# Supporting Information

## Zinc Porphyrin/Fullerene/Block-Copolymer Micelle for Enhanced Electron Transfer Ability and Stability

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## 1 Materials and instrumentation

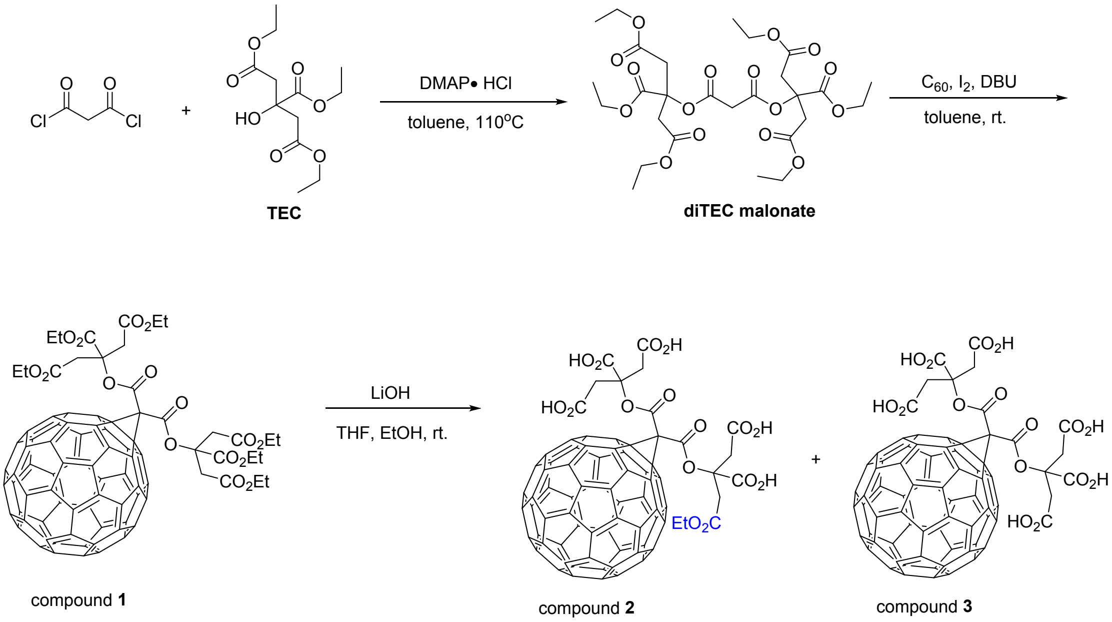
ZnTPPS was purchased from Sigma-Aldrich. Fullerene ($C_{60}$) was supplied by Yongxin Chemicals Corporation (Henan, China). Triethyl citrate and Malonyl dichloride were purchased from J&K. α-Methoxy-ω-aminopoly(ethylene glycol) ($CH_3O$-$PEG_{113}$-$NH_2$; $M$w = 5000; $M$w/$M$n = 1.05) was purchased from Aladdin and used after dried under vacuum. *ε*-(benzyloxycarbonyl)-L-lysine N-carboxyanhydride (Lys(Z)-NCA) were synthesized by the Fuchs-Farthing method using bis(trichloromethyl) carbonate (triphosgene). Trifluoroacetic acid, hydrogen bromide (HBr; 45% in acetic acid) were purchased from Sigma-Aldrich. Nitroblue tetrazolium (NBT), reduced nicotinamide adenine dinucleotide (NADH), methyl viologen ($MV^{2+}$), triethanolamine (TEOA), 2,2,6,6-tetramethyl-piperidine (TEMP), 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) were purchased from Aladdin and used as received. All aqueous solutions were prepared with ultrapure Milli-Q water (resistance >18 MΩ $cm^{-1}$).

$^1H$ NMR spectra were recorded on a Varian UNITY-plus 400 M NMR spectrometer at room temperature with tetramethylsilane (TMS) as an internal standard. Electron spray ionization (ESI) mass spectrometry was performed on a VG-ZAB-HS spectrometer (VG Company, England using the Fast Atom Bombardment (FAB) method. Dynamic light scattering (DLS) experiments at a 90° scatter angle were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 636 nm at required temperature. All samples were obtained by filtering through a 0.45 μm Millipore filter into a clean scintillation vial. Transmission electron microscopy (TEM) measurements were performed using a Philips T20ST electron microscope at an acceleration voltage of 100 kV. To prepare the TEM samples, the sample solution was dropped onto a carbon-coated copper grid and dried slowly at required temperature. The zeta potential values were measured on a Brookheaven ZetaPALS (Brookheaven Instrument, USA). Absorption spectra were performed on a Shimadzu UV-2401PC spectrometer (Shimadzu Corporation, Tokyo, Japan). Fluorescence spectra were carried out on a F4600 fluorophotometer (Hitachi, Japan). Time-resolved fluorescence measurements were run on a Fluorescence Lifetime Spectrometer (FL920).

# 2 The synthesis of materials

## 2.1 The synthesis of fullerene derivative.

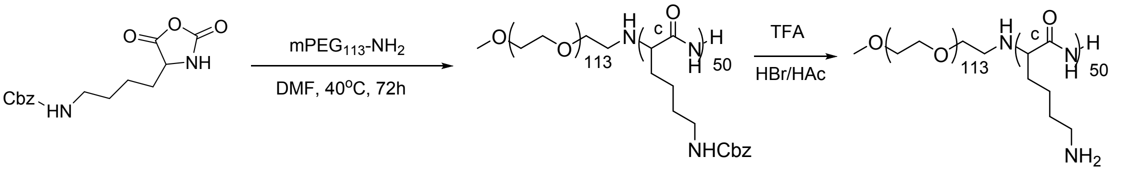
The synthesis route of m$C_{60}$ is shown in Scheme S1



**Scheme. S1.** Synthesis of fullerene derivative

# 3 The synthesis of block copolymer

The synthesis route of PEG-*b*-PLys is shown in Scheme S2.



**Scheme S2**. The synthesis route of PEG-*b*-PLys

# 4 Characterizations

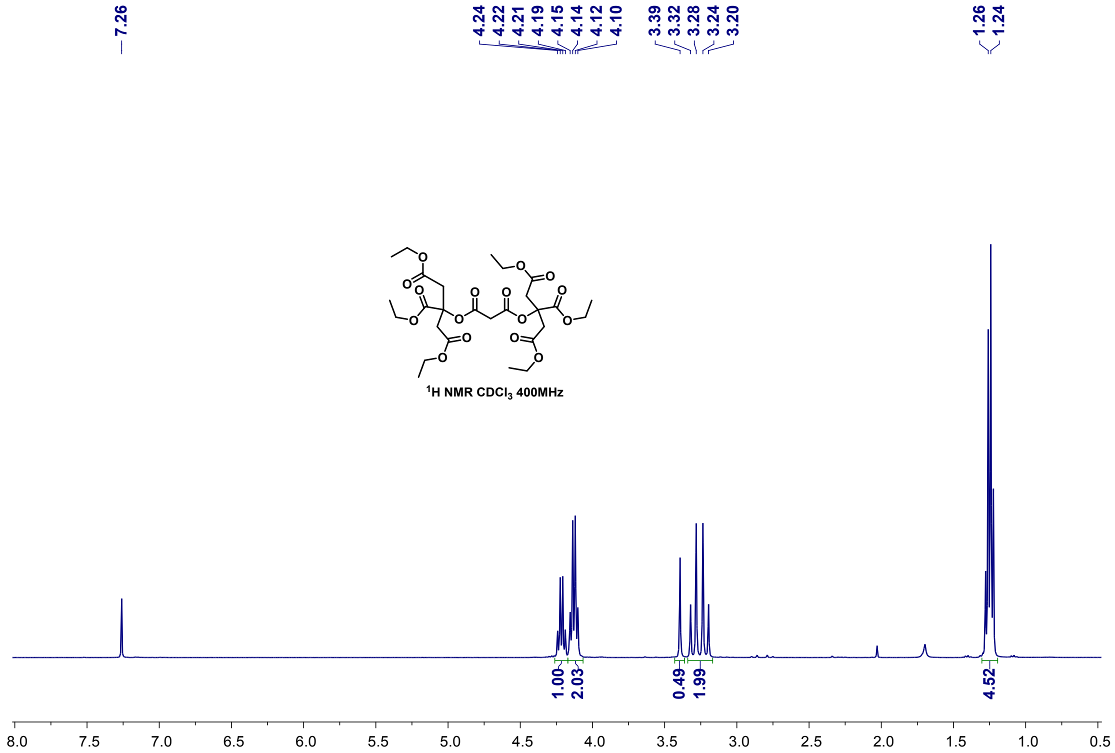


**Figure S1.** $^1$H NMR spectra of malonate.

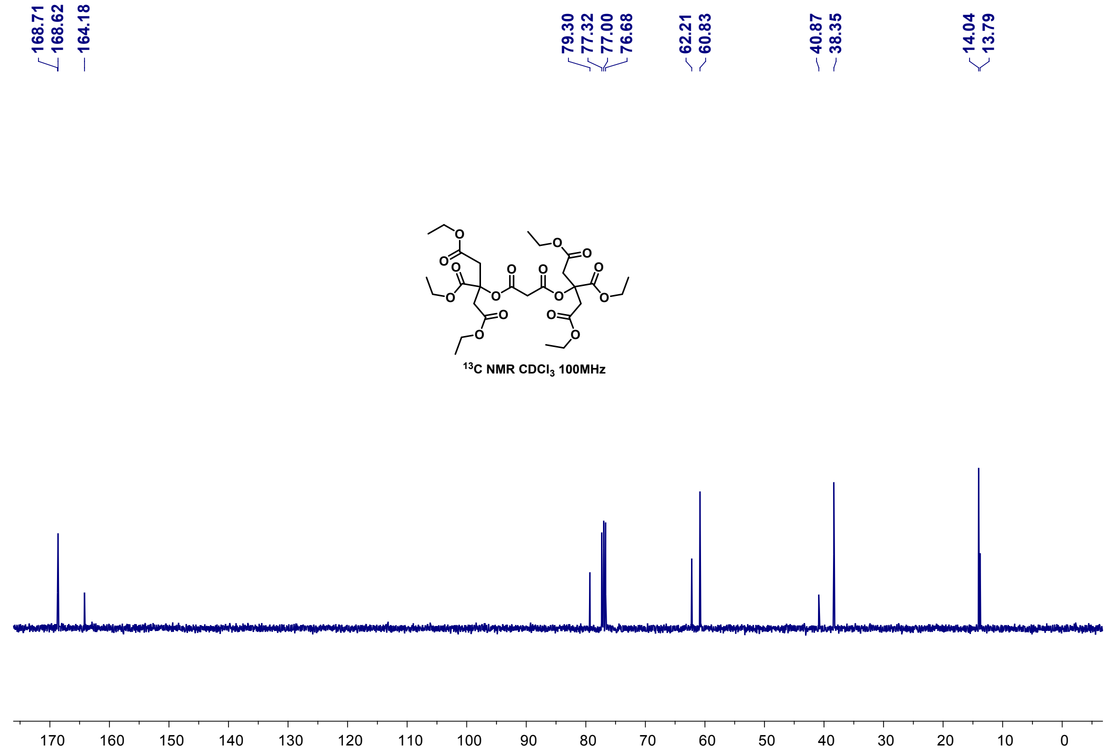


**Figure S2.** $^{13}$C NMR spectra of malonate.

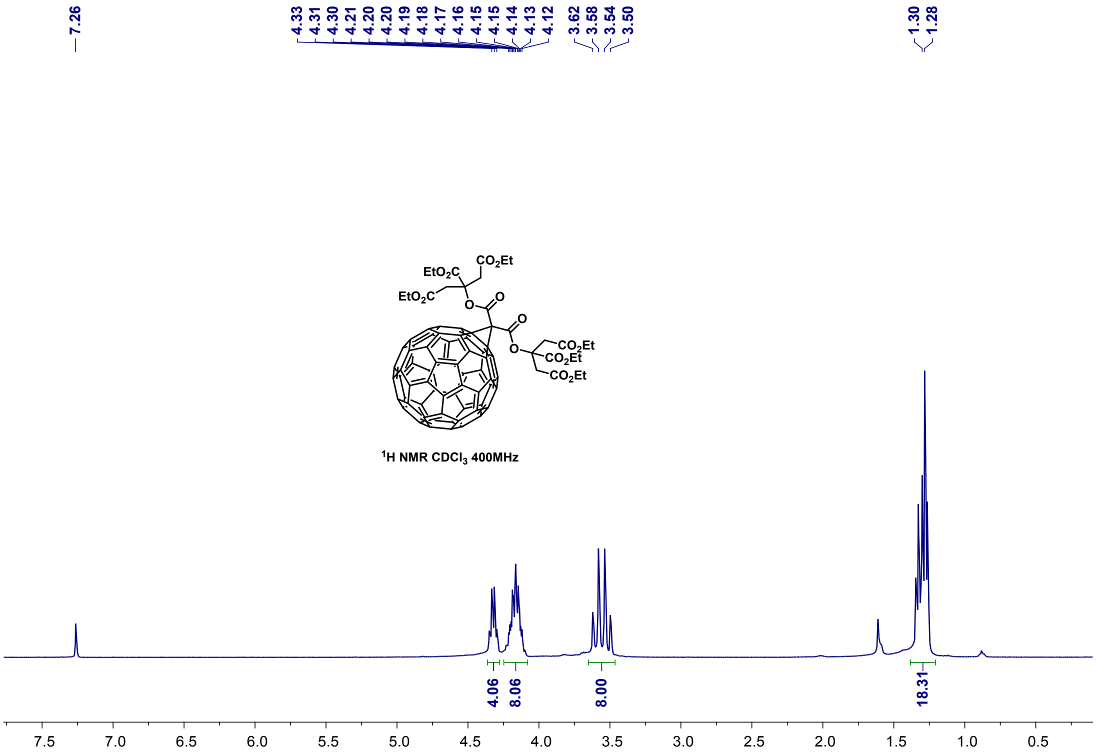


**Figure S3.** $^{1}$H NMR spectra of malonate fullerene.

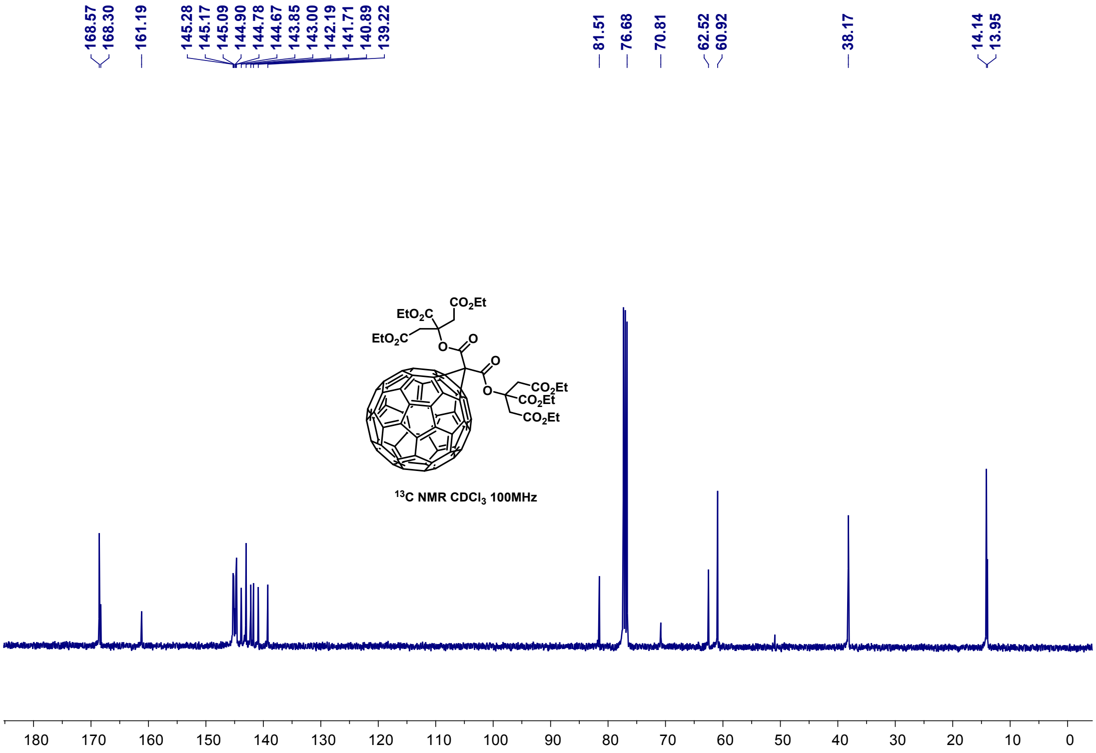


**Figure S4.** $^{13}$C NMR spectra of malonate fullerene.

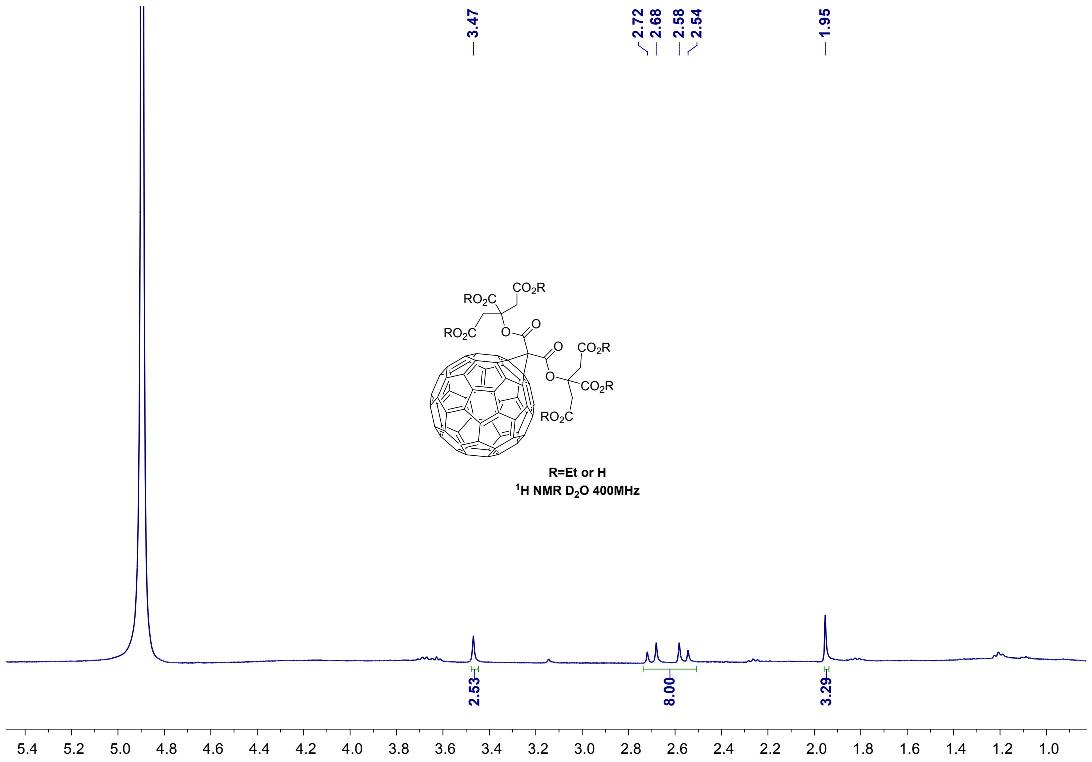


**Figure S5.** $^1$H NMR spectra of $mC_{60}$.

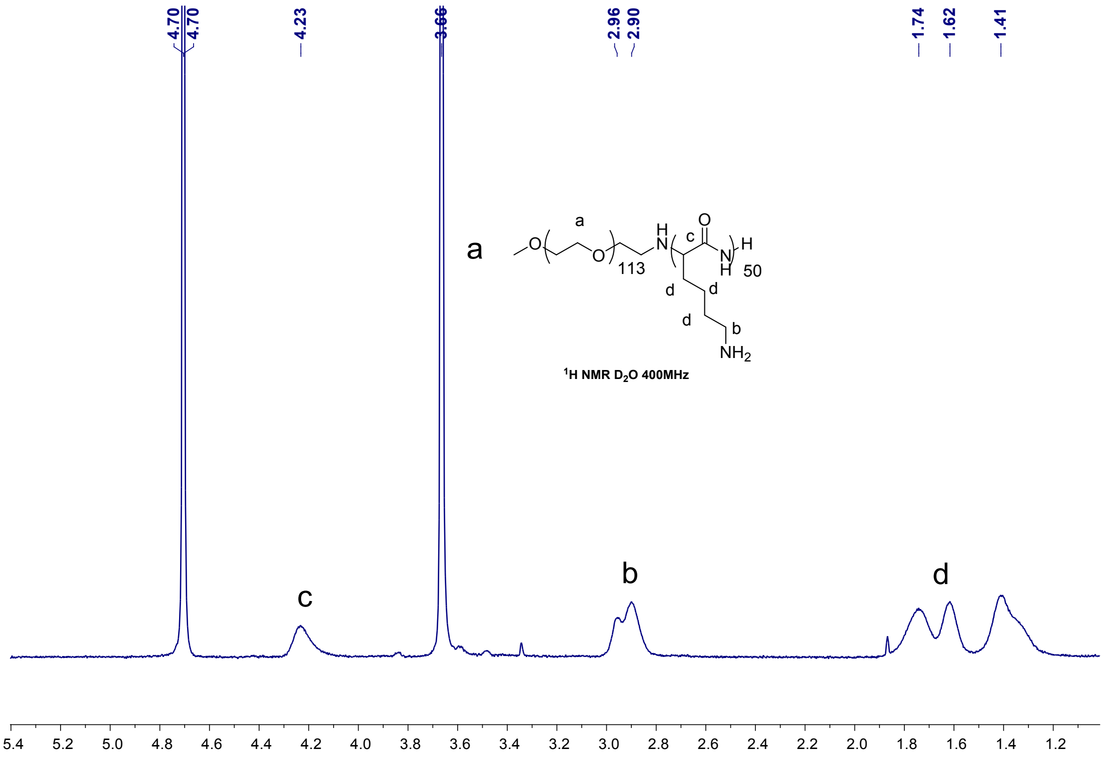


**Figure S6.** $^1$H NMR spectra of $PEG_{113}$-*b*-$PLys_{50}$.

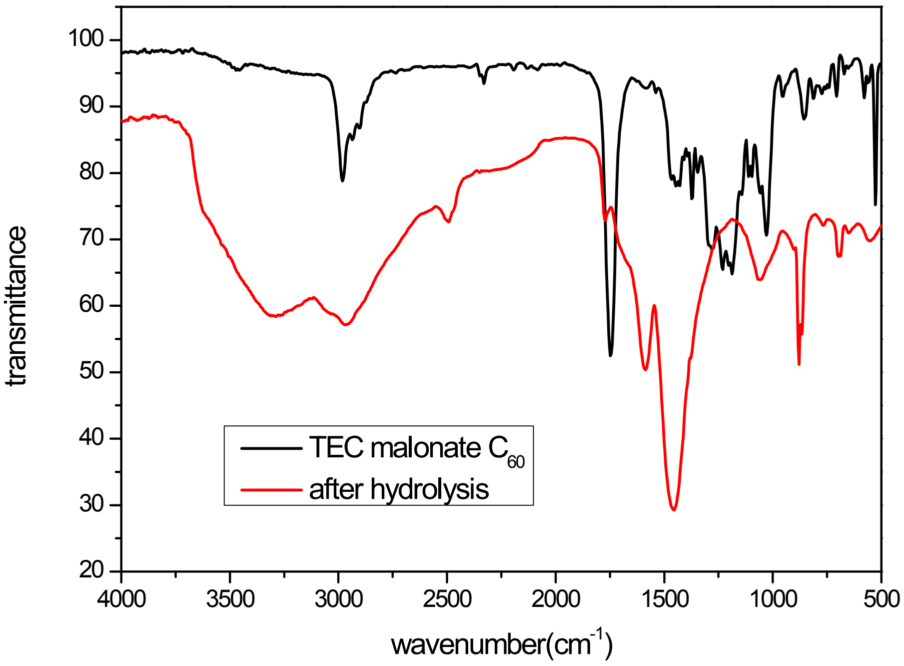
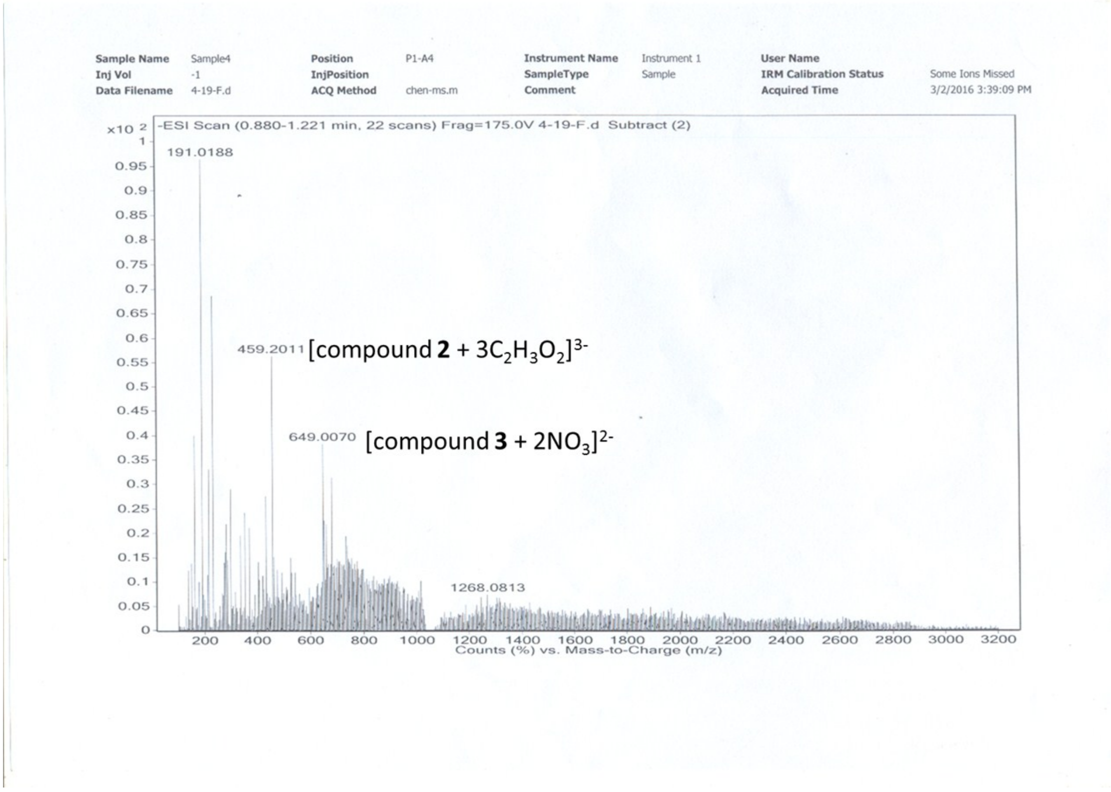


**Figure S7.** The FTIR spectroscopy of TEC malonate fullerene and its hydrolysis product ($mC_{60}$).



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Sample Name** | Sample4 | **Position** | P1-A4 | **Instrument Name** | Instrument 1 | **User Name** | |
| **Inj Vol** | -1 | **InjPosition** | | **SampleType** | Sample | **IRM Calibration Status** | Some Ions Missed |
| **Data Filename** | 4-19-F.d | **ACQ Method** | chen-ms.m | **Comment** | | **Acquired Time** | 3/2/2016 3:39:09 PM |

-ESI Scan (0.880-1.221 min, 22 scans) Frag=175.0V 4-19-F.d Subtract (2)

**Figure S8.** ESI-MS of $mC_{60}$ (negative mode).

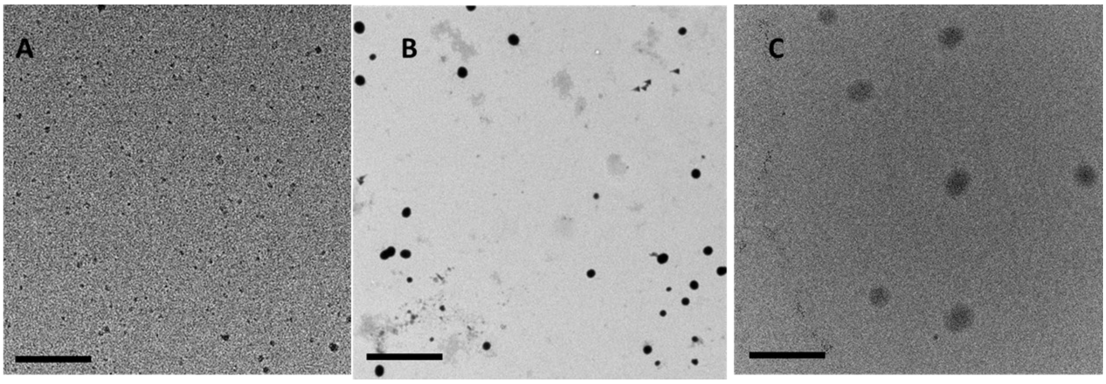


**Figure S9.** TEM micrograph of the (A)m$C_{60}$ solution, (B)ZnTPPS micelle, (C)m$C_{60}$ micelle. The scale bar is 200nm in A and 500nm in B and C, respectively.

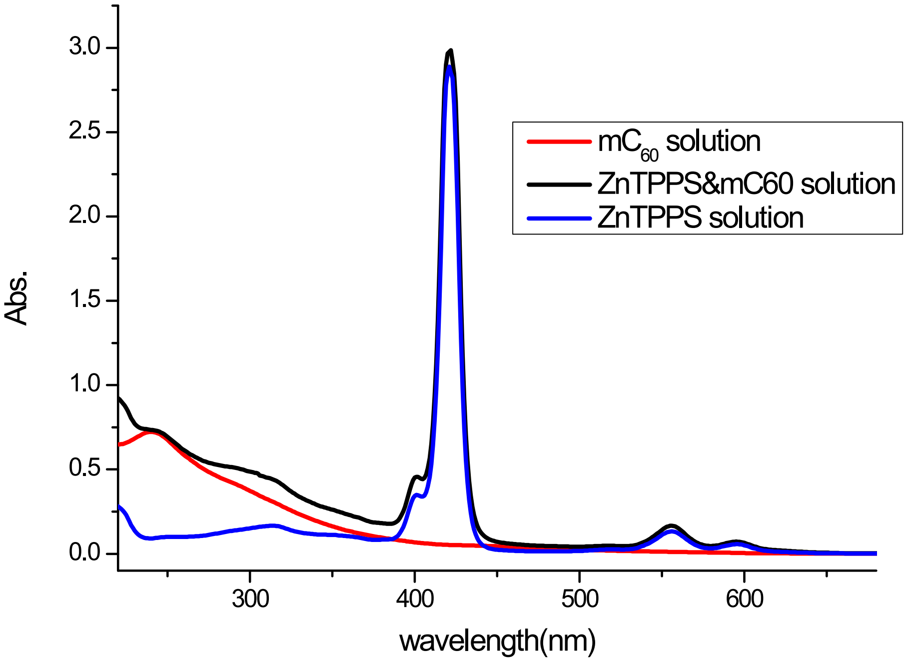
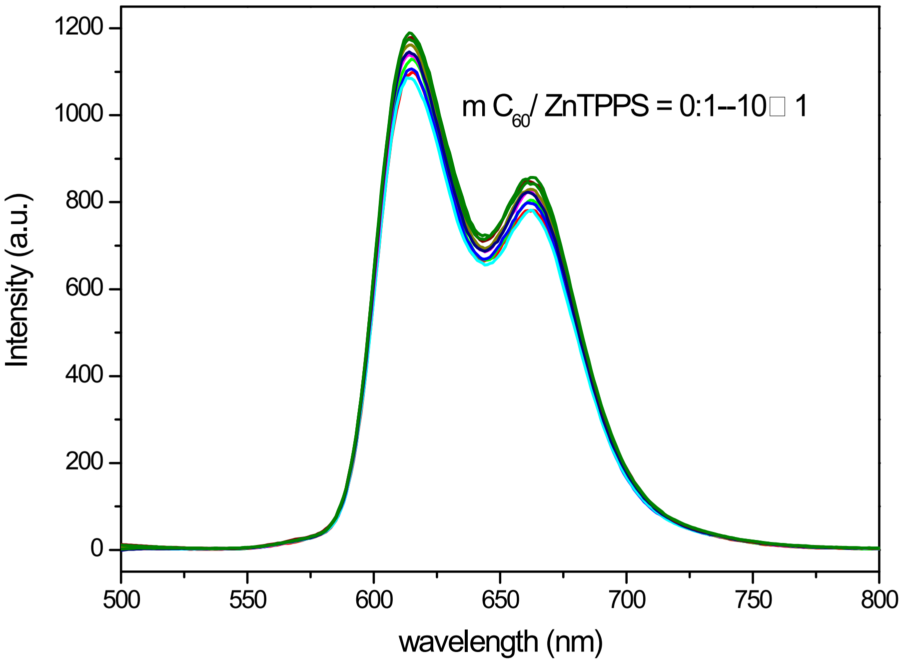


**Figure S10.** The UV-vis spectrum of m$C_{60}$ solution(~10 uM), ZnTPPS solution(~10 uM), and mixed solution (both m$C_{60}$ and ZnTPPS were 10 uM) in pure water.



**Figuer. S11.** Quenching of the steady-state fluorescence intensities of ZnTPPS on increasing addition of water-soluble fullerene in water, $\lambda_{ex.}$ = 430 nm.

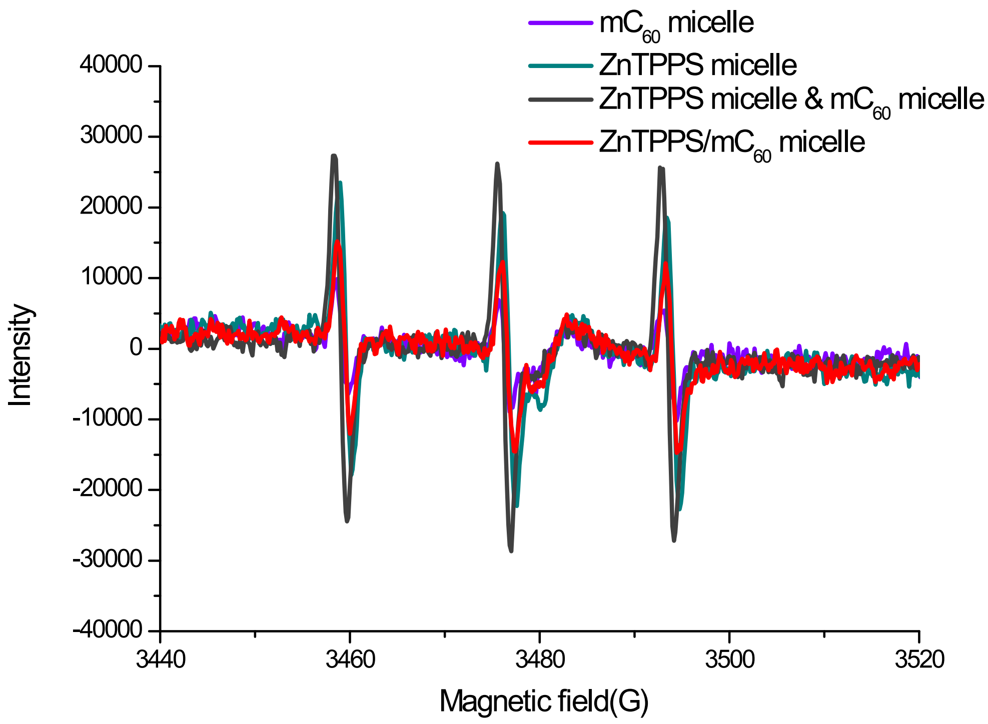


**Figure S12.** EPR spectra of the micelles solution in which trace TEMP acts to capture the $^1O_2$ generated upon photoirradiation.

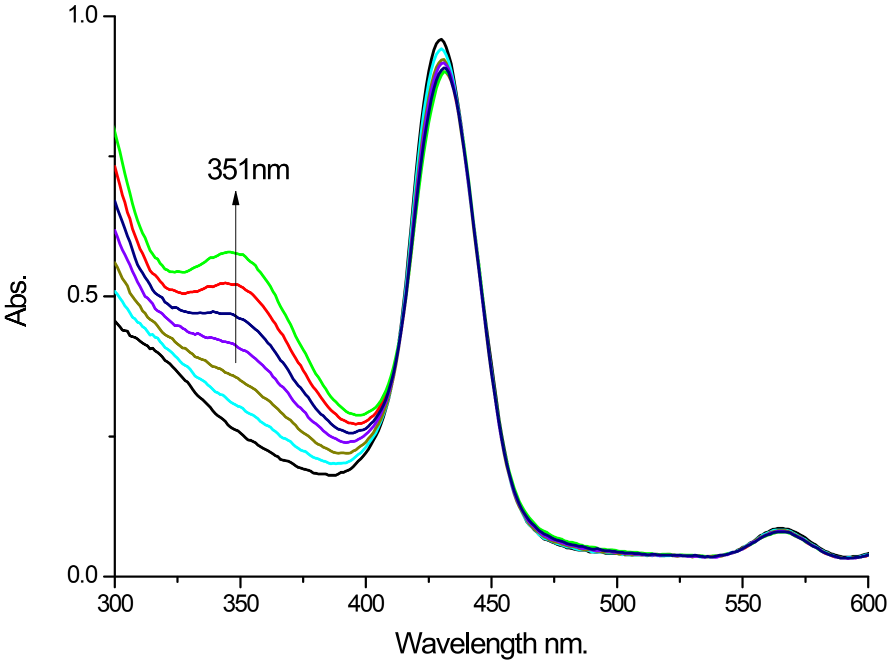


**Figure S13.** Changes in the UV-vis absorption spectra of the complex micelle (ZnTPPS:m$C_{60}$=1:1) with irradiation time in the presence of 0.1 M KI.

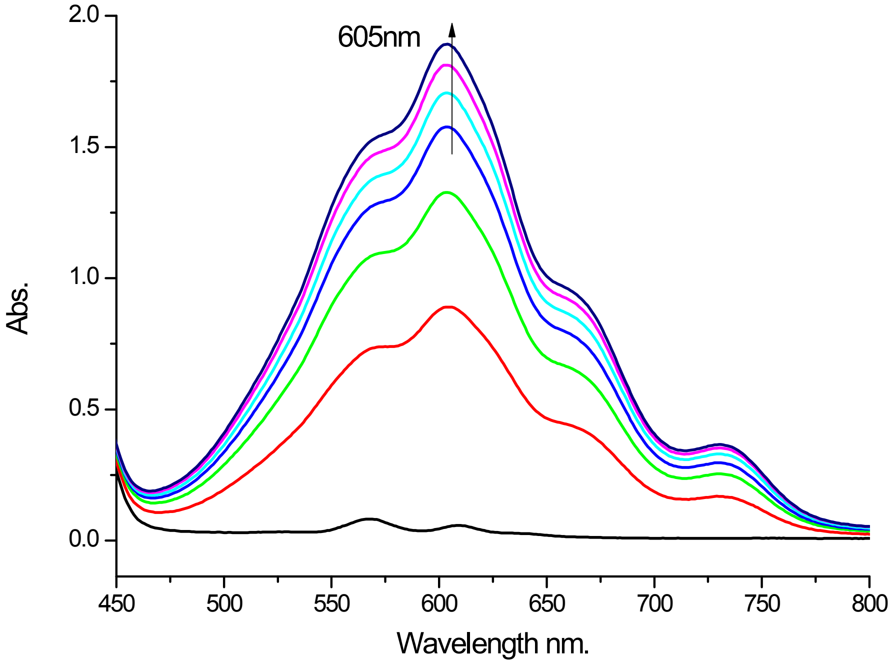


**Figure S14.** UV-vis spectral changes of the solutions of the mixture of the complex micelle (ZnTPPS:m$C_{60}$=1:1) and $MV^{2+}$ by the irradiation of light (0-30 min).

## 5 Light-harvesting properties of micelles.[1]

Calculation of fluorescence quantum yield of micelles in water.

The Fluorescence quantum yield of complex micelle in water was determined by using quinine sulfate in 1 M $H_2SO_4$ as a standard. The quantum yields were calculated with equation (1).

$\Phi = \Phi_s \times (I/I_s) \times (OD_s/OD) \times (\eta^2/\eta_s^2)$ (1)

where $\Phi$ is the quantum yield, $\Phi_s = 0.55$ for quinine sulfate, I is the integrated intensity of fluorescence emission peak, $\eta$ is the refractive index of solvents for sample and standard (water was used for both systems, $\eta_2 = \eta_{s2}$), and OD is the optical density determined by UV-vis spectroscopy. The subscript "s" refers to the standard. In this work, the fluorescence spectra of quinine sulfate were excited at 313 nm. The fluorescence quantum yield of complex micelle was calculated to be 2 %.

Energy transfer efficiencies based on donor quenching with steady-state fluorescence experiments were calculated according to following equation (2).

$E=1-I_{\text{ZnTPPS m.}}/I_{\text{complex m.}}$ (2)

where $I_{\text{ZnTPPS m.}}$ is the intensity of donor's (ZnTPPS micelle) fluorescence emission and $I_{\text{complex m.}}$ is the fluorescence emission of complex micelle.

Energy transfer rate constant according to equation (3).

$E=k_{ET}/(k_{ET}+\tau^{-1})$ (3)

where $k_{ET}$ is energy transfer rate constant, $\tau$ is the singlet state fluorescence lifetime of complex micelles. The $k_{ET}$ between donor and acceptor is calculated to be $1.26\times10^{8}$ $s^{-1}$.

## Reference

1 Y. Liu, J. Jin, H. Deng, K. Li, Y. Zheng, C. Yu and Y. Zhou, *Angew. Chem. Int. Ed*. **2016**, 55, 7952.