Electronic Supplementary Information

One-step synthesis of well-dispersed polypyrrole copolymers under gamma-ray irradiation

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Supplementary Experimental Section

S1 Materials and reagents

Polyethylene glycol 600 (PEG-600) (molecular weight: 570~630), pyrrole (AR), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, AR), methanol (AR), ethanol (AR) and dimethyl sulfoxide (DMSO, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were used as received without further purification and the deionized water (DI) was used for all experiments unless otherwise stated.

S2 Preparation of PEG-PPy copolymer and its purification

1 mL $FeCl_2$ aqueous solution (4.32 mmol mL^{-1}) was added to a mixture, consisted of 0.15 mL (2.16 mmol) of pyrrole, 3 g (5 mmol) of PEG-600, and 14 mL of DI, in a glass bottle. After completely stirring, the obtained mixture was irradiated by a ^{60}Co γ-ray source at a constant dose rate of 2.94 kGy h^{-1} at room temperature for 17 h under air atmosphere, and the total absorbed dose was 50 kGy. Then, the gamma-irradiated PEG-600/pyrrole/Fe^{2+} solution was directly centrifuged at 8000 rpm (6220 ×g, SF-TGL-20A, Shanghai Feiqiaer Analytical Instrument Co., Ltd, China) for 10 min to obtain supernatant (II) and sediment (I). The sediment (I) was purified by repeatedly water-washing and centrifugation at least three times, and freeze-dried,which was named as PPy-PEG-I. The supernatant (II) was dried by vacuum-assisted vaporization at 50 °C for 24 h, and then extracted by ethanol in Soxhlet extractor. A small amount black residue (III) was obtained after ethanol extraction, and labeled as PPy-PEG-III. After centrifuging the black ethanol extraction solution (IV) at 10000 rpm (9720×g) for 10 min, black sediment (V) and yellow supernatant were obtained. The sediment (V) also was purified by repeatedly water-washing and centrifugation at least three times, and denoted as PPy-PEG-V. All the above PPy-PEG samples were dried in vacuum oven at 50 °C over night.

S3 Control experiments

Neat PPy was prepared by Fe^{3+}-initiated redox polymerization of pyrrole. The detail of process as follows: 1 mL $FeCl_3$ aqueous solution (4.32 mmol mL^{-1}) was added to 14 mL pyrrole aqueous solution, which contained 2.16 mmol of pyrrole. After settling the above mixture in air for 17 h, it was separated by centrifugation at 3000 rpm (870 ×g) for 10 min. The obtained sediment was purified by repeated water-washing and centrifugation at least 3 times, and dried in vacuum oven at 50 °C over night.

Two control experiments were similarly conducted by the above way of PPy preparation. The difference is that 1 mL $FeCl_3$ (or $FeCl_2$) aqueous solution was added into 14 mL Py/PEG-600 solution, which contained 2.16 mmol of pyrrole, and 3 g of PEG-600. The product from $FeCl_3$/pyrrole/PEG-600 control experiment was marked as Ctl-1, and the other one was Ctl-2. It was found that both of the two control samples showed very poor stability in solution, and were unable to re-disperse in solvents completely (**Fig. S3**).

S4 Photothermal Tests

A 2 mL aqueous suspension of PPy-PEG (1 mg mL^{-1}) was injected in 1 × 1 × 4 cm quartz cuvette cell. The photothermal properties of different PPy-PEG copolymers aqueous suspensions were investigated by the temperature change under a 5 min laser irradiation. Water was used as a control. The temperature change was recorded by a thermal camera (FLIR A300: FLIR, Wilsonville, OR, USA) and the laser power and wavelength was 1 W cm^{-2} and 808 nm, respectively.

S5 Instruments and characterization

Fourier transform infrared spectrum (FT-IR) was characterized using transmission module of Bruker Optics TENSOR 27 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed on a TG 209 F3Tarsus (NETZSCH, Germany) instrument from 30 to 650 °C under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS) of neat PPy and PPy-PEG samples was taken out on a SHIMADZU Kratos AXIS Ultra DLD XPS instrument. Scanning electron microscopy (SEM) imaging was performed on a JEOL-JSM-6700F at 10kV. The nuclear magnetic resonance (NMR) spectra were operated at room temperature on a Bruker Avance 500 operating at a frequency of 500 MHz for ^{1}H-NMR spectra and all test samples were dissolved in deuterated DMSO. The particle size distribution was measured by a Malvern Zetasizer NanoZS.

Supplementary figures

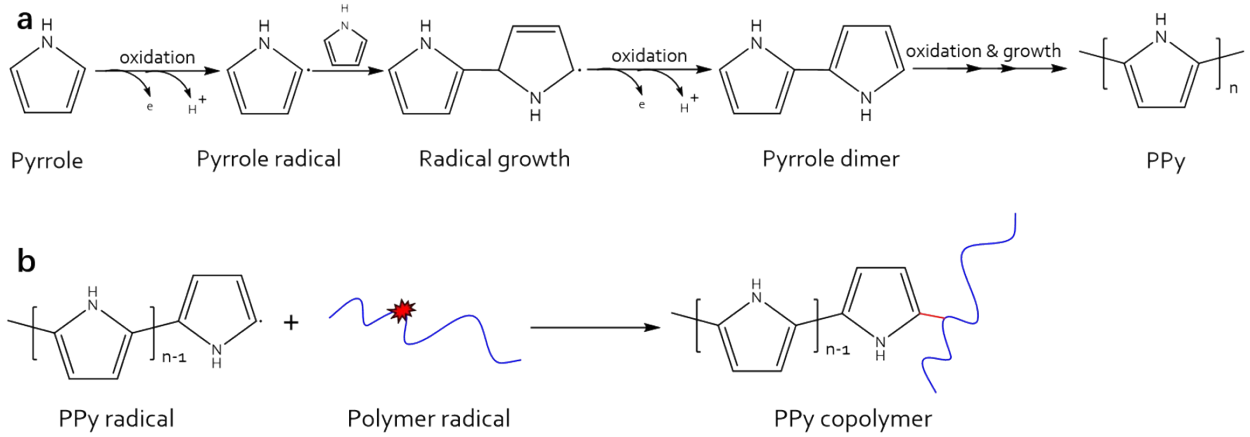

Fig. S1 (a)Schematic illustration of the synthesis mechanism of PPy by redox polymerization, and (b) the proposed synthesis strategy of PPy copolymer by coupling PPy radicals with additional polymeric radicals.

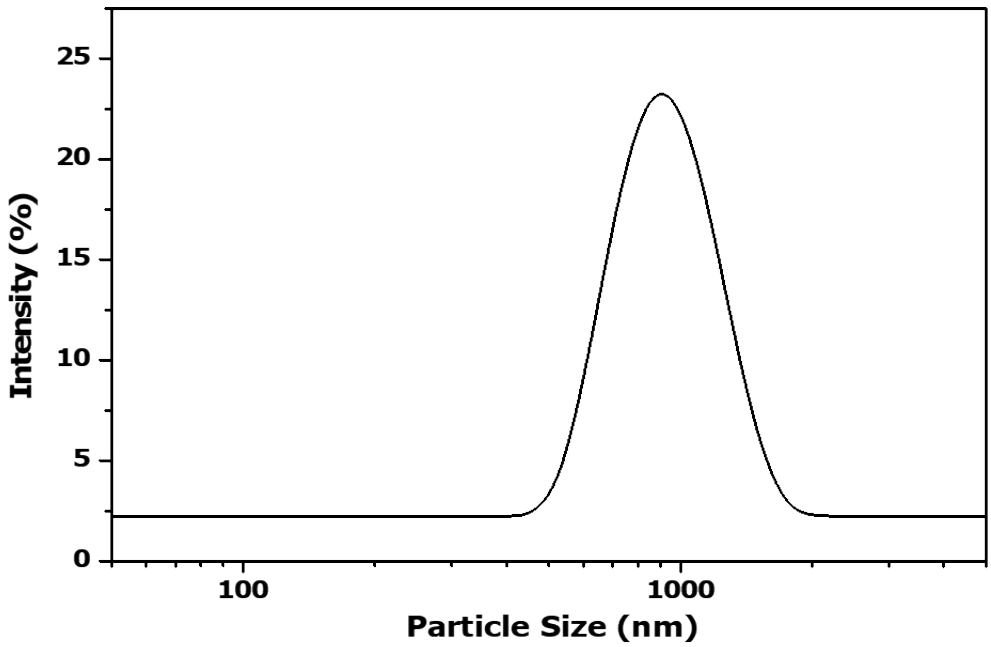

Fig. S2 The particle size distribution of PEG-PPy-I.

Fig. S3 The photo of ethanol extraction solution.

Fig. S4 Schematic illustration of control experiments processes: (a) PEG-600/pyrrole/ Fe^{2+}, and (b) PEG-600/pyrrole/ Fe^{3+}.

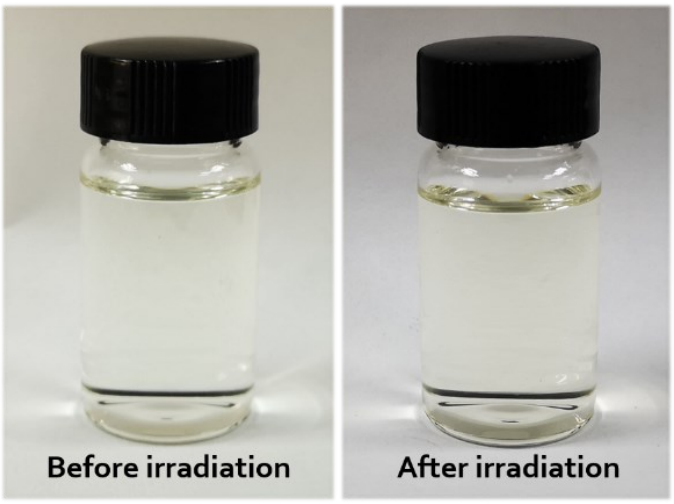

Fig. S5 The PEG-600/pyrrole aqueous solution without Fe^{2+} or Fe^{3+} before and after gamma-ray irradiation.

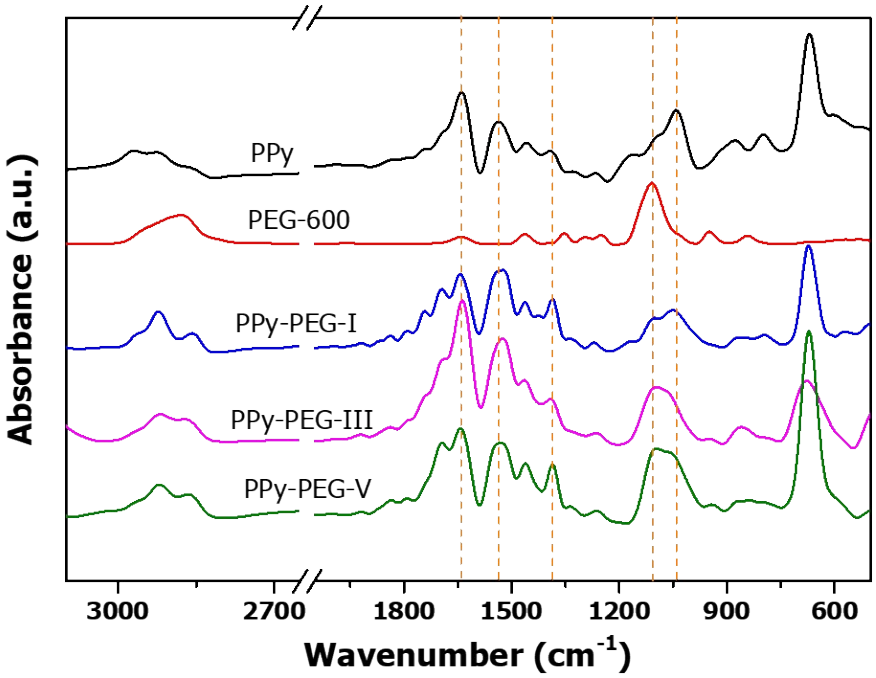

Fig. S6 FT-IR spectra of the PPy, PEG-600, PPy-PEG-I, PPy-PEG-III and PPy-PEG-V.

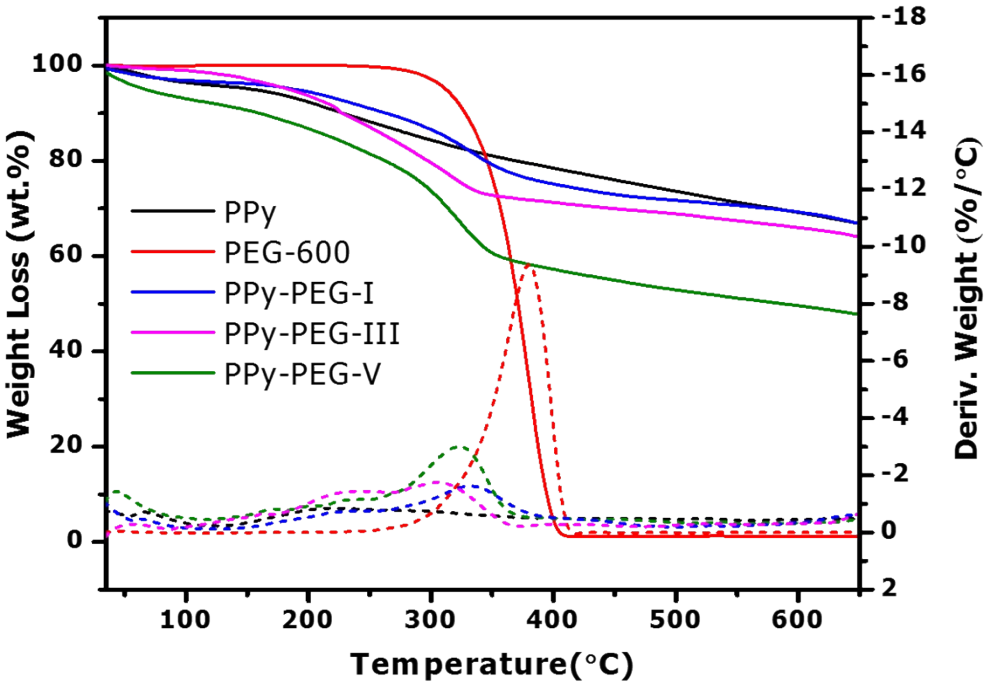

Fig. S7 TGA and DTG curves of the PPy, PEG-6oo, PPy-PEG-I, PPy-PEG-III and PPy-PEG-V.

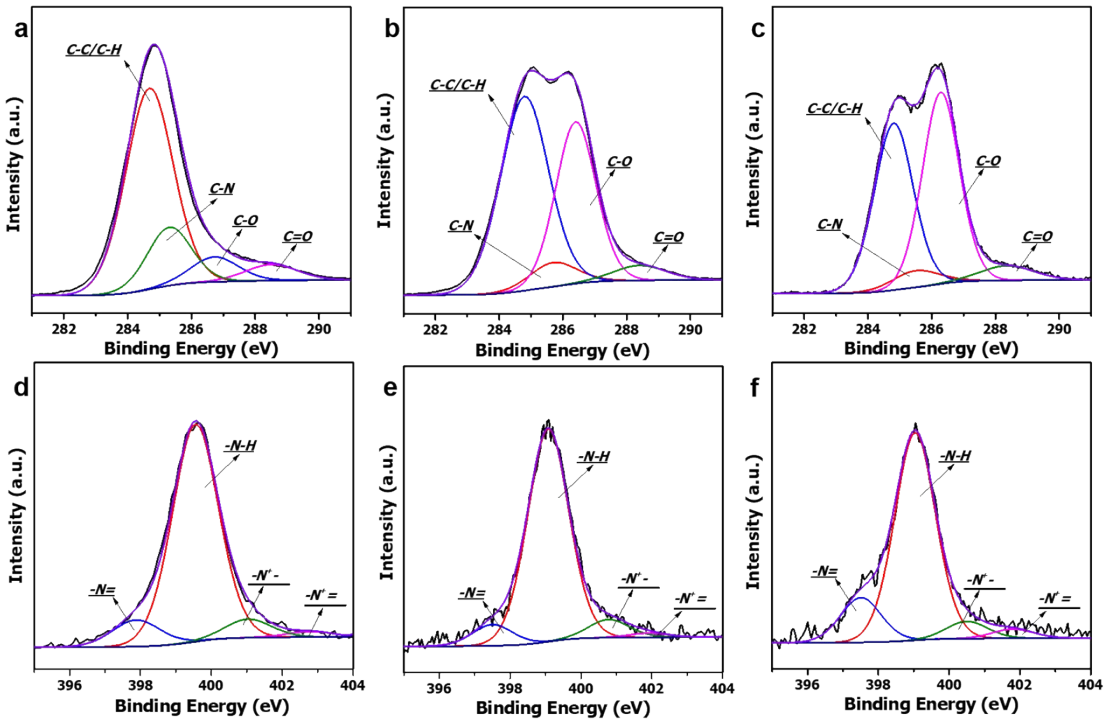

Fig. S8 XPS C1s spectra of (a)PPy, (b) PPy-PEG-III and (c) PPy-PEG-V; XPS N1s spectra of

(d)PPy, (e) PPy-PEG-III and (f) PPy-PEG-V.

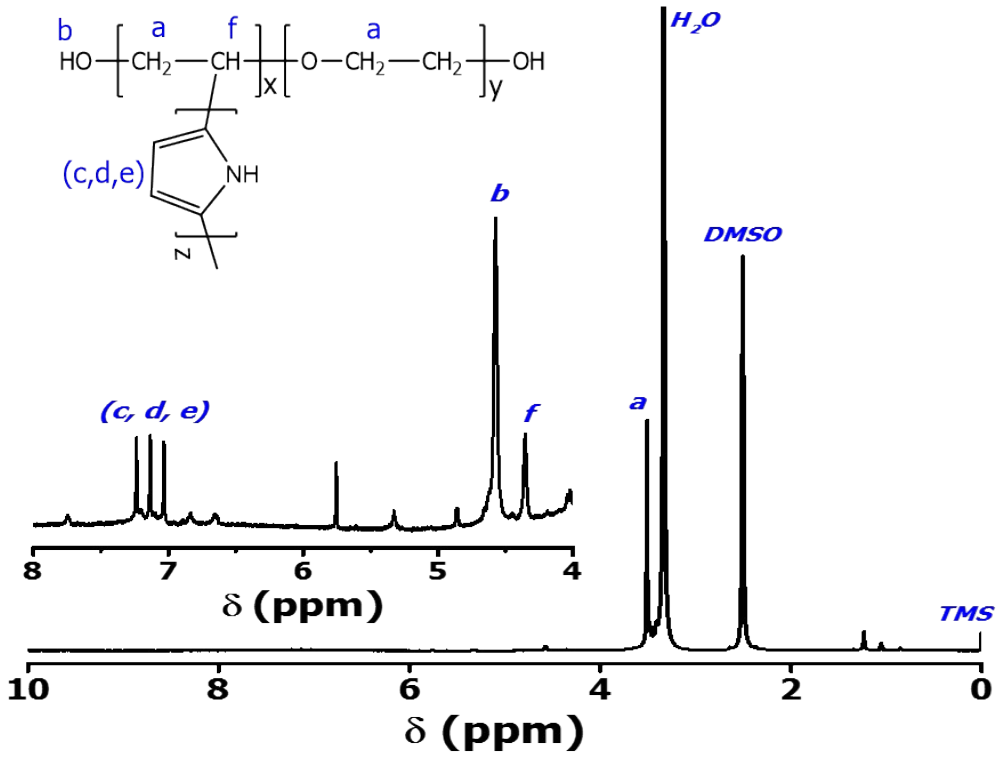

Fig. S9 H-NMR spectrum of PPy-PEG-V.

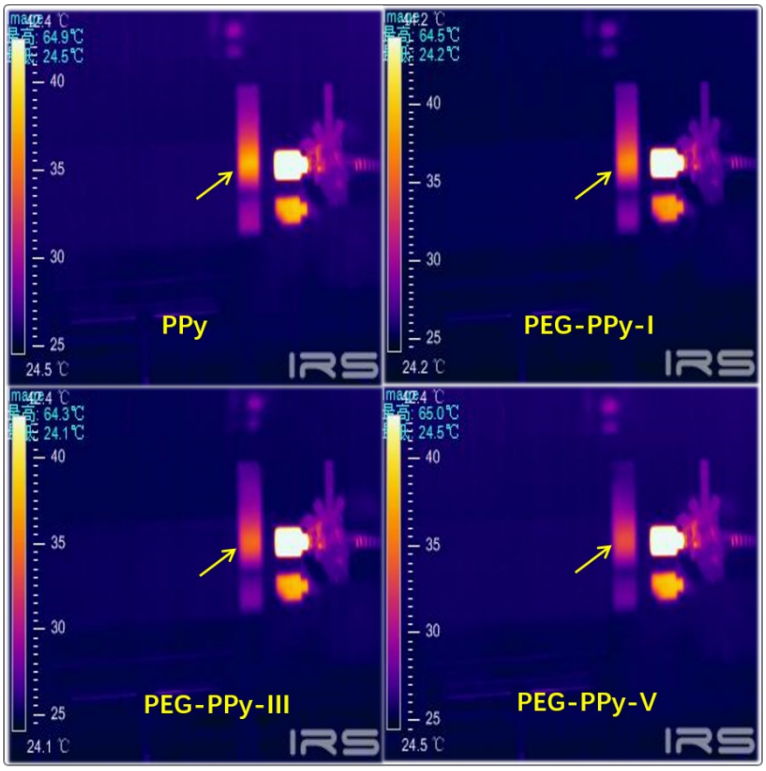

Fig. S10 Photothermal images of various samples dispersed in water (1 mg mL^{-1}) after 5 min laser irradiation (808 nm, 1 W cm^{-2}).

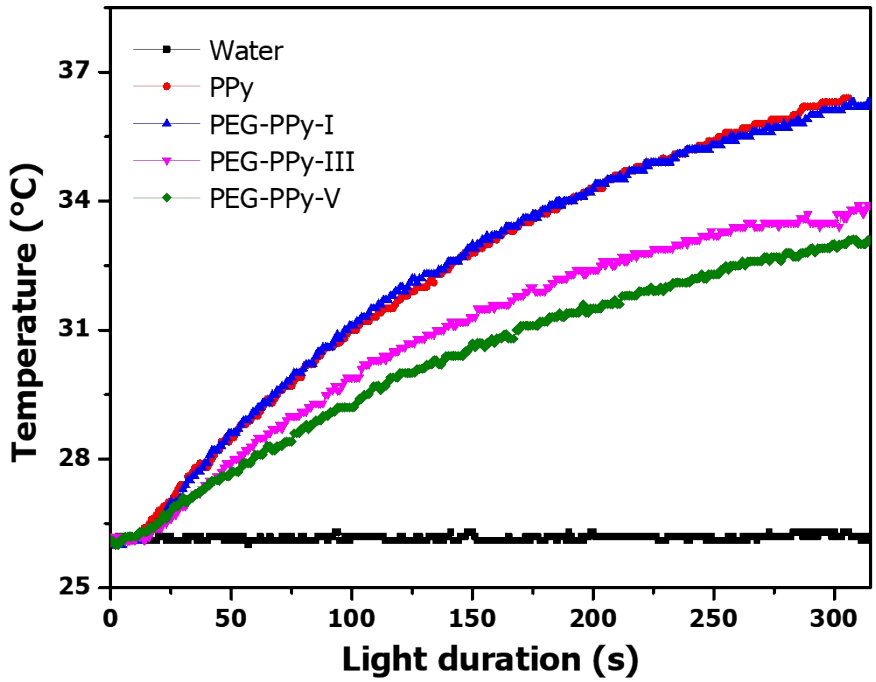

Fig. S11 Temperature change in various samples solutions (1 mg mL^{-1}) after 5 min laser irradiation (808 nm, 1 W cm^{-2}).

Supplementary tables

Table S1 Area percentage of fitted peaks from the C1s and N1s spectra of PPy, PPy-PEG-I, PPy-PEG-III and PPy-PEG-V.

Sample	C_{1s} fit [area%]				N_{1s} fit [area%]				N^+/N
	C-C/C-H	C-N	C-O	C=O	-N=	-N-H	$-N^+-$	$-N^+=$	
PPy	67.57	18.24	8.11	6.08	10.4	80	7.2	2.4	0.11
PPy-PEG-I	51.55	7.22	34.54	6.69	8	80	10.4	1.6	0.14
PPy-PEG-III	52.63	6.32	36.84	4.21	8.26	82.64	7.44	1.66	0.1
PPy-PEG-V	42.99	5.14	46.73	5.14	15.79	75.19	6.02	3	0.1

Table S2 Atomic percentage of the C, N, and O in PPy, PPy-PEG-I, PPy-PEG-III and PPy-PEG-V, which detected by XPS survey.

	Atomic [%]			PPy/PEG
	C 1s	N 1s	O 1s	(mole ratio)
PPy	72.96	8.82	18.22	-
PPy-PEG-I	71.44	6.47	22.09	0.73
PPy-PEG-III	67.38	5.65	26.97	0.37
PPy-PEG-V	64.26	5.66	30.08	0.31

Table S3 Integral area ratio peaks in the H-NMR spectra of PPy, PPy-PEG-I, PPy-PEG-III and PPy-PEG-V.

	a/b ratio	b/(c+d+e) ratio	Calculated MW of PEG segment
PEG-600	22.62	——	~520
PEG-600 (gamma)	20.11	——	~460
PPy-PEG-I	8.62	0.90	~210
PPy-PEG-III	10.14	2.08	~240
PPy-PEG-V	17.12	2.33	~390