Electronic Supplementary Material (ESI) for Polymer Chemistry.

Suppoting Information

Water-Soluble Fullerene-Functionalized Polymer Micelles for Efficient Aqueous-Processed Conductive Devices

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Experimental Section

Materials

Fullerene (purity 99.5%) and 3-thiopheneacetic acid (purity 98%) were purchased from Alfa Aesar (Ward Hill, MA, USA) and Acros Organics (Geel, Belgium), respectively. All other chemicals and solvents were of analytical reagent grade, purchased from Sigma-Aldrich (Louis, MO, USA) and used as received.

Characterization

Proton Nuclear Magnetic Resonance (^{1}H NMR). ^{1}H NMR spectra were captured using a Bruker AVIII-500MHz magnetic resonance spectrometer (Bruker Biospin AG, Fällanden, Zürich, Switzerland) at 25 °C. Samples (ca. 20 mg) were dissolved in deuterated solvents (0.8 mL) and placed in a NMR tube.

Gel Permeation Chromatography (GPC). Weight-average molecular weight (M_w), number-average molecular weight (M_n), and PDI (M_w/M_n) were measured using a Waters GPC system at 40 °C. The mobile phase for GPC was sodium nitrate ($NaNO_3$) solution. Elution time was 40 min. The system was calibrated using pullulan standards (Polymer Standards Service, Silver Spring, MD, USA).

Ultraviolet-Visible (UV-Vis) Spectroscopy. Light absorbance of samples was measured using a Jasco V-730 Spectrophotometer (Hachioji, Tokyo, Japan) between 900 and 200 nm at 0.5 nm intervals at 1000 nm/min.

Photoluminescence (PL) Spectroscopy. PL spectra were recorded using a Jasco FP-8300 Spectrofluorometer (Hachioji). Excitation wavelength was 400 nm; emission spectra were recorded between 420 nm and 790 nm at an interval of 1 nm.

Critical Micelle Concentration (CMC). CMC was determined by fluorescence spectroscopy using pyrene as a fluorescence probe following previously described procedures.[38.39]

Dynamic light scattering (DLS) and zeta potential measurements. Mean diameters and zeta potentials of micelles were measured using a Malvern Zetasizer Nano ZS (Herrenberg, Germany). Samples dissolved in deionized water were filtered through a 0.45 μm hydrophilic PTFE filter before measurement. Temperature-dependent DLS measurements were taken at various temperatures from 20 to 75 °C. After each temperature variation, 10 min equilibration was allowed before mean diameter measurement.

Scanning Electron Microscopy (SEM). SEM images were captured using a Nova NanoSEM 230 system (FEI, Eindhoven, Netherlands). Diluted samples in deionized water (25 μL) were dripped onto the copper grid and the solutions were allowed to evaporate slowly at ambient temperature. Platinum was sputtered onto the samples for 10 min before observation.

Transmission Electron Microscopy (TEM). TEM images were captured using a JEOL 2000 FX2 (Jeol USA, Inc., Peabody, MA, USA). Diluted samples in deionized water (25 μL) were dripped onto the copper grid and the solutions were allowed to evaporate slowly at ambient temperature.

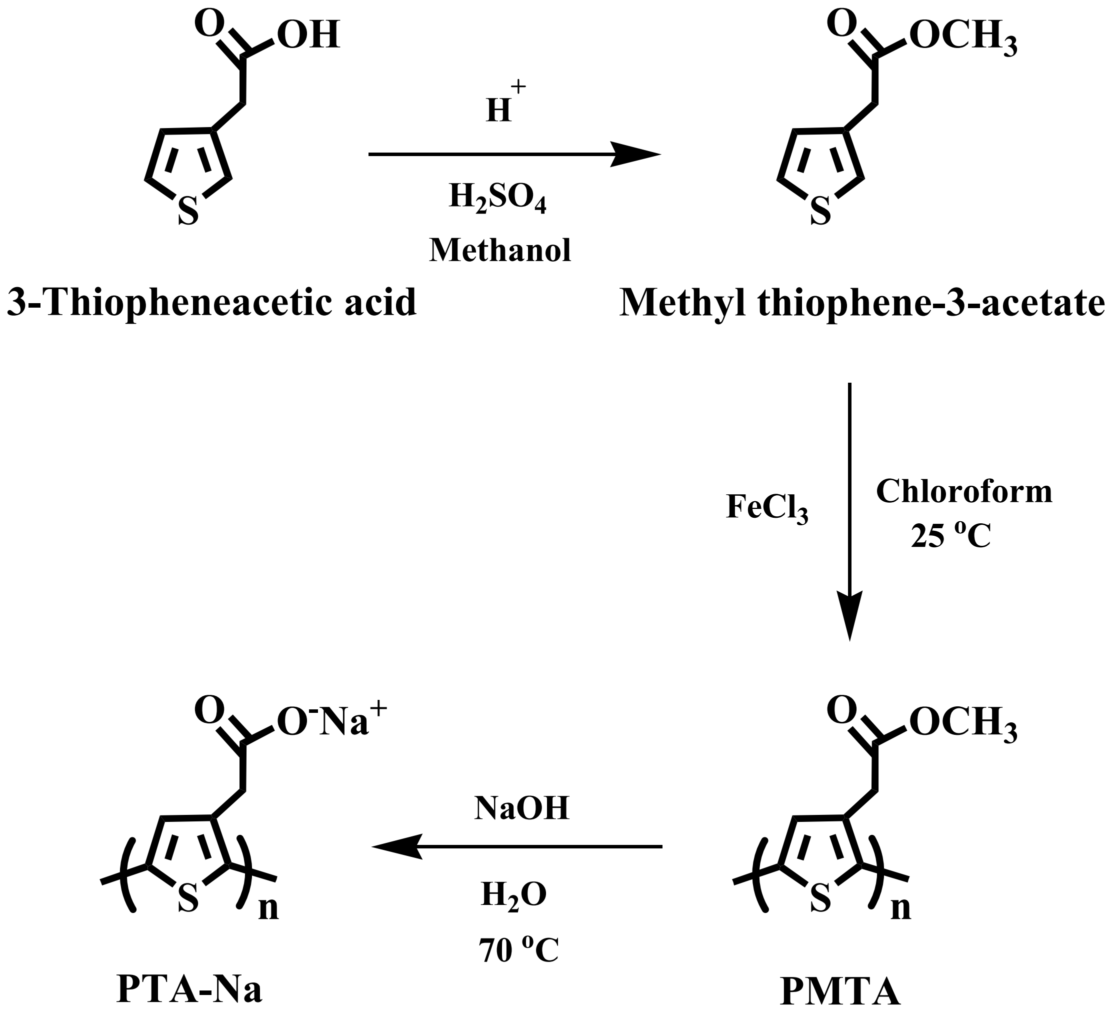
Raman Spectra were recorded using a G2D spectrophotometer (Uninanotech Co., Ltd, Republic of Korea). Samples were evaporated to a powder, placed on a microscope slide, and at 532 and 25 mW with scanning between 30 nm and 2260 nm. Exposure time was 1 sec with a cumulative total of 30 runs.

Cyclic Voltammetry (CV) was conducted using a CH Instruments 750 A (Austin, TX, USA) at a scan rate of 0.05 V/s from 0 V to 2 V, then turned back to 0 V. A three-electrode cell was used with indium tin oxide (ITO) as the working electrode, an Ag/Ag+ non-aqueous reference electrode (0.01 M $AgNO_3$) and platinum wire as the counter electrode. All electrochemical experiments were performed in acetonitrile with 0.1 M tetrabutylammonium perchlorate as an electrolyte. PTA-Na and PTA-NA/C60 were dissolved directly in aqueous solution, respectively. C60 was dissolved in toluene due to its hydrophobic nature and poor solubility in water. The CV films were deposited by spin-coating of the sample solutions on ITO electrodes.

Four-point probe method of measuring electrical conductivity. Electrical conductivity was measured using a four-point probe analyzer (KEITHLEY 2400 SourceMeter, Cleveland, OH, USA). Passing a current through the two outer probes and measuring the voltage through the inner probes enables measurement of sample resistivity, and conductivity can be calculated. Each solid sample was measured at 100 V and 5 mA over 1000 points. The PTA-Na/C60 thin films were prepared on a glass substrate by spin-coating technique and dried under vacuum at 50 °C for 12 h prior to the conductivity measurements.

*X-ray Photoelectron Spectroscopy (XPS)***.** XPS data were obtained with a MT-500 spectrometer (VG-Microtech, Uckfield, East Sussex, UK) using Al Kα X-ray radiation (1486.6 eV).

Measuring and Testing of Electrical Devices. Single-layer electrical devices were fabricated with the following structure: ITO/conducting layer (30 nm)/silver (Ag, 20 nm). PTA-Na and PTA-NA/C60 were dissolved in aqueous solution, respectively. C60 was dissolved in toluene due to its hydrophobicity. Solutions were deposited on an ITO glass via a spin-coating process as a conducting layer. Subsequently, Ag was deposited onto the conducting layer/ITO (spin-coated thin film on ITO) substrates by thermal evaporation at a rate of 4.0 Å s^{-1}. The electrical characteristics of the devices (depending the voltage and current of the device) were measured at 25 °C using an HP-4284 capacitance-voltage analyzer (Hewlett-Packard, Palo Alto, CA, USA) and Agilent-4156 probe station (Agilent Technologies, Palo Alto, CA, USA), respectively.



Scheme S1. Synthesis of PTA-Na.

Preparation of methyl thiophene-3-acetate[36,37]

3-Thiopheneacetic acid (10.0 g, 70 mmol) was dissolved in dry methanol (100 mL) in a 500 mL flask, then concentrated H_2SO_4 (0.8 mL) was slowly added as a catalyst, refluxed (6 h) under nitrogen, cooled to room temperature, then the solvent was removed using a rotary evaporator. The crude oil sample was dissolved in chloroform, extracted with deionized water, and the combined organic layers were dried over magnesium sulfate. An oily product was obtained after filtering and evaporation of the chloroform. Yield: 78 % (8.52 g).

Synthesis of PMTA

The methyl thiophene-3-acetate monomer (5.0 g, 32 mmol) was oxidatively polymerized using anhydrous ferric chloride ($FeCl_3$, 15.6 g, 96 mmol) in dry chloroform (100 mL), reacted for 16 h at 15 °C under nitrogen and the polymer was obtained after evaporation of chloroform. The crude polymer was purified by repeated washing with fresh methanol and deionized water, and collected by filtration. The final polymer was subjected to Soxhlet extraction with refluxing methanol for 2 days, and dried under vacuum. Yield: 3.6 g (72%).

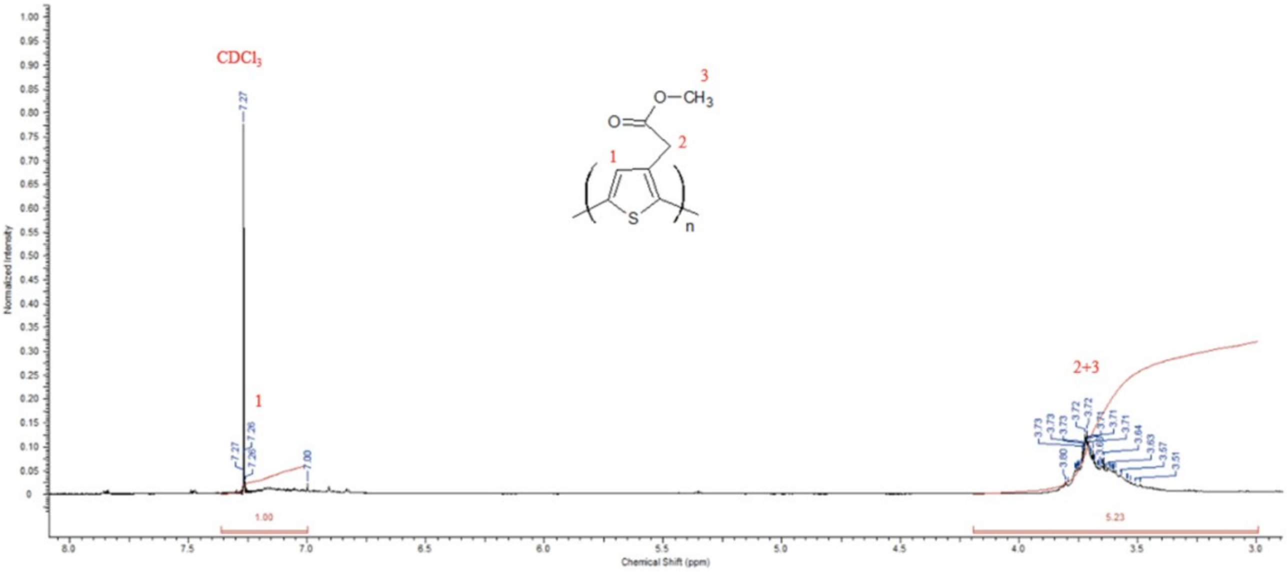


Fig. S1: ^{1}H NMR spectroscopy of PMTA in deuterated chloroform ($CDCl_3$).

Synthesis of sodium ion-functionalized PTA-Na

PMTA ($M_w \approx 8{,}000$, 7.0 g, 0.875 mmol) was placed in a 500 mL double-neck flask, followed by methanol (40 mL), deionized water (400 mL) and excess sodium hydroxide (NaOH, 7.12 g, 178 mmol), then stirred under nitrogen (24 h, 50 °C) to remove the methyl groups on the polymer side chains. The solution was filtered, evaporated to one-third of its volume, then transferred into 1000 dalton molecular weight cut-off dialysis tubing and dialyzed against deionized water for 3 days at 25 °C. PTA-Na was obtained after evaporating the deionized water. Yield: 6.4 g.

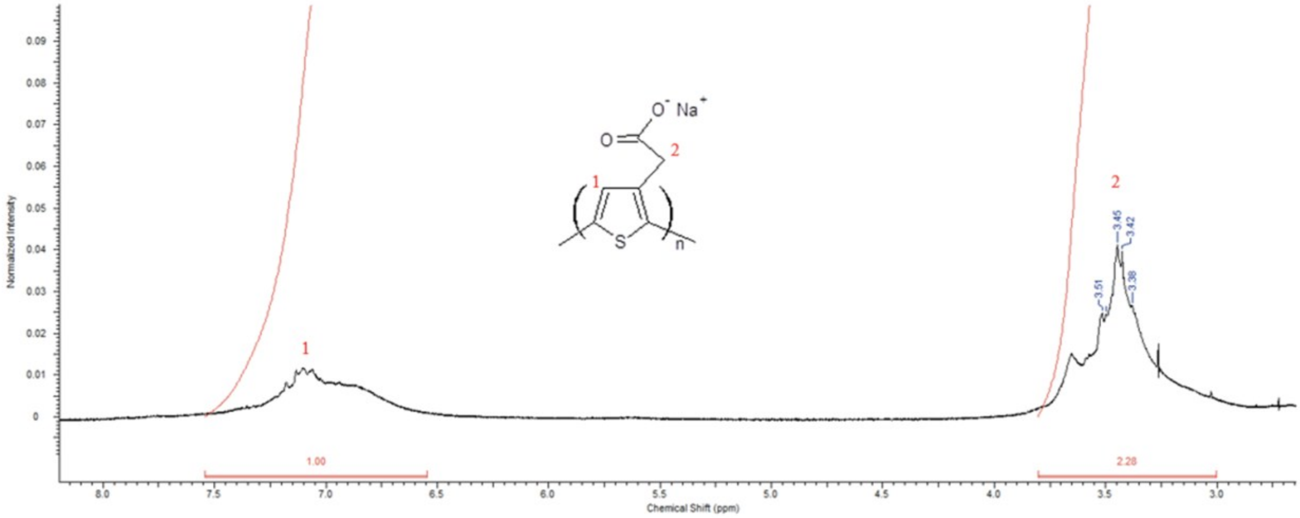


Fig. S2: ^{1}H NMR spectroscopy of PTA-Na in deuterium oxide (D_2O).

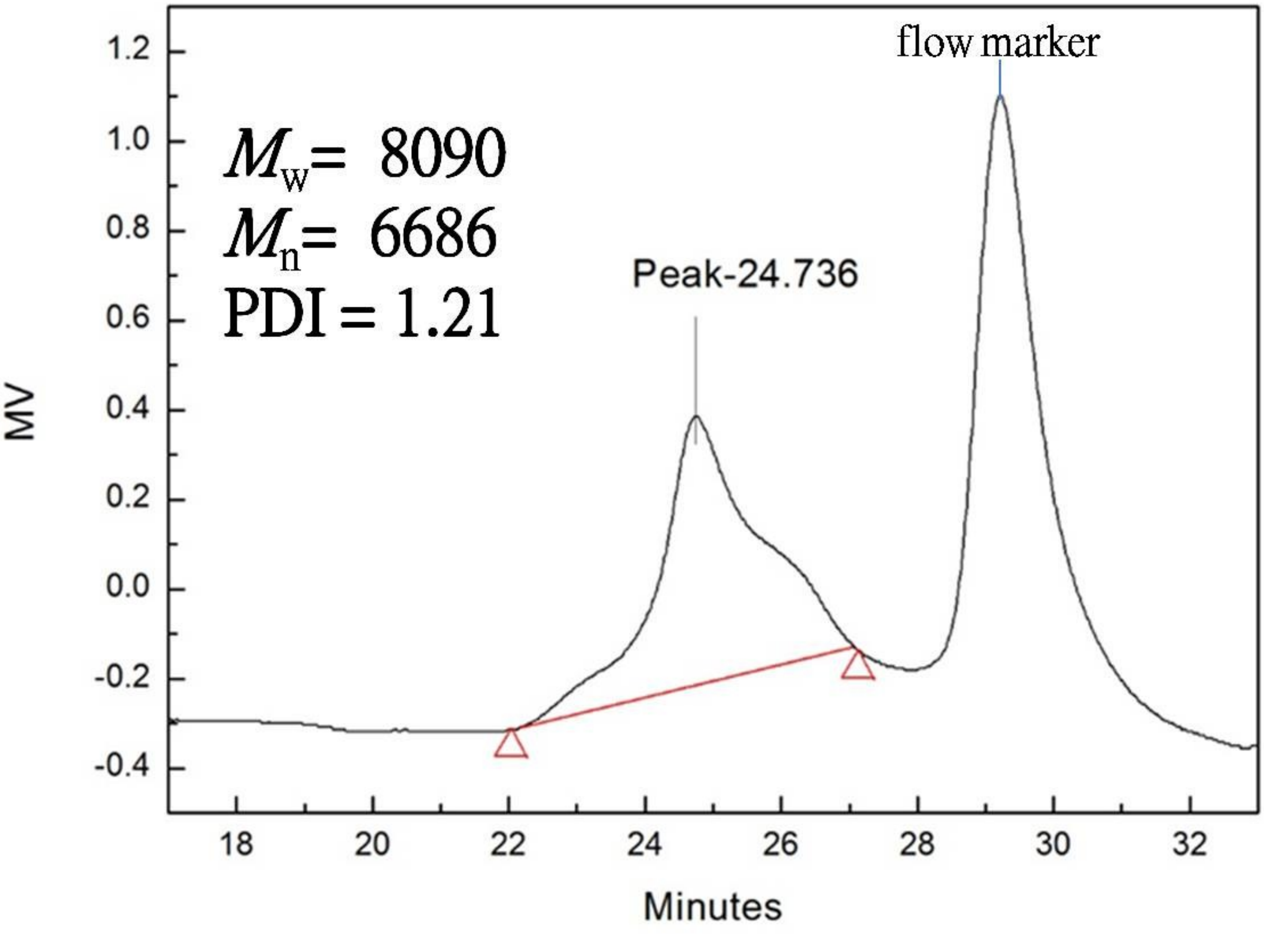


Fig. S3: GPC traces of PTA-Na in water.

Preparation of C60-loaded PTA-Na micelles

PTA-Na was used to encapsulate C60 via a simple solvent blending method. C60 (ranging from 0.2 to 10 mg) was mixed with 10 mg of PTA-Na in 20 mL deionized water with stirring at 100 °C for 24 h, cooled to room temperature and free C60 was removed by filtration through a 0.45 μm PTFE filter. The solutions were stored in a dry box. To further evaluate the C60 loading content of micelles, water was removed by rotary evaporation under reduced pressure at 40 °C, then the residue was dissolved in toluene, insoluble PTA-Na was removed by filtration through a 0.45 μm PTFE filter, and the solution was analyzed by UV-Vis spectroscopy at 540 nm to detect C60. The loading content of fullerene was calculated according to equation 1:

$$\text{Loading content} = W_t / W_s \times 100\% \qquad \text{Equation (1)}$$

where, W_t, is the weight of C60 loaded into micelles; W_s, the weight of the C60-loaded micelles after filtration.

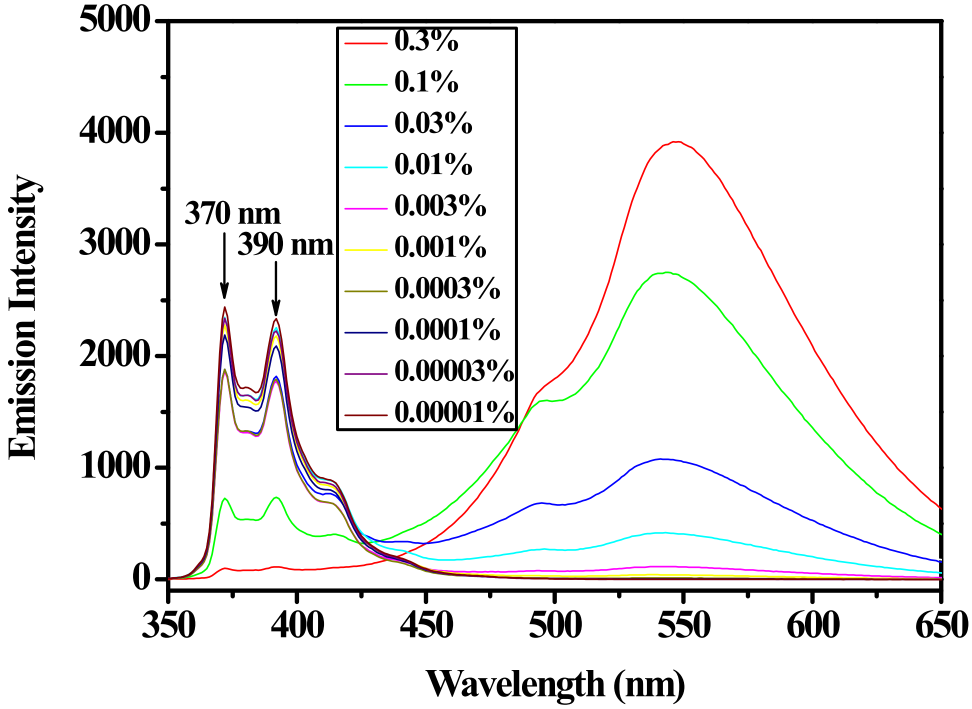


Fig. S4: Fluorescent emission of pyrene in different concentrations of PTA-Na in water.

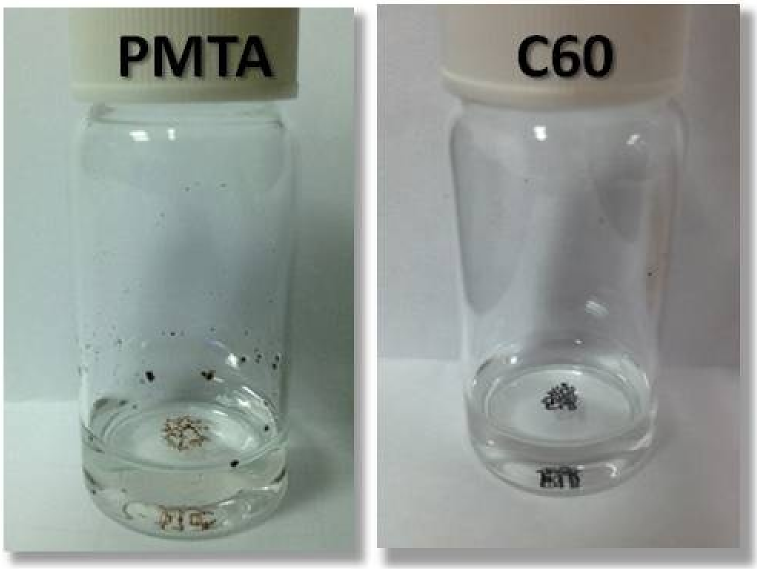
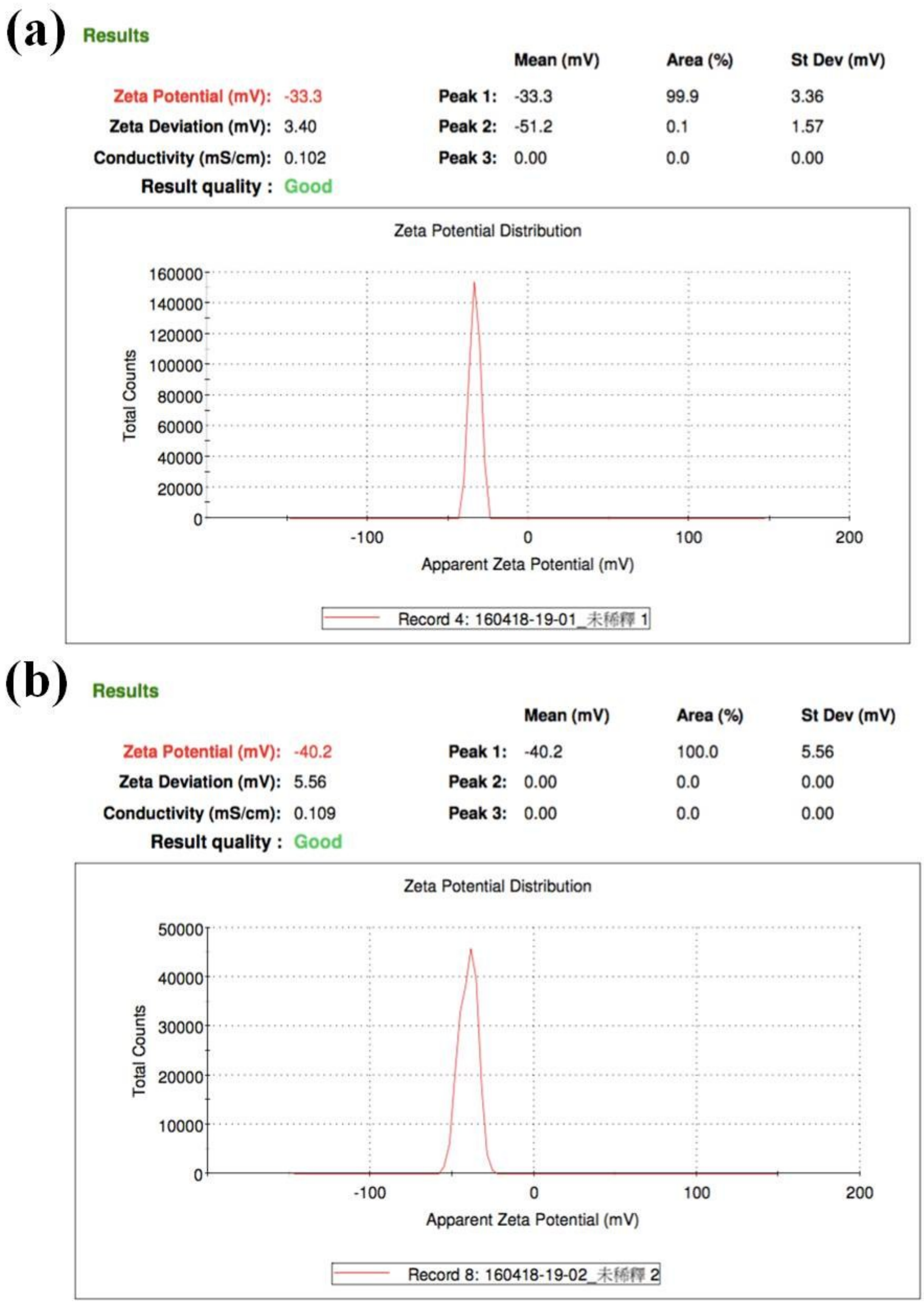


Fig. S5: Photos of (a) PMTA and (b) C60 in water.



(a) **Results**

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-33.3	**Peak 1:**	-33.3	99.9	3.36
Zeta Deviation (mV):	3.40	**Peak 2:**	-51.2	0.1	1.57
Conductivity (mS/cm):	0.102	**Peak 3:**	0.00	0.0	0.00
Result quality :	Good				

(b) **Results**

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-40.2	**Peak 1:**	-40.2	100.0	5.56
Zeta Deviation (mV):	5.56	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.109	**Peak 3:**	0.00	0.0	0.00
Result quality :	Good				

Fig. S6: Zeta potentials of **(a)** PTA-Na and **(b)** 1/1 PTA-Na/C60 in water at 25 °C.

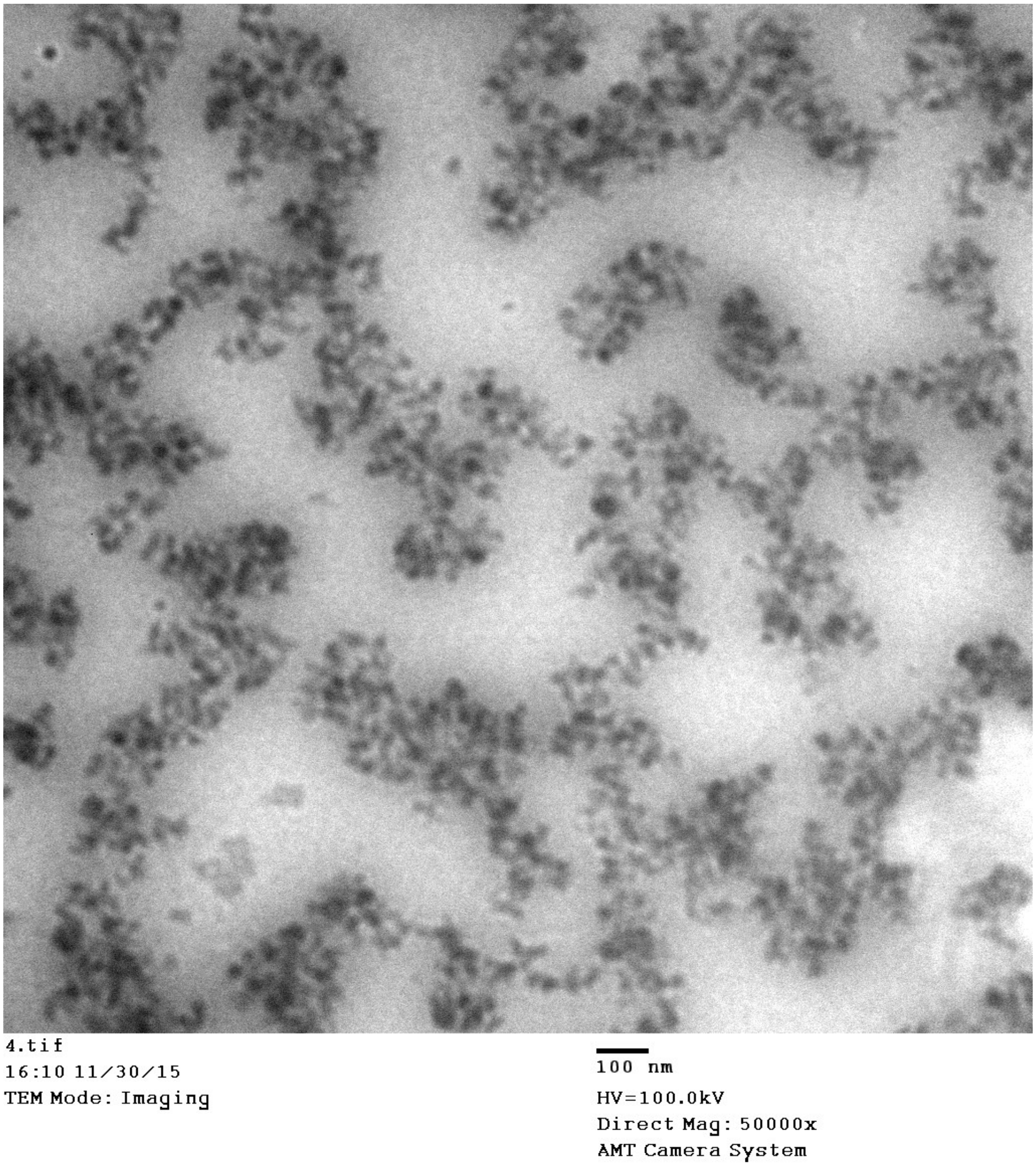


Fig. S7: TEM image of PTA-Na.

Table S1. C60-loading capacity of PTA-Na/C60 micelles.

PTA-Na/C60 blending ratio (weight/weight ratio, mg/mg)	C60 loading content
1:0.2	4.64% (0.06 mg)
1:0.5	5.33% (0.08 mg)
1:1	6.47% (0.13 mg)

Table S2. Electrical conductivity of free C60, PTA-Na and 1/1 PTA-Na/C60 recorded at 25 °C.

Sample	Conductivity (S/cm)
C60	2.02×10^{-7}
PTA-Na	2.74×10^{-2}
1/1 PTA-Na/C60	1.85×10^{-1}