Supplementary Information for

Brush-Modified Fluorescent Organic Nanoparticles by ATRP with Rigidity-Regulated Emission

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I. Experimental Section

Materials. HMTPE (hydroxymethyl-TPE, also [4-(1,2,2-triphenylethenyl)phenyl]methanol, 97%, Ambeed), THBPE (tetrakis(4-hydroxybiphenyl)ethylene, also 4-[4-[1,2,2-tris]4-(4-98 (BRIJ[®]O20, hydroxyphenyl)phenyl]ethenyl]phenyl]phenol, 97%. Ambeed), Brij polyoxyethylene (20) oleyl ether average, $M_n \sim 1,150$, Aldrich), ascorbic acid (AsAc, 99%, Aldrich), methanol (MeOH, > 99.8%, Aldrich), tetrahydrofuran (THF, 99.5%, Aldrich), N,Ndimethylformamide (DMF, 99.9%, Acros), benzyl alcohol (BnOH, 99%, Aldrich), acetone-d6 (99.96%, Cambridge Isotope Laboratories), chloroform-d (CDCl₃, 99.96%, Cambridge Isotope Laboratories), ethyl a-bromoisobutyrate (EBiB, 98%, Aldrich), 2-bromoisobutyryl bromide (BiBB, 98%, Aldrich), sodium bicarbonate (NaHCO₃, ACS grade, Fisher Chemical), dichloromethane (DCM, 99.5%, Fisher), sodium chloride (NaCl, ACS grade, Fisher Chemical), sodium sulfate (Na₂SO₄, 99%, anhydrous, granular, Aldrich), alumina (neutral, Super I, 50-200µm, Sorbtech), alumina (basic, Super I, 50-200µm, Sorbtech), copper(II) bromide (Cu^{II}Br₂, 99.9%, Aldrich), tris(2-pyridylmethyl)amine (TPMA, 99%. KOEI), tris(2dimethylaminoethyl)amine (Me₆TREN, 99%, KOEI), tin(II) 2-ethylhexanoate (Sn(Oct)₂, 95%, Aldrich), and anisole (99%, Aldrich), were used as received unless otherwise stated. The stock solution of Cu^{II}Br₂(TPMA) was prepared by dissolving Cu^{II}Br₂ and TPMA in a 1: 1.1 molar ratio in water (0.05 M). Poly(ethylene glycol) methyl ether methacrylate (OEOMA₅₀₀, average M_n = 500, Aldrich) and ethylene glycol dimethacrylate (EGDMA, 98%, Aldrich) were passed through a column filled with basic alumina prior to use to remove any polymerization inhibitor. 2-Hydroxyethyl methacrylate (HEMA, 99%, Aldrich) was pre-washed to remove the residual ethylene glycol dimethacrylate. Details are written in the following section. The water used in this study is 18.2 M Ω ·cm ultrapure water.

Size exclusion chromatography (SEC). Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by SEC (also known as gel permeation chromatography, GPC). THF SEC was measured via a PSS GPC system with an Agilent 1260 Infinity II isocratic pump, a column set containing 3 PSS SDV analytical columns (pore sizes: 10³ Å, 10⁵ Å, 10⁶ Å), a Waters 2410 refractive index (RI) detector, and a PSS SLD9000 multi-angle light scattering (MALS) detector. The column set was kept with THF as the eluent at a flow rate of 1.00 mL/min (T = 35 °C). Analysis of polymer signals was based on PSS WinGPC software (build 9666) for molecular weight analysis. The calibrations for linear poly(ethylene glycol) methyl ether methacrylate samples (linear POEOMA₅₀₀) were first based on linear poly(methyl methacrylate) (PMMA) standards, followed by Mark-Houwink calibration. The calibrations for fluorescent organic nanoparticles (FoNPs) were based on the MALS detector using the injected sample mass concentration. DMF SEC was measured via a PSS GPC system with an Agilent 1260 Infinity II isocratic pump, a column set containing 3 PSS GRAM analytical columns (pore sizes: 3000 Å, 3000 Å, 100 Å), an Agilent 1260 Infinity II refractive index (RI) detector, and a PSS SLD2020 multi-angle light scattering (MALS) detector. The column set was kept in a column oven thermostated at 50 °C. DMF containing 0.05 M LiBr was used as the eluent. Analysis of polymer signals was based on PSS WinGPC software (build 9666) for molecular weight analysis. All FoNP and FoNP-g-POEOMA₅₀₀ (with linear POEOMA₅₀₀ as mixtures) samples were diluted and then processed through a 0.45 µm PTFE filter before SEC measurement.

Nuclear magnetic resonance spectroscopy (NMR). The synthesized inimer 2-(2bromoisobutyryloxy)ethyl methacrylate (BiBEM) (in CDCl₃), purity of HMTPE and THBPE (in acetone-d6), and OEOMA₅₀₀ monomer conversion (in CDCl₃) during SI-ARGET ATRP were analyzed by proton NMR (¹H NMR) using Bruker Avance[™] III 500 MHz (¹H Frequency) NMR Instrument.

Dynamic light scattering (DLS). FoNP size distributions were determined using a Zetasizer Ultra (Malvern Instruments Ltd) at 25 °C with THF as dispersant. Samples were diluted prior to the measurement (around 10 mg·mL⁻¹).

Helium pycnometer (referred to our previous work).¹ The densities of solid oNPs were determined via dividing the sample weight by the volume measured using a Micromeritics Accupyc II 1340. The skeletal volume of oNP is measured by helium gas displacement using the volume-pressure relationship of Boyle's Law. The oNP sample (as powder form) is placed in a sealed cup of a known volume. This cup is then placed into the sample chamber. Helium gas is introduced to the sample chamber and expanded into a second empty chamber with a known volume. The pressure observed after filling the sample cell, and the pressure discharged into expansion chamber are measured. The volume of oNP is then calculated.

Steady-state UV-Vis-NIR measurements. The UV-Vis-NIR spectra of samples were collected on a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu).

Steady-state photoluminescence measurements. The steady-state photoluminescence spectra were measured on an FLS-1000 spectrofluorometer (Edinburgh). Visible photoluminescence was measured using a photomultiplier (PMT) as the detector. The absolute photoluminescence quantum yield (QY) of THBPE_{0.3}B90E10 in benzyl alcohol (BnOH) was determined by an integrating sphere. The QYs of other samples were determined by the comparison of emission intensities of THBPE_{0.3}B90E10 in BnOH (as the reference) and other samples.²

Pre-washing of HEMA. 2-Hydroxyethyl methacrylate (HEMA), was pre-washed to remove the residual ethylene glycol dimethacrylate. First, 90 mL of HEMA was diluted with 210 mL water. Then, 100 mL hexane was mixed with the diluted HEMA solution, and the mixture was stirred for 5 min. Next, the mixture was transferred into a 500 mL separation funnel, and the aqueous layer after stabilized phase separation was collected. These mixing and separation procedures were repeated four times. After that, an excessive amount of NaCl was added into the separated aqueous layer with 10 min stirring. Once stabilized, HEMA phase-separated from the saline water, and was dried using anhydrous Na₂SO₄ for the subsequent inimer BiBEM synthesis.

Synthesis of inimer BiBEM. The purity check of BiBEM can be referred to our previous work.¹ HEMA (prewashed, 30 mL, 1.0 equiv) and 250 mL DCM were added to a 500 mL round bottom flask. Then, 41.6 g (2.0 equiv) NaHCO₃ was added into the flask. The mixture was then put into an ice bath, and degassed using nitrogen for 30 min. After that, BiBB (33.6 mL, 1.1 equiv) was slowly injected into the flask dropwise using a syringe pump (injection rate around 0.5 mL/min). The ice bath was kept for 2 h, and the reaction proceeded overnight with its temperature gradually increasing to room temperature. The synthesized inimer BiBEM was purified with the following steps: (1) 3 times washing of saturated NaHCO₃ solution (in water); (2) 3 times washing of water; and (3) washing of saturated NaCl solution (in water). Finally, BiBEM was dried using anhydrous Na₂SO4, passed a short period of basic alumina, and kept in the freezer (-20 °C).

General procedure for the FoNP synthesis by microemulsion ATRP. Take the synthesis of HMTPE₃B60E40 as an example. BiBEM (0.30 g, 45.8 μ L), EGDMA (0.14 g, 135.1 μ L), and HMTPE (19.5 mg) were mixed to form the oil phase under sonication. Cu^{II}Br₂(TPMA) stock solution (0.05 M in water) 28.7 μ L (800 ppm compared to comonomers), and Brij 98 (0.50 g) were added into 12.00 mL of ultrapure water to form the aqueous phase under sonication. The oil phase

was added dropwise into the aqueous solutions (total volume $\approx 12.50 \text{ mL}$) and homogenized by a vortex mixer. The mixture was transferred to a 25 mL Schlenk flask and purged with nitrogen for 15 min. The flask was then immersed in a 50 °C oil bath, and the AsAc stock solution (0.25 mL, 0.005 g/mL in water) was incorporated. [AIEgen]_0: [BiBEM + EGDMA]_0: [CuBr₂(TPMA)]_0: [AsAc]_0 = 3: 100: 0.08: 0.4. After 2 h reaction, the final FoNP products were purified through precipitation in methanol, dissolution in THF, centrifugation, and repeated dialysis (1 cycle of MeOH/THF 50/50 %v/v, 1 cycle of MeOH/THF 33/67 %v/v, and 3 cycles of THF).

General procedure for the FoNP-g-POEOMA₅₀₀ synthesis by SI-ARGET ATRP. Take the synthesis of HMTPE3B60E40-g-POEOMA500 as an example. OEOMA500 (6.48 g, 6.00 mL, 12.96 mmol, 50.0 vol% in anisole), HMTPE₃B60E40 as FoNP-Br macroinitiator (50.1 mg), EBiB as the sacrificial initiator in anisole stock solution (0.01 mL/mL) 19 µL (0.0013 mmol), Cu^{II}Br₂ in DMF stock solution (0.005 g/mL in DMF) 0.17 mL (300 ppm compared to monomer), and Me₆TREN in anisole stock solution (0.01 mL/mL) 0.31 mL, were mixed together. Then around 5.37 mL anisole was added into the mixture so that the OEOMA₅₀₀ concentration was around 50 vol% in anisole. The mixture was then transferred to a 25 mL Schlenk flask and purged with nitrogen for 15 min. After that, the freshly prepared $Sn(Oct)_2$ in anisole stock solution (0.05 mL/mL) 0.13 mL was slowly added into the flask to start the SI-ARGET ATRP. The flask was then immersed in a 60 °C oil bath for 1 h. In short, FoNP-Br ~50 mg, $[OEOMA_{500}]_0$: $[EBiB]_0 = 10000$: 1, $[CuBr_2]_0$ 300 ppm compared to monomer concentration, $[CuBr_2]_0$: $[Me_6TREN]_0$: $[Sn(Oct)_2]_0 = 1$: 3: 5. The partial final FoNP-g-POEOMA500 and linear POEOMA500 mixtures were diluted in DMF for DMF SEC analysis. To separate the linear POEOMA₅₀₀ from FoNP-g-POEOMA₅₀₀, ultrahigh speed centrifugation (Thermo Fisher Scientific, Sorvall ST16 Centrifuge, equipped with a Thermo Fisher Scientific Fiberlite F15 - 6×100y rotor) (13000 rpm for 2 h) was employed.



II. Fluorescent Organic Nanoparticles (FoNP) Synthesis by Microemulsion ATRP

Figure S1. Proton nuclear magnetic resonance (¹H NMR) spectroscopy of (a) HMTPE and (b) THBPE (in acetone-d6). The impurities are mainly from residual water since the integrations of phenyl protons are proportional.



Figure S2. Volume-averaged hydrodynamic diameters of (a) HMTPE- and (b) THBPEencapsulated FoNPs redispersed in THF measured by DLS.



Figure S3. (Normalized) THF SEC elution with time of FoNPs.

III. Quantum Yield (QY) Determination



Figure S4. Absolute quantum yield determination of THBPE_{0.3}B90E10 in benzyl alcohol (BnOH).

Relative Quantum Yield Determination

$$\phi_{S} = \phi_{R} \left(\frac{I_{S}}{I_{R}}\right) \left(\frac{1 - 10^{-A_{R}}}{1 - 10^{-A_{S}}}\right) \left(\frac{n_{S}}{n_{R}}\right)^{2}$$
(eqn. S1)

The method of relative quantum yield determination was referred to the reference.²

Where,

 Φ_S and Φ_R are the quantum yields of the sample and reference.

 I_S and I_R are the integrated photoluminescence intensities of the sample and reference.

 A_S and A_R are the absorbances at the excitation wavelength of the sample and reference.

 n_S and n_R are the refractive indices of the solvents used for the sample and reference.

Entry	I (× 10 ⁵) ^b	Solvent ^c	Absorbance ^d	k ^e	QY (%)
THBPE0.3B90E10 ^a	252	BnOH	0.055839	1.0000	19.2
THBPE0.3B75E25	350	BnOH	0.077016	0.7425	19.8
THBPE0.3B60E40	281	BnOH	0.053949	1.0328	22.1
Control B90E10	34	THF	0.040079	1.1439	3.0
Control B75E25	44	THF	0.067482	0.7007	2.4
Control B60E40	41	THF	0.047556	0.9723	3.0
HMTPE3B90E10	45	THF	0.066961	0.7058	2.4
HMTPE ₃ B75E25	189	THF	0.067447	0.7011	10.1
HMTPE3B60E40	246	THF	0.056331	0.8290	15.5
HMTPE2B60E40	345	THF	0.080865	0.5936	15.6
THBPE0.3B90E10	118	THF	0.121534	0.4131	3.7
THBPE0.3B75E25	100	THF	0.080314	0.5973	4.6
THBPE _{0.3} B60E40	152	THF	0.101326	0.4846	5.6

Table S1. Relative Quantum Yield Determination

^{*a*} THBPE_{0.3}B90E10 in BnOH is the reference shown as Figure S4. ^{*b*} Integrated photoluminescence intensities. ^{*c*} The refractive indices for BnOH and THF are 1.539 and 1.407 at 20 °C, respectively.

^{*d*} The absorbance is measured at the excitation wavelength $\lambda_{ex} = 336$ nm. ^{*e*} $k = \left(\frac{1-10^{-A_R}}{1-10^{-A_S}}\right) \left(\frac{n_S}{n_R}\right)^2$.

IV. Photoluminescence of oNP Backbones, AIEgens, and FoNPs



Figure S5. Fluorescent emission spectra evolution of bare oNPs (without encapsulating AIEgen) with increasing intraparticle rigidity (excitation wavelength $\lambda_{ex} = 336$ nm).



Figure S6. Absorbance and emission spectra evolution of copper catalyst complex in mixed THF and water with 50/50 % v/v. The photoluminescence intensities were normalized according to the main peak position for comparison. The excitation wavelength was 336 nm for the emission spectrum.



Figure S7. Absorbance and emission spectra evolution of (a) HMTPE and (b) THBPE in THF, (c) HMTPE and (d) THBPE as solid, and (e) HMTPE- and (f) THBPE-encapsulated FoNP in THF (HMTPE₃B60E40 and THBPE_{0.3}B60E40 as the example, respectively). The photoluminescence intensities were normalized according to the main peak position for comparison. The excitation wavelength was 336 nm for all the emission spectra.



Figure S8. Fluorescent emission spectra evolution of bare oNPs (without encapsulating AIEgen) and FoNP sample HMTPE₃B90E10. The photoluminescence intensities were normalized according to the largest peak position for comparison. The excitation wavelength was 336 nm for all the emission spectra. After comparing the shapes and positions of the emission peaks above 475 nm (highlighted within the red circle), the low QY of HMTPE₃B90E10 (ϕ = 2.4%) was ascribed to the low FoNP rigidity leading to free intramolecular motion thus weak emission of HMTPE despite a successful encapsulation.



Figure S9. Fluorescent emission spectra evolution of HMTPE-encapsulated FoNP samples with different HMTPE compositions (HMTPE₃B60E40 and HMTPE₂B60E40) (excitation wavelength $\lambda_{ex} = 336$ nm).



Figure S10. THBPE-encapsulated FoNP with increasing intraparticle rigidity. (a) Digital photos (shown as inset in Figure 2c) of FoNPs under UV irradiation ($\lambda_{ex} = 365$ nm). (b) CIE 1931 chromaticity diagram.

V. THBPE-Encapsulated FoNP in BnOH

Entry	B90E10	B75E25	B60E40
$^*M_{n,MALS}$ (×10 ³ g·mol ⁻¹)	6028	4261	2850
*Mass of solid oNPs tested in He pycnometer (g)	0.1680	0.1047	0.1941
Number of solid oNPs tested in He pycnometer (×10 ¹⁶)	1.68	1.48	4.10
*"Skeletal" volume of oNPs measured in He pycnometer (cm ³)	0.116	0.074	0.135
*Hydrodynamic diameter of oNP (THF solutions) by DLS (nm)	36.4	27.2	20.9
Hydrodynamic volume of oNP (THF solutions) (× 10 ⁻¹⁸ cm ³)	25.3	10.5	4.8
If all oNPs used in He pycnometer are dissolved in THF, the estimated total hydrodynamic volume of oNPs (cm ³)	0.425	0.155	0.197
The difference between "skeletal" and hydrodynamic volume (cm ³)	0.309	0.081	0.062
Estimated porosity (% v/v)	72.7	52.3	31.5

Table S2. Porosity Estimation of Solid oNP Backbones

* The absolute molecular weights, the mass and "skeletal" volumes measured with the pycnometer, and the hydrodynamic diameters of oNPs dissolved in THF measured by DLS, were referred to our previous work.¹



Figure S11. Dry THBPE-encapsulated FoNP sample THBPE_{0.3}B60E40 under (a) ambient conditions and (b) UV irradiation ($\lambda_{ex} = 365$ nm). Digital photo of THBPE-encapsulated FoNPs redispersed in BnOH (~ 5 mg·mL⁻¹) using ultrasonication with increasing intraparticle rigidity under (c) ambient conditions and (d) UV irradiation ($\lambda_{ex} = 365$ nm, shown as inset in Figure 3b).





Figure S12. (Normalized) SEC elutions with time of FoNP (in THF, dark) and mixtures of POEOMA₅₀₀-grafted FoNP with linear POEOMA₅₀₀ (in DMF, light), and deconvoluted molecular weights (assumed to follow a normal distribution, red) using PMMA standards from DMF SEC RI detector. The $M_{n,RI}$ (PMMA-based) was subsequently calibrated as $M_{n,abs}$ (POEOMA₅₀₀-based) using Mark-Houwink equation. (a, b) HMTPE₃B90E10-*g*-POEOMA₅₀₀. (c, d) HMTPE₃B75E25-*g*-POEOMA₅₀₀. (e, f) HMTPE₃B60E40-*g*-POEOMA₅₀₀. (g, h) THBPE_{0.3}B90E10-*g*-POEOMA₅₀₀. (e, f) HMTPE₃B60E40-*g*-POEOMA₅₀₀. (g, h) THBPE_{0.3}B90E10-*g*-POEOMA₅₀₀. Reaction conditions were listed in Figure 4.

VII. Mark-Houwink Calibration

Use HMTPE₃B60E40-*g*-POEOMA₅₀₀ as an example.

Entry	x, BiBEM (mol %)	x, EGDMA (mol %)	x, HMTPE (mol %)	M _{n, RI} (×10 ³)	<i>M</i> _w / <i>M</i> _n	<i>М</i> п, MALS (×10 ³)	D _{oNP, THF} (nm)
HMTPE3B60E40	60	40	3	41	1.19	3,244	16.4 ± 0.3

The information of FoNP HMTPE₃B60E40 as in Figure 2.

Apparent molecular weight and distribution (M_w/M_n)

The apparent molecular weight (based on the PMMA standards from DMF SEC RI detector) of deconvoluted linear POEOMA₅₀₀, $M_{n,RI} = 82650$, $M_w/M_n = 1.24$.

Using the Mark-Houwink equation,

$$K_1 M_1^{a_1+1} = K_2 M_2^{a_2+1}$$
 (eqn. S2)

Rearranging eq. S2 gives the molecular weight M_2 .

$$\log M_2 = \frac{1}{1+a_2} \left(\log \frac{K_1}{K_2} \right) + \frac{1+a_1}{1+a_2} \log M_1$$
 (eqn. S3)

For PMMA, $K_1 = 20.94$, $a_1 = 0.642$. For POEOMA₅₀₀, $K_2 = 354$, $a_2 = 0.355$. The values were referred to the reference.³ The recalibrated molecular weight of linear POEOMA₅₀₀ $M_{n,abs} =$ 112840. Since POEOMA₅₀₀ initiated from FoNP-Br and sacrificial initiator (EBiB) should polymerize at similar rate,⁴ the $M_{n,abs}$ of linear POEOMA₅₀₀ was also regarded as the molecular weight of the grafted brush layer ($M_{n,brush}$) of HMTPE₃B60E40-g-POEOMA₅₀₀.

VIII. Grafting Density Calculation

The calculation for HMTPE₃B60E40-g-POEOMA₅₀₀ is shown as an example.

Monomer conversion (conv.).

OEOMA₅₀₀ monomer conversion was measured by ¹H NMR – 21.0%

The "active" -Br concentration of FoNP-Br macroinitiator ([xFoNP-Br]0)

Since [OEOMA₅₀₀]₀: [EBiB]₀: [FoNP-Br]₀ = 10000: 1: *x*,

$$\frac{[OEOMA_{500}]_0}{[EBiB]_0 + [x_{FONP-Br}]_0} \times M_{w,OEOMA_{500}} \times conv. + M_{w,EBiB} = M_{n,brush}$$
(eqn. S4)

Therefore,

$$\frac{10000}{1+x} \times 500 \times 21.0\% + 209.05 = 112840, \ x = 8.32$$

Average number of grafted chains per FoNP, Nbrush

(Molar amount of total active -Br, n_{FoNP-Br})

$$n_{FoNP-Br} = n_{EBiB} \times \frac{x_{FoNP-Br}}{x_{EBiB}} = 0.0013 \times \frac{8.32}{1} = 0.0108 \, mmol$$
 (eqn. S5)

(Number of FoNP, N_{FoNP})

$$N_{FoNP} = \frac{m_{FoNP}}{M_{n,MALS,FoNP}} \times N_A = \left(\frac{0.0501 \ g}{3244000 \ g/mol}\right) \times 6.022 \times 10^{23}$$

$$= 9.30 \times 10^{15}$$
(eqn. S6)

(Average number of grafted chains per FoNP, Nbrush)

$$N_{brush} = n_{FoNP-Br} \times N_A \div N_{FoNP}$$

= (0.0108 × 10⁻³) × (6.022 × 10²³) ÷ (9.30 × 10¹⁵) (eqn. S7)
= 698

Grafting density, σ (chains nm⁻²)

$$\sigma = \frac{N_{brush}}{S_{FoNP}} = \frac{698}{4\pi \times (\frac{16.4}{2})^2} = 0.83$$
 (eqn. S8)

Average molecular weight of components in HMTPE3B60E40, Mw,ave

$$M_{w,ave} = f_{BiBEM} \times M_{w,BiBEM} + f_{EGDMA} \times M_{w,EGDMA}$$

$$+ f_{HMTPE} \times M_{w,HMTPE} = 257.64$$
(eqn. S9)

Weight fractions of FoNP "core" and POEOMA500 brush "shell" in HMTPE3B60E40-g-

POEOMA500, ω_{oNP} and $\omega_{POEOMA500}$

(Molecular weight of FoNP HMTPE₃B60E40 core)

$$M_{core} = M_{n,MALS,FoNP} = 3.244 \times 10^6 \ g/mol$$

(Average molecular weight of grafted POEOMA₅₀₀ chain)

 $M_{n,POEOMA_{500},single} = 112840 \ g/mol$

(Molecular weight of the entire grafted POEOMA₅₀₀ layers)

 $M_{n,brush,total} = M_{n,POEOMA_{500},single} \times N_{brush} = 112840 \times 698 = 79 \times 10^6 \ g/mol$

(Weight fraction of FoNP core)

$$\omega_{FoNP} = \frac{M_{core}}{M_{core} + M_{n,brush,total}} = 0.04$$
 (eqn. S10)

(Weight fractions of PMMA brush shell, $\omega_{POEOMA500} = 0.96$)

Average molecular weight of a single particle brush HMTPE₃B60E40-g-POEOMA₅₀₀, $M_{n,PGFoNP}$ and weight percentage of AIEgen loading ω_{AIEgen} (wt%)

(Average molecular weight of a single POEOMA₅₀₀-grafted FoNP)

$$M_{n,PGFoNP} = M_{POEOMA_{500}, total} + M_{core} = 82 \times 10^6 \, g/mol$$

Number of encapsulated AIEgen per FoNP

$$N_{AIEgen} = \frac{M_{n,MALS,FoNP}}{M_{w,ave}} \times f_{HMTPE} = \frac{3244000}{257.64} \times 0.03 = 378$$
(eqn. S11)

Weight percentage of AIEgen loading ω_{AIEgen}

$$\omega_{AIEgen} = \frac{N_{AIEgen} \times M_{w,HMTPE}}{M_{w,PGFoNP}} \times 100\% = 0.17\%$$
(eqn. S12)

Assume evenly distributions of AIEgens, the volume that each AIEgen takes, VAIEgen

$$V_{AIEgen} = \frac{V_{FoNP}}{N_{AIEgen}} = 6.1 \ nm^3$$
(eqn. S13)

Distance of any two AIEgens as the diameter of VAIEgen, dAIEgen

$$d_{AIEgen} = 2 \times \sqrt[3]{\frac{3 \times V_{AIEgen}}{4\pi}} = 2.3 nm$$
 (eqn. S14)

Entry	HMTPE3B90E10- g-POEOMA500	HMTPE ₃ B75E25- g-POEOMA ₅₀₀	HMTPE3B60E40- <i>g</i> -POEOMA500	THBPE _{0.3} B90E10- <i>g</i> -POEOMA ₅₀₀	THBPE _{0.3} B75E25- <i>g</i> -POEOMA ₅₀₀	THBPE _{0.3} B60E40- <i>g</i> -POEOMA ₅₀₀
X BiBEM	0.90	0.75	0.60	0.90	0.75	0.60
Хедрма	0.10	0.25	0.40	0.10	0.25	0.40
XAIEgen	0.03	0.03	0.03	0.003	0.003	0.003
m _{FoNP} (mg)	49.9	50.2	50.1	50.2	49.9	50.2
D _{FoNP, THF} (nm)	27.2	19.9	16.4	25.8	19.5	18.0
conv. (%)	33.0	25.9	21.0	29.8	23.2	21.0
$M_{ m n,abs,brush}$	82000	101700	112840	73520	99700	116000
$M_{ m w}/M_{ m n}$	1.21	1.38	1.24	1.29	1.35	1.38
M _{n,MALS,FoNP} (×10 ³)	3183	3218	3244	3261	3470	4252
XFoNP-Br	19.17	11.76	8.32	19.32	10.66	8.07
S _{FoNP} (nm ²)	2324	1244	845	2091	1195	1018
n _{FoNP-Br} (mmol)	0.0248	0.0152	0.0108	0.0250	0.0138	0.0105
N _{FoNP} (×10 ¹⁵)	9.44	9.39	9.30	9.27	8.66	7.11
$N_{ m brush}$	1585	977	698	1627	961	886
σ (nm ⁻²)	0.68	0.79	0.83	0.78	0.80	0.87
M _{w,ave}	281.91	269.78	257.64	273.14	261.00	248.87

 Table S3. Detailed Sample Information of SI-ARGET ATRP from FoNP-Br with EBiB.

M _{n,brush,total} (×10 ⁶)	130	99	79	120	96	103
ω _{FoNP} (%)	2.4	3.1	4.0	2.7	3.5	4.0
<i>Ш</i> роеома500 (%)	97.6	96.9	96.0	97.3	96.5	96.0
M _{n,PGFoNP} (×10 ⁶)	133	103	82	123	99	107
NAIEgen	339	358	378	36	40	51
ω _{AIEgen} (wt%)	0.09	0.13	0.17	0.02	0.03	0.03
V _{AIEgen} (nm ³)	31.1	11.5	6.1	251.1	97.3	59.6
dAIEgen (nm)	3.9	2.8	2.3	7.8	5.7	4.8

IX. HMTPE3B60E40-g-POEOMA500 in Aqueous Media



Figure S13. Digital photo of brush-modified FoNP, HMTPE₃B60E40-*g*-POEOMA₅₀₀ (20 mg·mL⁻¹ ¹ in water, left), and unmodified FoNP, HMTPE₃B60E40 (0.8 mg·mL⁻¹ in THF, right), with equivalent HMTPE concentration ($9.2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) under (a) ambient conditions and (b) UV irradiation ($\lambda_{ex} = 365 \text{ nm}$, shown as Figure 4e).

X. References

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