K. Poddutoori,[c] Art van der Est,*[d] and Francis D'Souza*[a]

[a]*Department of Chemistry, University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, United States; E-mail: Francis.dsouza@unt.edu*

[b]*Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Sibirsky Tract 10/7, Kazan 420029, Russian Federation.*

[c]*Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, 1038 University Drive, Duluth, MN 55812, USA.*

[d]*Department of Chemistry, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, Ontario, L2S 3A1, Canada. Email: avde@brocku.ca*

Experimental Section

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. Tetra-n-butylammonium perchlorate, $(n\text{-}Bu_4N)ClO_4$, used in electrochemical studies was from Fluka Chemicals.

Synthesis

5-(4'-hydroxyphenyl)-10, 15, 20-tri(N, N-diphenylaminophenyl)porphyrin (TPAPhOH), a

Propionic acid (51 ml) was taken in a 250 ml round bottom flask and heated for 15 mins followed by the addition of diphenylaminobenzaldehyde (2.5g, 9.15 mmol), 4-hydroxybenzaldehyde (0.375g, 3.05 mmol) and pyrrole (0.85 ml, 12.2 mmol). Then the whole contents were allowed to reflux for 5h until the TLC showed the consumption of starting material. The mixture was stored at 0ºC for 12 hr, ~~warmed to room temperature~~ and filtered to get the solid compound which was purified using silica column with chloroform (100%) as the eluent. Yield 28.5%. ^{1}H NMR in CDCl3: δ (ppm) 9.0 (m, 8H, β-pyrrole-H), 8.1 (m, 8H, ortho-phenyl-H), 7.48 (m, 6H, meta-phenyl-H), 7.40 (d, 2H, substituted phenyl-H), 7.1-7.46 (m, m, 30 H, N-phenyl), -2.67 (s, 2H, imino-H).

5-(4"-formyl benzoic acid-4'-phenyl ester)-10, 15, 20-tri(N, N-diphenylaminophenyl) porphyrin (TPA Ester), b

Porphyrin a (0.380g, 0.335 mmol), 4-carboxybenzaldehyde (0.251g, 1.67 mmol), and 4-di(methylamino)pyridine (DMAP, 0.205g, 1.67 mmol) were dissolved in dry dichloromethane (40 ml) under N_2 gas in an ice bath and stirred for a few minutes before adding N, N'dicyclohexylcabodiimide (DCC, 0.346g, 1.67 mmol). The reaction mixture was then stirred for 24h at room temperature. In the work up process, the crude compound was extracted with chloroform. Then the compound was purified on silica column using toluene (100%) as eluent. Yield 33%. ^{1}H NMR in CDCl3, δ (ppm) 10.20 (1H, -CHO), 8.9-9.1 (m, 8H, β-pyrrole-H), 8.1 (m, 6H, ortho-phenyl-H), 7.45 (m, 6H, metaphenyl-H), 8.55, 8.3 (d, d, 4H, substituted phenyl-H), 7.67-7.45 (d, d, 4H, phenyl-CHO), 7.10-7.46 (m, 30 H, N-phenyl), -2.67 (s, 2H, imino-H).

5-(4"-formyl benzoic acid-4'-phenyl ester)-10, 15, 20-tri(N, N-diphenylaminophenyl) porphyrinato platinum(II) (PtTPA), c

$PtCl_2$ (0.080g, 0.296 mmol) was dissolved in benzonitrile and refluxed for 1.5h under N_2 gas. Subsequently, 5-(4"-formyl benzoic acid-4'-phenyl ester)-10, 15, 20-tri(N, N-diphenylaminophenyl) porphyrin, b (0.250g, 0.197 mmol) was added and refluxed for additional 1.5h until the UV showed that the four Q-

bands of the free base porphyrin had been reduced to the two Q-bands expected for a metalloporphyrin. The solvent was then removed under vacuum and the metallated compound was purified on silica gel column with toluene (100%) as the eluent. The yield thus obtained was 30%. ^{1}H NMR in CDCl3, δ (ppm) 10.20 (1H, -CHO), 8.9-9.1 (m, 8H, β-pyrrole-H), 8.0 (m, 6H, ortho-phenyl-H), 7.44 (m, 6H, metaphenyl-H), 8.55, 8.3 (d, d, 4H, substituted phenyl-H), 8.13,7.67 (d, d, 4H, phenyl-CHO), 7.10-7.46 (m, 30 H, N-phenyl). MS (MALDI): Calcd. 1456.4327 [M+]; found 1462.4480, 1461.4441, 1460.4415, 1459.4397, 1458.4379, 1457.4353, 1455.4294, 1453.4137[M+].

5-[2-(4′′-Benzoic acid-4′-phenyl ester)-N-methyl-3, 4-fulleropyrrolidine]-10, 15, 20-tri (N, N-diphenylaminophenyl)porphyrinato platinum(II), (C_{60}TPA), d

To 20 ml of dry toluene, compound c (0.100g, 0.00686 mmol), C_{60} (0.148g, 0.205 mmol) and sarcosine (0.06g, 0.086 mmol) were added and the mixture was refluxed for 12h. The solvent was removed under vacuum and the crude product was purified using a silica column with toluene and hexane (80:20 v/v) as the eluent. Yield 33%. ^{1}H NMR in CDCl3, δ (ppm) 8.9 (m, 8H, β-pyrrole-H), 8.0 (m, 6H, ortho-phenyl-H), 7.44 (m, 6H, meta-phenyl-H), 8.55, 8.24 (d, d, 4H, substituted phenyl-H), 8.15, 7.67 (d, d, 4H, phenylpyrrolidine), 7.10-7.46 (m, 30H, N-phenyl), 4.87 (s, 1H, pyrrolidine-H), 4.1, 4.92 (d, d, 2H, pyrrolidine-H) 2.80 (s, 3H, pyrrolidine N-CH3). ^{13}C NMR (500 MHz, CS2/CDCl3) δ 147.79, 147.51, 143.09, 134.95, 129.68, 129.61, 124.95, 123.45, 121.31, 30.00. MS (MALDI): Calcd, 2203.4800 [M+]; found 2208.4939, 2207.4922, 2206.4908, 2205.4879, 2204.4840, 2202.4758, 2201.4696, 2200.4687 (M+-C60)

Spectral measurements

All reagents were obtained from commercial sources, and used as received unless otherwise stated. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) 400 MHz instrument using $CDCl_3$, and Acetone-d_6 and Methanol-d_4 as solvents. ^{1}H NMR chemical shifts are reported in parts per million (ppm) using the chemical shift of the residual solvent peak as a reference or tetramethylsilane (TMS) as an internal standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants, J, are given in Hz. ^{13}C NMR chemical shifts were obtained using the residual solvent peak as a referenced. HRMS was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer.

The UV-visible spectral measurements were carried out with a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right angle detection method was used. Differential pulse voltammograms 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 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 and spectral measurements using nitrogen gas.

Femtosecond Transient Absorption Spectroscopy. 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 a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is $\pm$10%.

Nanosecond Laser Flash Photolysis: The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with 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 Xplorer 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[1,2]. 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 the liquid crystal 4′-pentyl-4-biphenylcarbonitrile (5CB) at room temperature to a nominal concentration of ~ 1 mM. The solution was then warmed to about 60ºC and filtered to remove any undissolved compound, purged with N_2 and placed in a flat cell, which was sealed to reduce contact with oxygen.

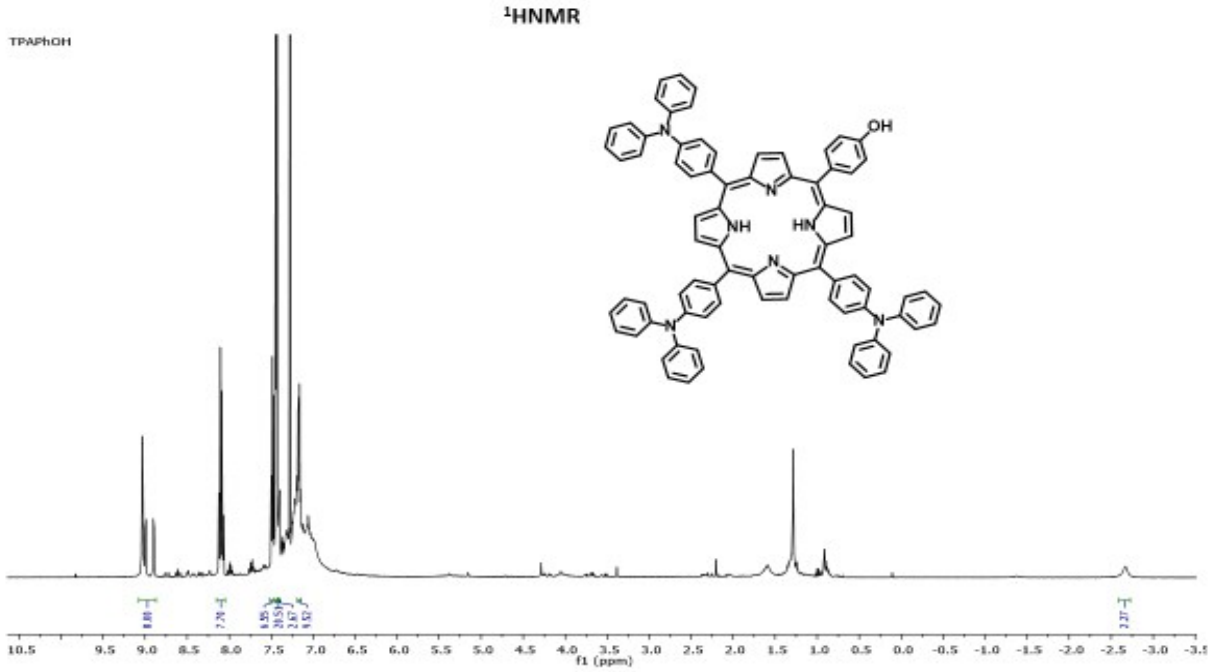

Figure S2: ^{1}H NMR of free-base $(TPA)_3P$-OH in $CDCl_3$.

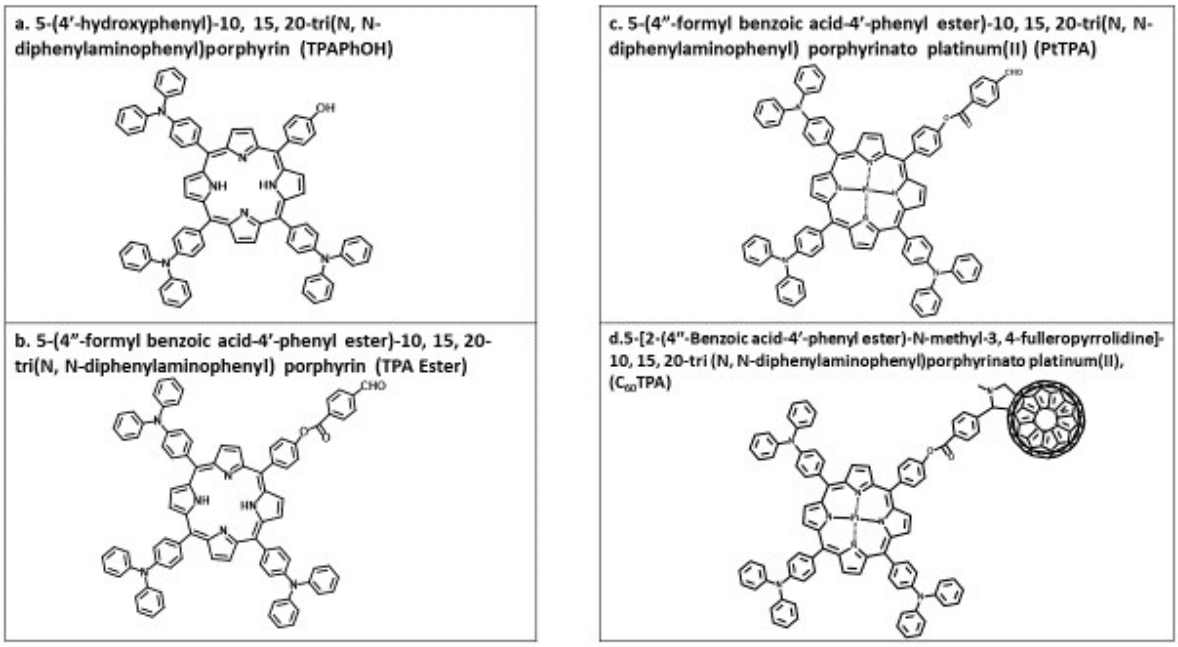

Figure S1. Structures of the synthesized compounds.

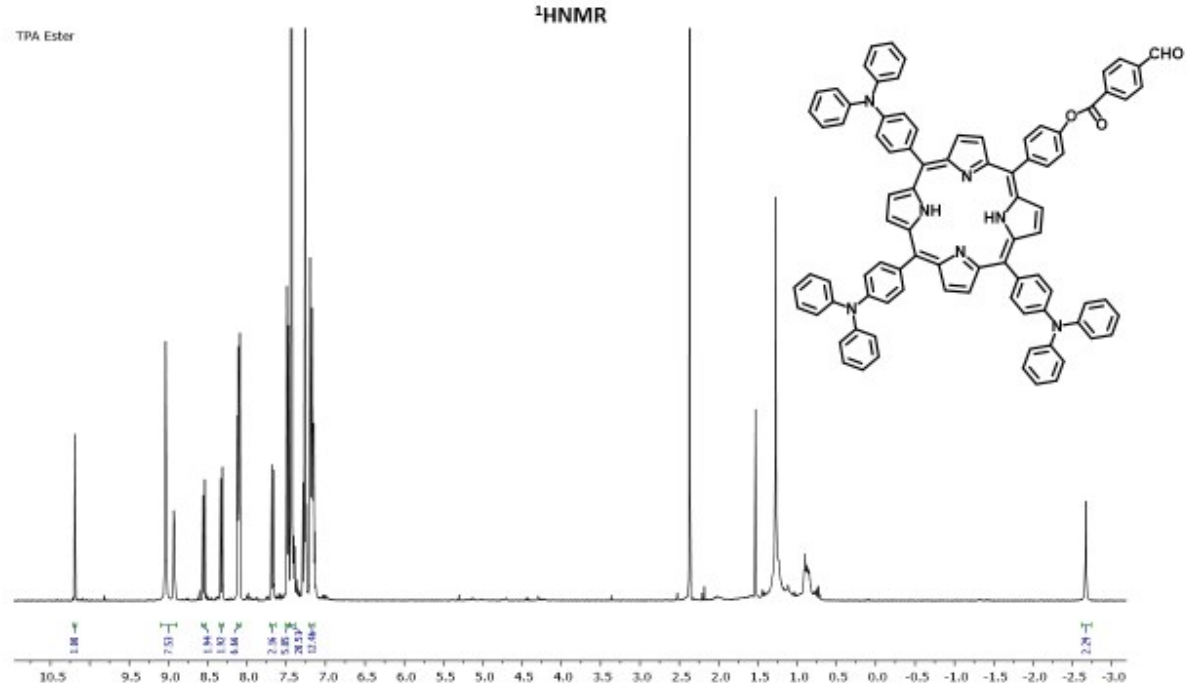

Figure S3: ^{1}H NMR of free-base $(TPA)_3P$-CHO in $CDCl_3$.

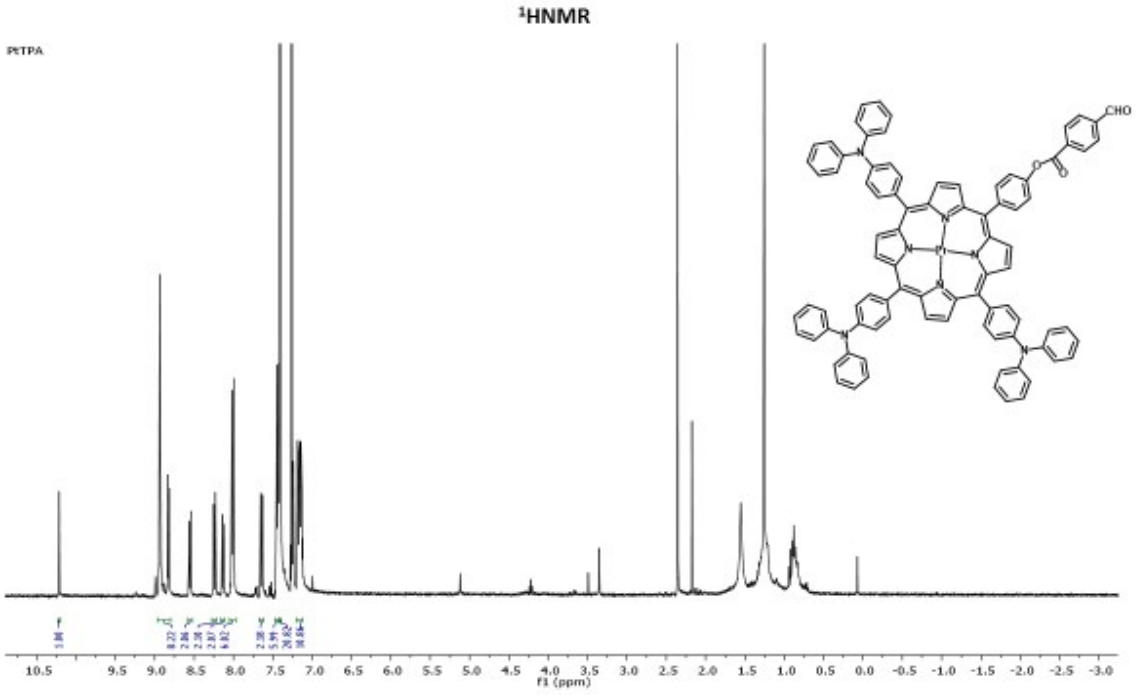

Figure S4: ^{1}H NMR of $(TPA)_3PPt$-control in $CDCl_3$.

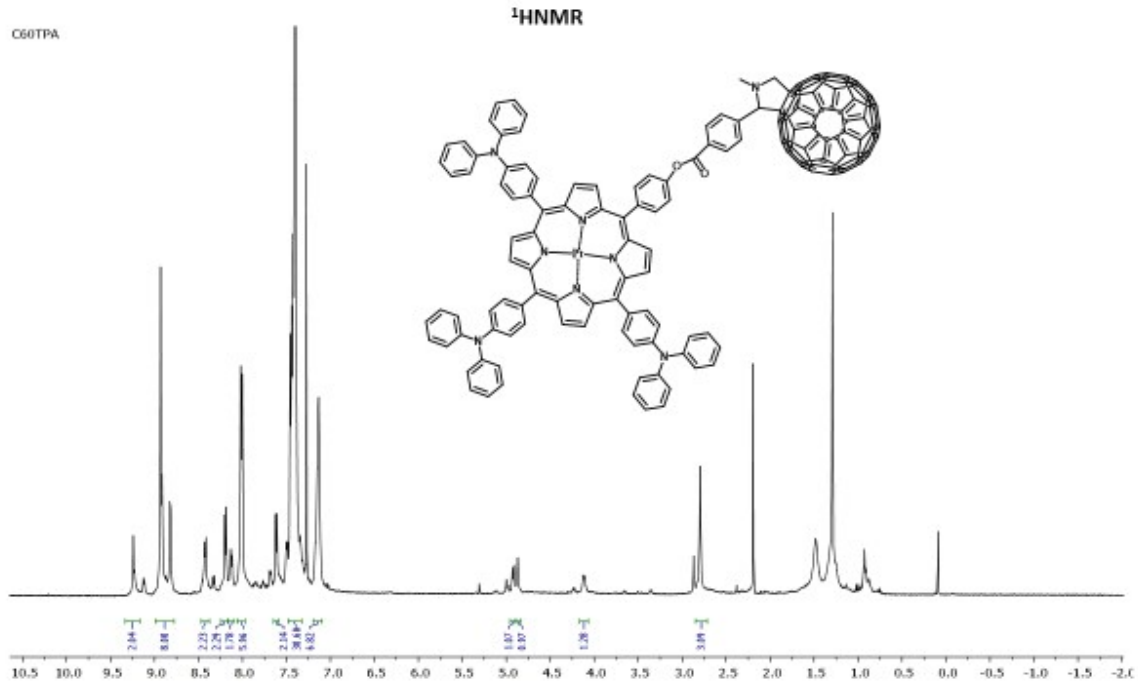

Figure S5: ^{1}H NMR of $(TPA)_3PPt\text{-}C_{60}$ in $CDCl_3$.

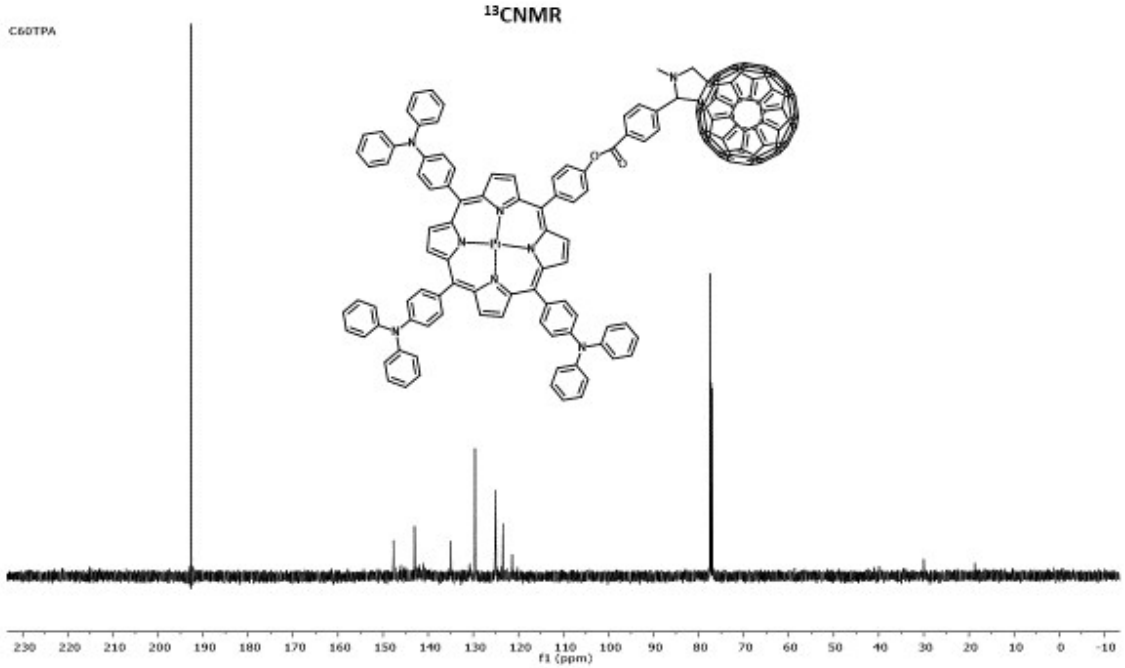

Figure S6: ^{13}C NMR of $(TPA)_3PPt\text{-}C_{60}$ in $CDCl_3$.

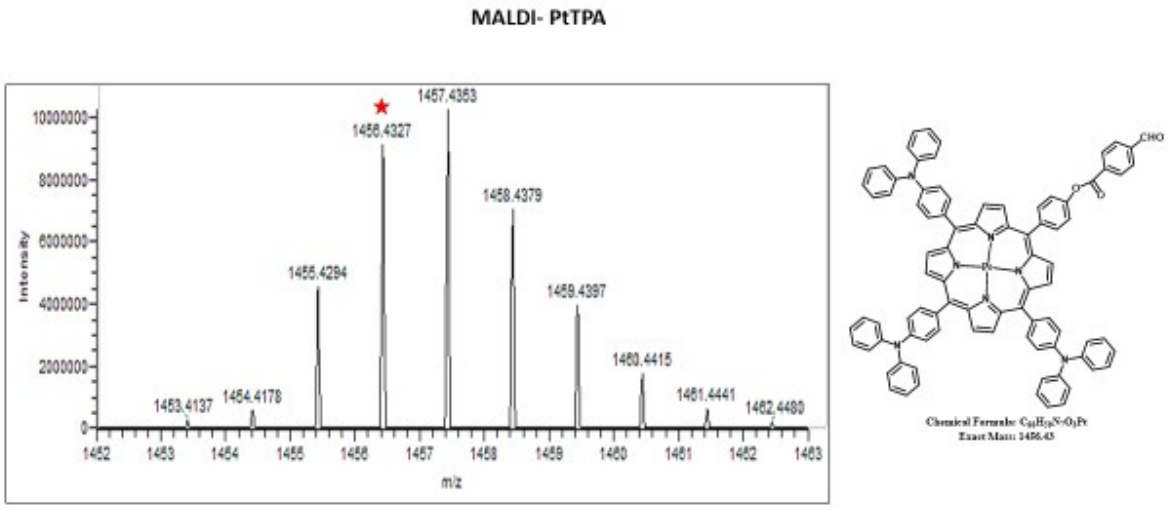

Figure S7: MALDI mass of of $(TPA)_3PPt$-Control.

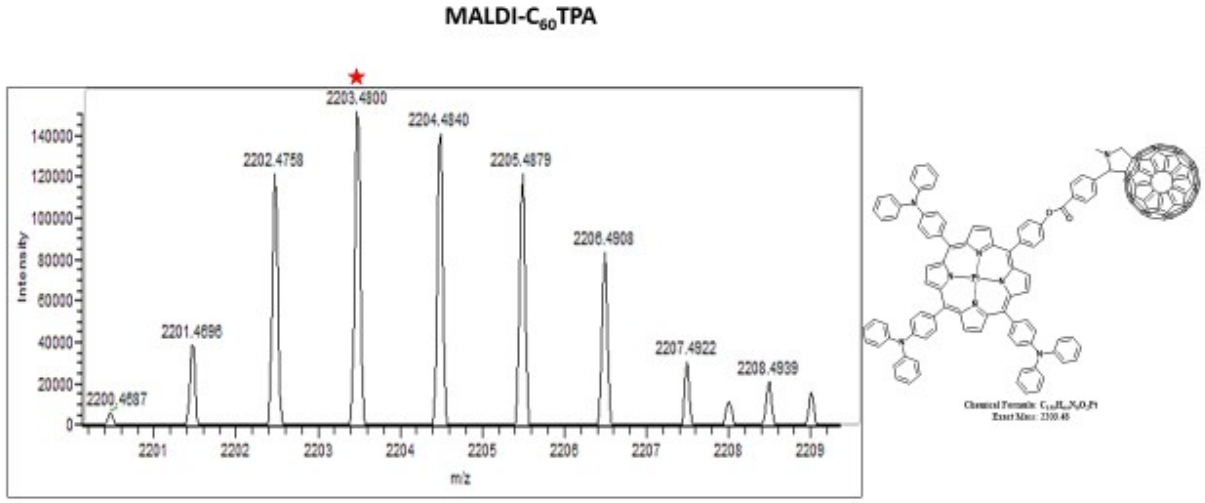

Figure S8: MALDI of $(TPA)_3PPt$-C_{60}.

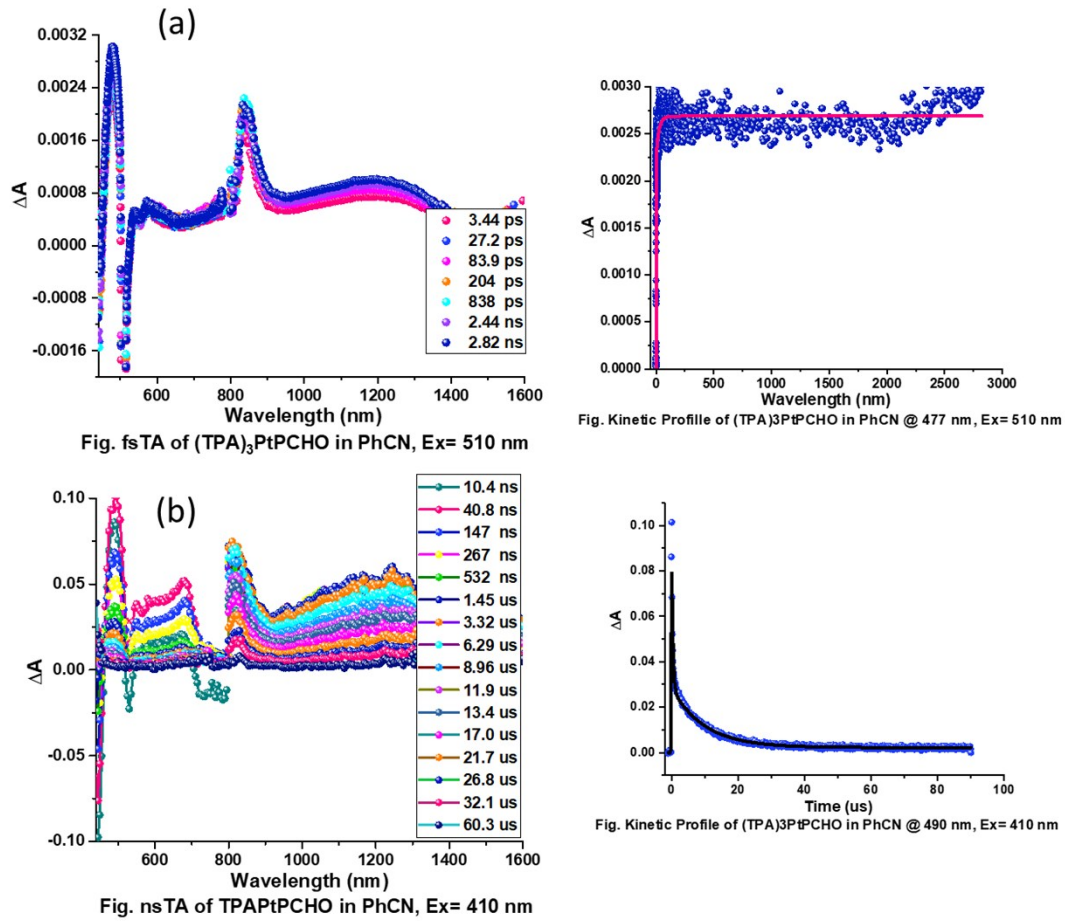

Figure S9. (a) Fs-TA spectra of $(TPA)_3PPt$ control at the indicated delay times (λ_{ex} = 510 nm), Time profile of the 477 nm peak is shown at right hand side. (b) Ns-TA spectra of $(TPA)_3PPt$ control at the indicated time intervals (λ_{ex} = 410 nm). Time profile of the 490 nm peak is shown at right hand side. All spectra were recorded in Ar-saturated benzonitrile.

References

1. 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.
2. 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.