Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Tetraphenylethene and Maltoheptaose Conjugate with Aggregation-Induced Emission (AIE) Characteristic for Temperature Sensor

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Experimental section

Materials

1-Bromo-1,2,2-triphenylethylene (98%), 4-(hydroxymethyl)phenylboronic acid (98%), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 97%) were purchased from J&K Scientific (Beijing, China). *N*-Maltoheptaosyl-*N*-(prop-2-yn-1-yl)acetamide (Mal-alkyne)[1,2] and 4-(1,2,2-triphenylethenyl)benzenemethanol (TPE-OH)[3] were synthesized according to the methods reported in the literatures. All other regents were purchased from J&K Scientific or Aladdin Reagent Co., and were used without further purification.

Synthesis of 4-(1,2,2-triphenylvinyl)benzyl methanesulfonate (TPE-OMs)

TPE-OMs was synthesized by mesylation of THE-OH. TPE-OH (1 g, 2.8 mmol) and pyridine (0.88 g, 11.2 mmol) were dissolved in 20 mL of dichloromethane. Methanesulfonyl chloride (1.28 g, 11.2 mmol) was mixed with dichloromethane (10 mL), and the solution was added dropwise into the reaction mixture. The reaction mixture was stirred at room temperature for 24 h, diluted with dichloromethane (30 mL), and washed twice with 60 mL of deionized water. The collected organic phase was dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed on a silica gel column using dichloromethaneo/hexane (v/v = 3:1) as the eluent to give a white powder. ^1H NMR (600 MHz, $CDCl_3$-*d*, δ, ppm): 3.67 (CH_2-SO_3-CH_3, 3H), 4.50 (CH_2-OMs, 2H), 6.90 - 7.17 (aromatic protons, 19H).

Synthesis of (2-(4-(azidomethyl)phenyl)ethene-1,1,2-triyl)tribenzene (TPE-N_3)

TPE-OMs (660 mg, 1.5 mmol) was dissolved in 10 mL of *N*,*N*-dimethylformamide (DMF), followed by the addition of sodium azide (293 mg, 4.5 mmol). The solution was stirred at 90 °C for 24 h. The reaction mixture was diluted with dichloromethane (50 mL), and washed with deionized water (50 mL) thrice. The collected organic phase was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column using dichloromethane/hexane (v/v = 1:1) as the eluent to give a white powder. ^{1}H NMR (600 MHz, $CDCl_3$-*d*, δ, ppm): 4.25 (CH_2-N_3, 2H), 6.96 - 7.15 (aromatic protons, 19H).

'Click' Synthesis of Mal-TPE

TPE-N_3 (122 mg, 0.32 mmol), Mal-alkyne (328.3 mg, 0.27 mmol), and CuCl (27 mg, 0.27 mmol) were placed in a Schlenk flask. Eight mL of DMF was added to dissolve the mixture. The flask was then evacuated and backfilled with argon. This process was repeated three times to eliminate oxygen from the reaction system. After that, PMDETA (111.36 μL, 0.53 mmol) was quickly introduced. The reaction mixture was sealed and stirred at 50 °C for 24 h. After cooling down to room temperature, the solution was dripped into 40 mL of cold diethyl ether and the precipitate was collected by centrifugation. The crude product was re-dissolved in deionized water, and dialyzed against ethylenediaminetetraacetic acid (EDTA) aqueous solution for 2 days and deionized water for 3 days. The solution was filtered through a 0.2 μm filter membrane, and lyophilized to give a white powder. ^{1}H NMR spectrum of Mal-TPE is shown in

Figure S1 (ESI). Mass: m/z 1619.63 ([M + H$^+$], Figure S2, ESI).

Fluorescence responsiveness and reversibility of Mal-TPE

Mal-TPE was dissolved in phosphate-buffered saline (PBS) solution to prepare a sample solutions with a concentration of 40 μM. Two mL of the solution was added to a quartz cuvette, and the cuvette was heated from 20 to 65 °C in a water bath. Upon reaching the predetermined temperature, the fluorescence intensity of the sample solution was recorded immediately on a Shimadzu RF-5301PC spectrophotometer at different temperatures.

To determine the fluorescence reversibility of Mal-TPE, the sample solution was heated to 55 °C in a water bath and sent for the fluorescence measurement immediately. After that, the sample solution was cooled down to 20 °C by exposure to room temperature, and its fluorescence intensity was recorded again. The heating and cooling processes were repeated for 9 times.

Characterization

The chemical structures of synthetic compounds were characterized by ^{1}H NMR spectroscopy on a Bruker DRX 400 MHz spectrometer. The UV-visible absorption spectra of Mal-TPE were conducted with a Shimadzu UV-2550 spectrophotometer. The fluorescence spectra were measured on a Shimadzu RF-5301PC spectrophotometer. An absolute photoluminescence quantum yield measurement system (Quantaurus-QY, Hamamatsu Photonics, Japan) with an excitation wavelength of 350 nm was used to determine the absolute quantum yield (Φ) of the Mal-TPE conjugate. Fluorescence lifetime was measured on a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer. Sample was excited at 350 nm, emission for time-correlated single photon counting (TCSPC) was detected at 466 nm. The hydrodynamic diameter of Mal-TPE in water was obtained by DLS measurements performed with a Nano ZS90 Zetasizer (Malvern Instruments, UK). The transmission electron microscopy (TEM) image was obtained from a JEOL JEM-2100 TEM (JEOL Ltd., Tokyo, Japan).

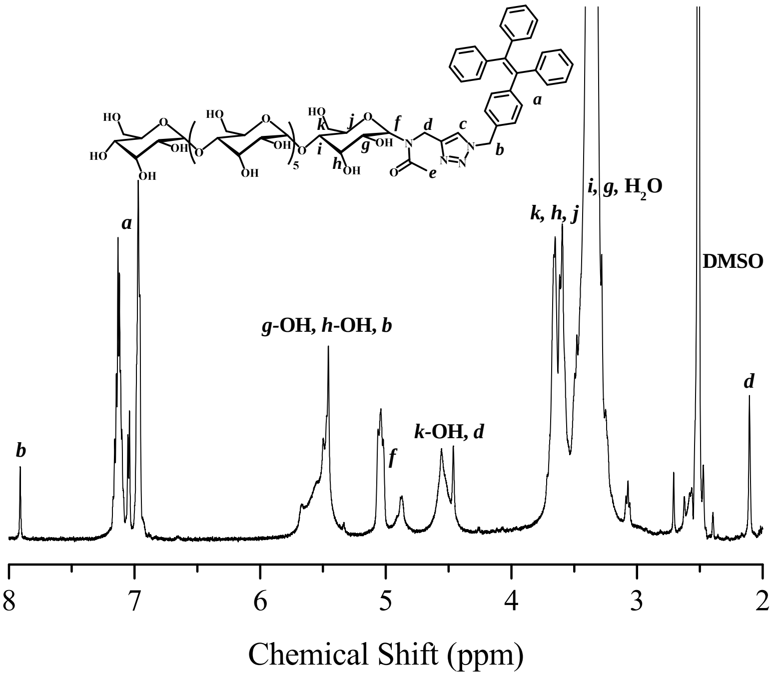


Figure S1. ^{1}H NMR spectrum of the Mal-TPE conjugate in DMSO-d_6.

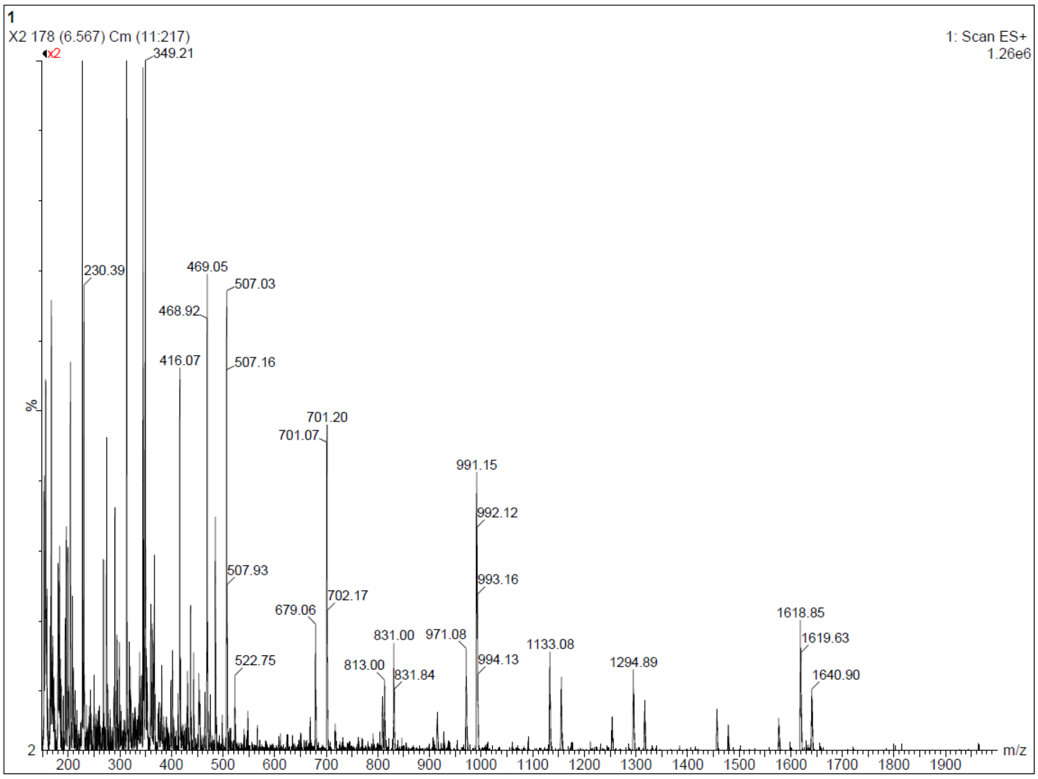


Figure S2. Mass spectrum of the Mal-TPE conjugate.

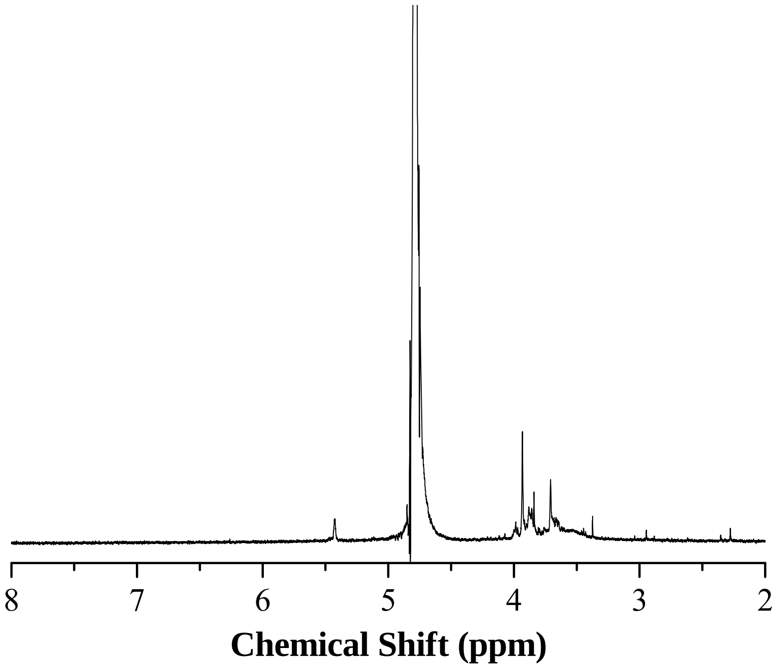


Figure S3. ^{1}H NMR spectrum of the Mal-TPE conjugate in D_2O.

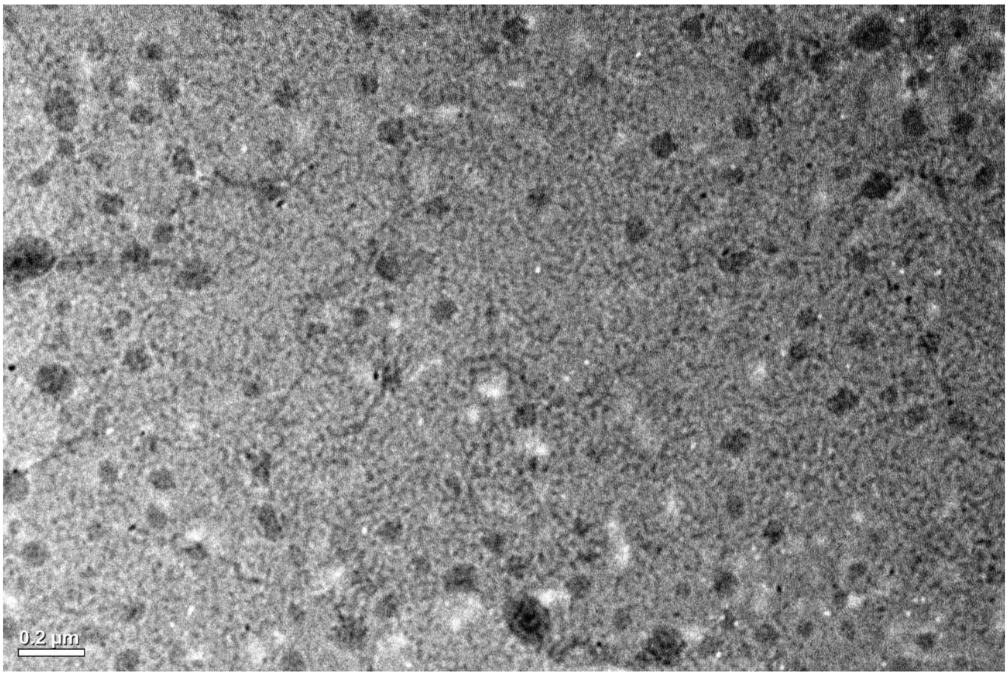


Figure 4. TEM image of Mal-TPE aggregate (40 μM) in deionized water. Mal-TPE was dissolved in deionized water at a concentration of 40 μM. Twenty μL of the solution was dropped on a carbon-coated copper grid. After drying at room temperature, the sample was sent for TEM observation.

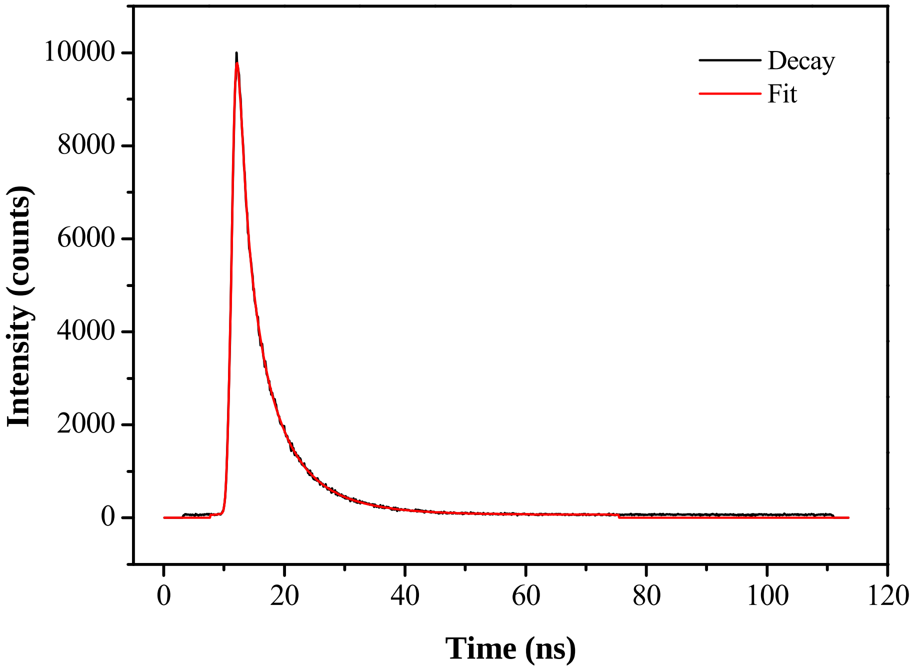


Figure S5. Fluorescence lifetime of Mal-TPE (40 μM) in PBS solution.

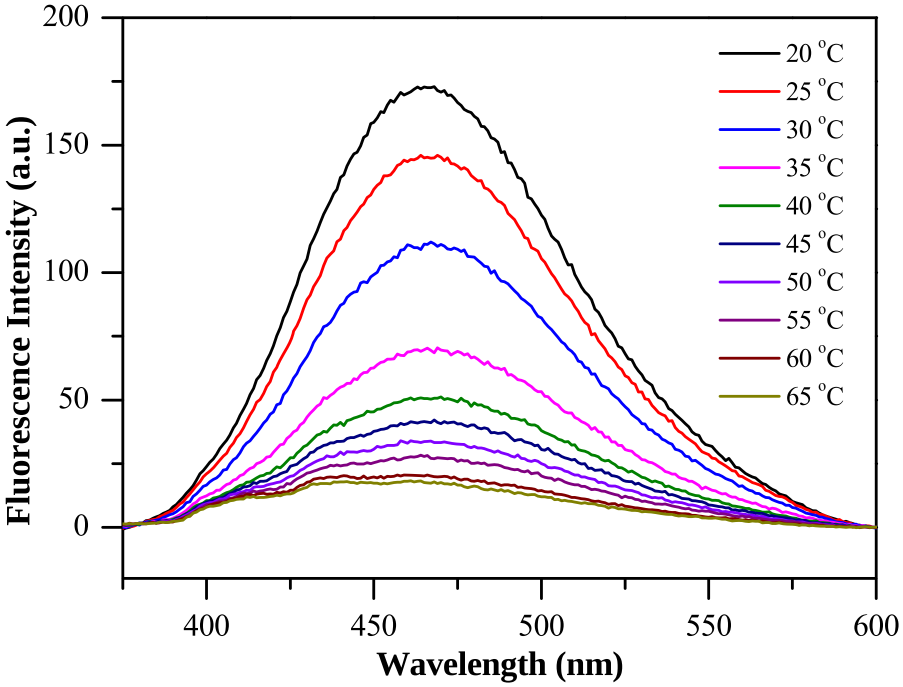
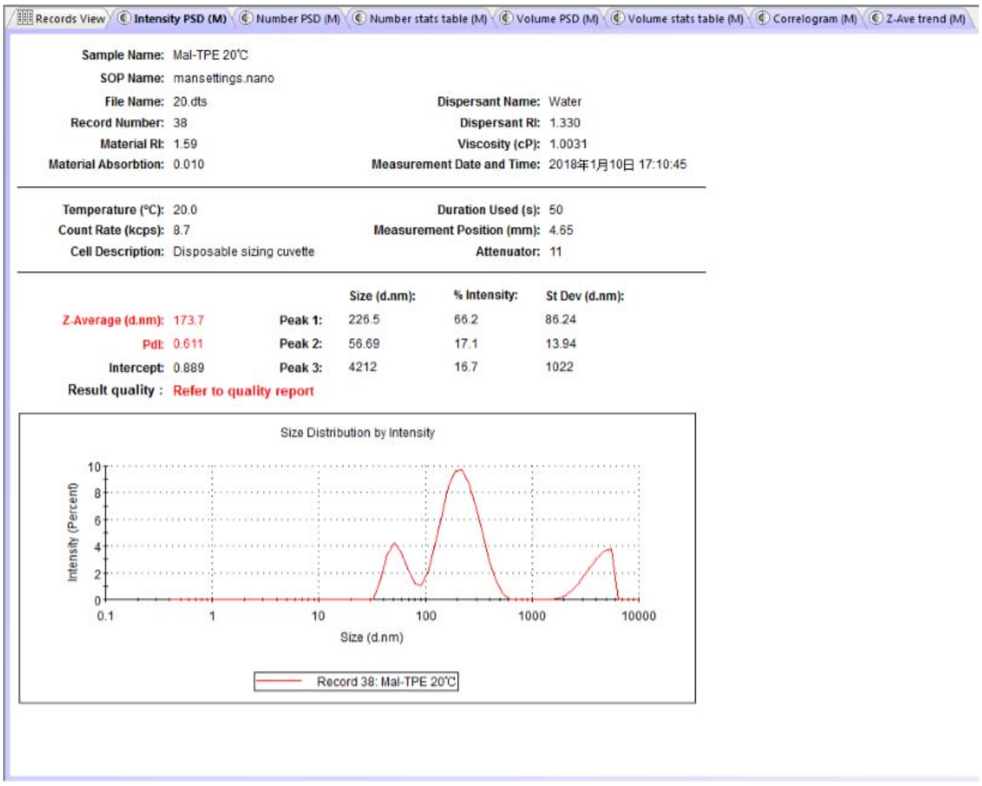


Figure S6. Fluorescence spectra of Mal-TPE (20 μM) in PBS solution at different temperatures with an excitation wavelength of 350 nm.



Sample Name: Mal-TPE 20℃
SOP Name: mansettings.nano
File Name: 20.dts
Record Number: 38
Material RI: 1.59
Material Absorbtion: 0.010

Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 1.0031
Measurement Date and Time: 2018年1月10日 17:10:45

Temperature (°C): 20.0
Count Rate (kcps): 8.7
Cell Description: Disposable sizing cuvette

Duration Used (s): 50
Measurement Position (mm): 4.65
Attenuator: 11

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	173.7	**Peak 1:**	226.5	66.2	86.24
PdI:	0.611	**Peak 2:**	56.69	17.1	13.94
Intercept:	0.889	**Peak 3:**	4212	16.7	1022

Result quality : **Refer to quality report**

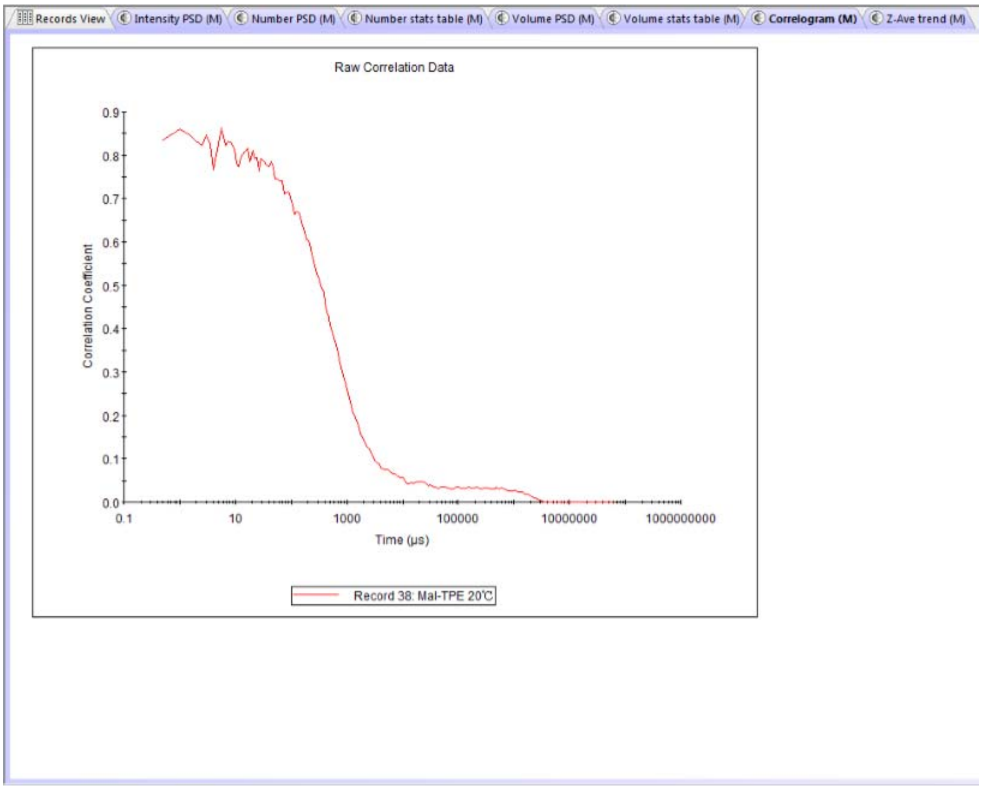
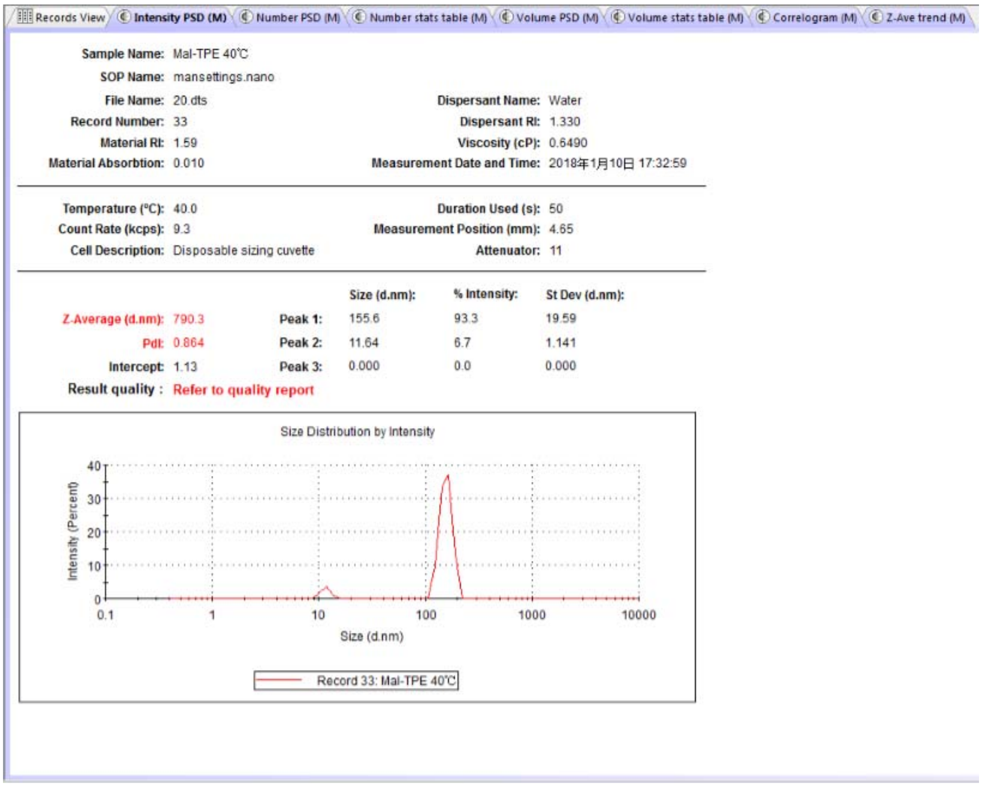


Figure S7. DLS report and raw correlation data of Mal-TPE at 20 ºC.



Sample Name: Mal-TPE 40℃
SOP Name: mansettings.nano
File Name: 20.dts
Record Number: 33
Material RI: 1.59
Material Absorbtion: 0.010
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.6490
Measurement Date and Time: 2018年1月10日 17:32:59

Temperature (°C): 40.0
Count Rate (kcps): 9.3
Cell Description: Disposable sizing cuvette
Duration Used (s): 50
Measurement Position (mm): 4.65
Attenuator: 11

Z-Average (d.nm): 790.3
PdI: 0.864
Intercept: 1.13
Result quality : **Refer to quality report**

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	155.6	93.3	19.59
Peak 2:	11.64	6.7	1.141
Peak 3:	0.000	0.0	0.000

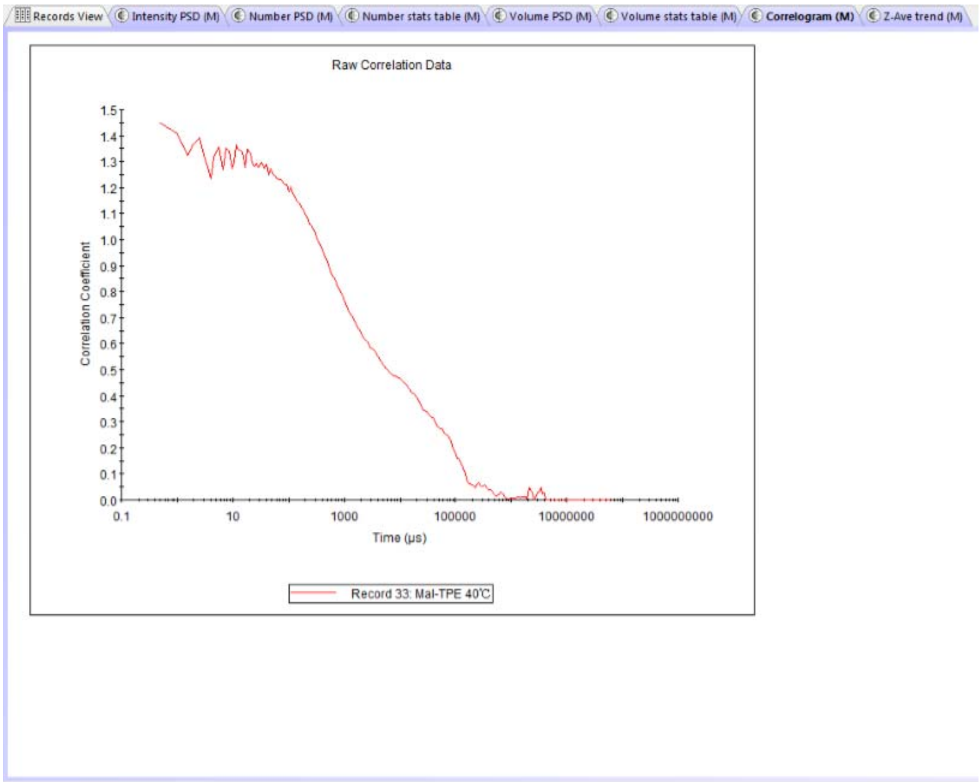
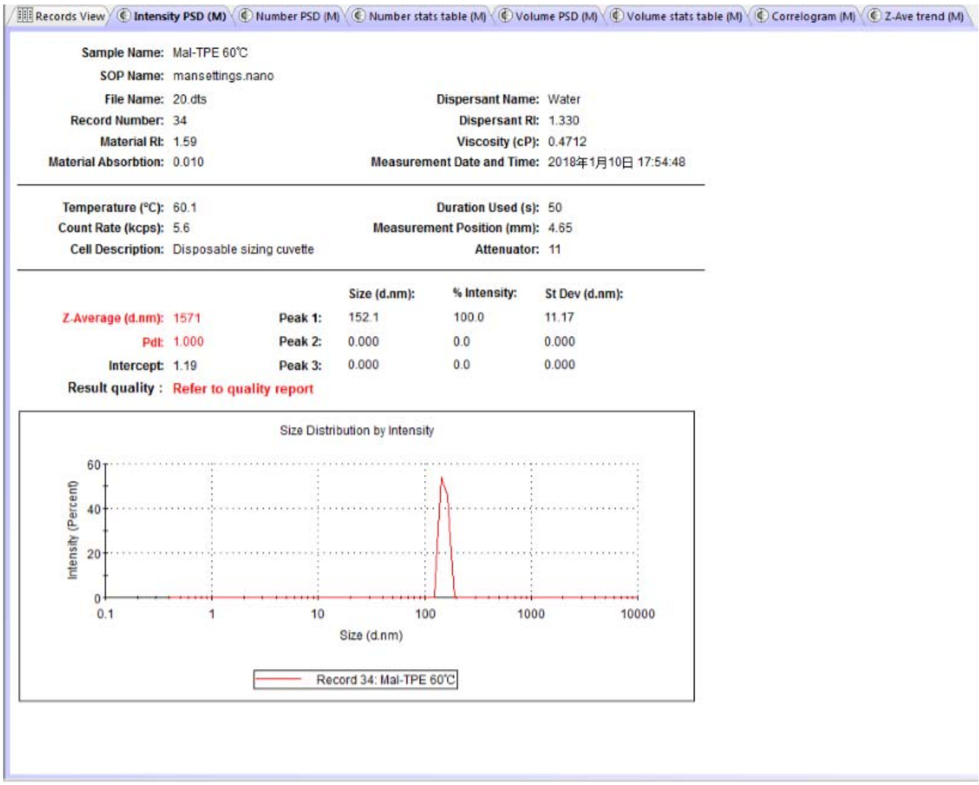


Figure S8. DLS report and raw correlation data of Mal-TPE at 40 ºC.



Sample Name: Mal-TPE 60℃
SOP Name: mansettings.nano
File Name: 20.dts
Record Number: 34
Material RI: 1.59
Material Absorbtion: 0.010
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.4712
Measurement Date and Time: 2018年1月10日 17:54:48

Temperature (°C): 60.1
Count Rate (kcps): 5.6
Cell Description: Disposable sizing cuvette
Duration Used (s): 50
Measurement Position (mm): 4.65
Attenuator: 11

Z-Average (d.nm): 1571
PdI: 1.000
Intercept: 1.19
Result quality : Refer to quality report

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	152.1	100.0	11.17
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

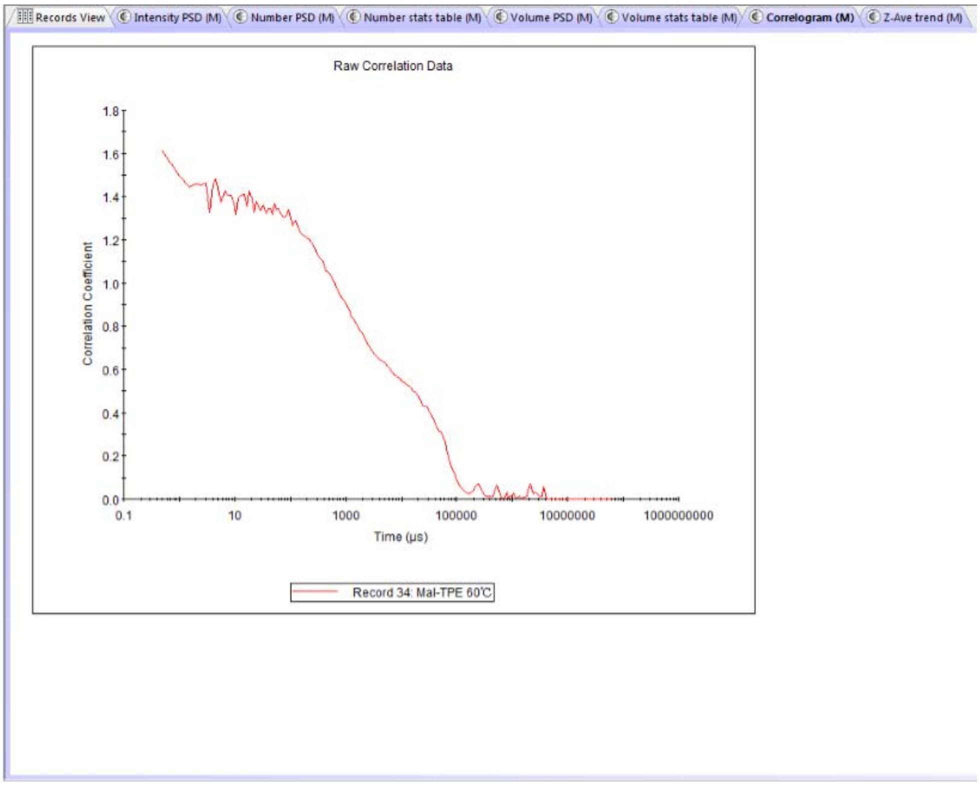


Figure S9. DLS report and raw correlation data of Mal-TPE at 60 ºC.

References

1. R. Eising, W. C. Elias, B. L. Albuquerque, S. Fort and J. B. Domingos, *Langmuir*, 2014, **30**, 6011-6020.
2. Y. Shi, H. Li, J. Cheng, T. Luan, D. Liu, Y. Cao, X. Zhang, H. Wei, Y. Liu and G. Zhao, *Chemical Communications*, 2017, **53**, 12302-12305.
3. N. N. Li, J. Z. Li, P. Liu, D. Pranantyo, L. Luo, J. C. Chen, E.-T. Kang, X. F. Hu, C. M. Li and L. Q. Xu, *Chemical Communications*, 2017, **53**, 3315-3318.