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Supporting information

# **Exciton and Charge Transfer Processes within Singlet Fission Micelles**

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### I. Transient absorption spectroscopy

### Instrumentation

A detailed description of the transient absorption (TA) spectroscopy employed for these studies has been previously reported.<sup>1–3</sup> A resonant pump pulse of ~100 fs was generated with a 1 KHz amplified Ti:Sapphire system with an optical parametric amplifier. A femtosecond supercontinuum probe in a thin sapphire plate is also generated from the laser. The delay in the probe is controlled mechanically. A fiber laser (Leukos) is used to generate a nanosecond supercontinuum probe pulse. Longer delay times are measured using an electronically delayed configuration. In the two probe measurements, the pump pulse is the same. All sample solution concentrations were below 500  $\mu$ M.

# Solution phase experiments

In toluene solution, the TA spectra of **TEGPNo40-***b***-TePNo[n]** display similar features to those of the previously reported TePNo homopolymer. However, the rate of singlet fission is significantly reduced with the addition of the extended TEGPNo40 block. This effect is greater with shorter TePNo block size.

Singlet fission is determined according to well-established protocols. Here, we photoexcited the **TEGPNo40-***b***-TePNo[n]** compounds with an excitation wavelength of 540 nm, which corresponds to a vibrational excited state of the S<sub>1</sub> exciton. Transient optical spectra show a spectral evolution on nanosecond timescales (Figure S1). The singlet state can be readily identified in the raw data (Figure S1) and from global analysis using a sequential kinetic model. Due to inhomogeneity, this model does not yield pure spectral decompositions. However, it is useful for identified characteristic timescales and conversion processes. Singlet excitons can be identified by their strong stimulated emission signals near 595 nm. This feature is observed in the first two spectra obtain from global analysis (**Figure S2**). Their decay is characterized by two timescales of ~ 50 ps and ~ 1 ns. These time constants are found to decrease with increasing n, from 1237 ps in n = 5 to 680 ps in n = 25.

Similarly, the triplet pair can be distinguished from the free triplet by its decay rate. As we have previously reported for a homopolymer of **TePNo[n]**, the triplet pair recombination follows a secondary geminate process in which mobile triplets separate along the backbone of the polymer and then recombine. As such, the time constant for triplet-triplet annihilation is slower for longer polymers, with a lifetime of 0.6  $\mu$ s for n = 5 and 1.8  $\mu$ s for n =25. The free triplet lifetime exceeds 130  $\mu$ s as is found in sensitization measurements.

	$ au_{ m SF}$ (ps)	$ au_{\mathrm{TT}}$ (µs)	$ au_{\mathrm{T}}\left(\mathrm{\mu s} ight)$
TEGPNo40-b-TePNo5	45, 1237	0.6	164
TEGPNo40-b-TePNo25	28, 720	1.8	135

Table S1: SF time constants of diblock copolymers in toluene solution



Figure S1: TA spectra of **TEGPNo40-***b***-TePNo[n]** in dilute toluene solution



Figure S2: Single-wavelength kinetics of **TEGPNo40**-*b*-**TePNo5** and **TEGPNo40**-*b*-**TePNo25** at 450 nm in dilute toluene solution, representing singlet decay. Global analysis of **TEGPNo40**-*b*-**TePNo25** in dilute toluene solution does not yield pure spectral decompositions due to the inhomogeneity of the SF process. The first principal spectrum (orange) corresponds to a pure singlet exciton, which can be identified by its strong stimulated emission signal at 595 nm. The second principal spectrum reflects a linear combination of singlet and triplet pair excitons. As such, singlet fission occurs over both time constants. The third component is a pure triplet pair, which exhibits a length dependent annihilation process, and the fourth component is the long-lived free triplet. Time constants are summarized in Table S10.

Kinetics and peak position analysis

£(1)

Ground state bleach (GSB) peak minima were determined in Igor Pro using the multipeak fitting function. Desired time cuts were extracted from the bulk dataset and fit between the wavelengths of 460 and 530 nm. Fit was initialized using two gaussian peaks centered at 475 and 506 nm, along with a linear baseline. The data are summarized in Figure S3a.

Stimulated emission (SE) kinetics at 593 nm were fit according to the following function:

$$= y0 + 0.5 * a1 * Exp\left(-k1 * \left((t-t0) - \frac{pw^2 * k1}{2}\right)\right) * \left(1 + Erf\left(\frac{(t-t0) - pw^2 * k1}{pw * sqrt(2)}\right)\right) + 0.5 * a2 * Exp\left(-k2 * \left((t-t0) - \frac{pw^2 * k3}{2}\right)\right) * \left(1 + Erf\left(\frac{(t-t0) - pw^2 * k3}{pw * sqrt(2)}\right)\right) + 0.5 * a4 * Exp\left(-k4 * \left((t-t0) - \frac{pw}{2} * \frac{k3}{2}\right)\right) * \left(1 + Erf\left(\frac{(t-t0) - pw^2 * k3}{pw * sqrt(2)}\right)\right) + 0.5 * a4 * Exp\left(-k4 * \left((t-t0) - \frac{pw}{2} * \frac{k4}{2}\right)\right) + 0.5 * a4 * Exp\left(-k4 * \left(\frac{t-t0}{2} + \frac{1}{2} + \frac{$$

Fixed values of  $y_0 = 0$  and  $k_1 = 6$  were used for all data sets. The impulsive generation of the SE signal is described by  $k_1$ ; the biexponential decay of the SE signal is described by  $k_2$  and  $k_3$ ; and longer timescale kinetics are described by  $k_4$ . Time constants for selected **TEGPNo40-***b*-**TePNo[n]** polymers, **TeM[n]** micelles, and *s***TeM[n]** swollen micelles are summarized in Table S2, and are recorded as  $\tau = k^{-1}$ . Selected traces for TeM[n] micelles are displayed in Figure S3b.

Excited state absorption (ESA) kinetics were averaged over the region of 700 to 750 nm. The resultant traces were each normalized at 20 ps to visually compare the relative rate of decay of the triplet pair in Figure S3c.

Table S2: Summary of singlet fission decay dynamics. When multiple analyses are used based on both the ESA and SE features, we report the average values.

	Morphology $\tau_{\text{SF},1}$ (ps)		$ au_{\text{SF,2}}$ (ps)
	Polymer solution	45	1240
TEGPNo40-b-TePNo5	Micelle	5	51
	Swollen micelle	1.9	7.1
TEGPNo40-b-TePNo10	Micelle	2.5	17.3
TEGPNo40-b-TePNo15	Micelle	2.1	19.8
	Polymer solution	28	720
TEGPNo40-b-TePNo25	Micelle	2.1	13
	Swollen micelle	1.6	7.1



Figure S3: Kinetic analysis of TeM[n] micelles, including a) GSB minima shift, b) SE rise, and c) ESA decay.



Figure S4: TA spectra of **TeM[n]** micelles in water.



Figure S5: TA spectra of **sTeM[n]** swollen micelles in water.

Kinetics of doped micelles:

Global analysis was performed using the Glotaran software package<sup>4</sup> to identify SF kinetics of doped **TeM[n]** micelles. Pentacene-doped micelles excited at 480 nm produced three meaningful components:  $\tau_1$  describes the decay of the tetracene singlet by some combination of singlet fission or singlet transfer pathways;  $\tau_2$  describes the decay of a mixed state consisting of excited species derived from both tetracene and pentacene; and  $\tau_3$  describes the decay of the pentacene free triplet (Table S3). Excitation of the same micelles at 600 nm produces only two meaningful components:  $\tau_1$  describes the decay of the pentacene singlet by SF; and  $\tau_2$  describes the decay of the pentacene free triplet (Table S4). TAA-doped micelles excited at 545 nm produced four meaningful components:  $\tau_1$  describes the decay of the tetracene singlet by SF;  $\tau_2$  describes the decay of tetracene m(TT) by charge transfer;  $\tau_3$  describes the decay of the [Tet]-/[TAA]<sup>+</sup> charge transfer state; and  $\tau_4$  describes the decay of residual tetracene triplets (Table S5).

	Pen %	Toluene?	$ au_1$ (ps)	$ au_2$ (ps)	$ au_3$ (µs)
	5	N	8.5	228	36
T.M.[5]		Y	4.4	111	34
1 ewi[5]	10	Ν	4.6	322	29
		Y	6.7	263	35
	5	Ν	5.4	159	40
T.M[25]	5	Y	4.5	429	39
1 6141[25]	10	N	3.7	361	36
		Y	4.7	280	36

Table S3: Kinetics of Pen-doped TeM[n] micelles, 480 nm excitation.



Figure S6: TA spectra of **TeM[5]** and *s***TeM[5]** micelles, co-assembled with Pen, 480 nm excitation



Figure S7: TA spectra of TeM[25] and sTeM[25] micelles, co-assembled with Pen, 480 nm excitation

	Pen %	Toluene?	$ au_1$ (ps)	$ au_2$ (µs)
	5	N	166	30
T.M.[5]	5	Y	117	26
1 ew1[5]	10	Ν	132	24
		Y	119	29
	5	Ν	163	31
T.M[25]	5	Y	106	32
1 6141[25]	10	N	131	30
	10	Y	116	29

Table S4: Kinetics of pentacene-doped TeM[n] micelles, 600 nm excitation



Figure S8: TA spectra of TeM[5] and sTeM[5] micelles, co-assembled with Pen, 600 nm excitation



Figure S9: TA spectra of TeM[25] and sTeM[25] micelles, co-assembled with Pen, 600 nm excitation

	Toluene?	$\tau_1$ (ps)	$ au_2$ (ps)	$\tau_3$ (ns)	$ au_4$ (µs)
T.M(5)	N	7	180	8	30
I eM[5]	Y	5	176	10	45
TeM[25]	N	3	246	10	29
	Y	3	193	10	33

Table S5: Kinetics of TAA-doped TeM[n] micelles, 545 nm excitation



Figure S10: TA plots of TeM[n] and sTeM[n] micelles, co-assembled with 1 equiv. TAA

# II. Polymer and assembly characterization

### Instrumentation

Gel permeation chromatography (GPC) was performed on a Waters Alliance 2695 separation module using a PL-aqua gel-OH 8-micron Mixed-M column (300 x 7.5 mm), with a Waters 2998 Photodiode Array Detector and a Waters 2414 Refractrometer Detector. Measurements were taken using THF stabilized with dibutylhydroxytoluene as the mobile phase, and an elution rate of 1 mL/minute. Molecular weight data and dispersities were determined from monodisperse polystyrene standards.

UV/vis spectra were taken on an Agilent Cary 60 UV-Vis Spectrophotometer. Measurements of micelles were performed as-is without further dilution.

Dynamic light scattering (DLS) was performed on a Malvern Zetasizer Nano-ZS equipped with a 10 mW 632.8 nm laser. Measurements were performed in water at 25°C using a 173° backscatter. Particle sizes are reported as the Z-average diameter, averaged over three measurements.

Particle morphology images was obtained on an FEI Talos F200X transmission electron microscope. Samples were prepared using carbon film on 200 mesh copper grids from Ted Pella.

	$M_n$ (kg/mol)	Đ	Theoretical TePNo %	Actual TePNo %
TEGPNo40-b-TePNo5	13.5	1.42	11	9
TEGPNo40-b-TePNo10	17.1	1.38	20	16.5
TEGPNo40-b-TePNo15	20.8	1.28	27	24.5
TEGPNo40-b-TePNo25	27.2	1.31	38	36

Table S6: Polymer size and TeNo incorporation

GPC results confirm the expected increase in polymer molecular weight for **TEGPNo40-***b***-TePNo[n]** with increasing n. Dispersities remain relatively consistent among all polymers.

Theoretical percentages of the TePNo blocks were calculated as n/(40 + n), in accordance with the stoichiometric inputs. Actual percentage was determined using <sup>1</sup>H NMR, by comparing the ratio between a representative tetracene signal at 9.3 ppm to the cumulative vinyl backbone signal from 5.8 - 5.1 ppm (Figure S23-26). For a TePNo homopolymer, this ratio is 1:1.



Figure S11: GPC traces of **TEGPNo40-***b***-TePNo[n**]



Figure S12: UV/vis spectra over a period of ten days of **TeM[10]** micelle in water at room temperature. Sample was kept in a sealed, degassed cuvette and stored in the dark between measurements.



Figure S13: UV/vis spectra of **TeM[5]**, co-assembled with TIPS-Pen in water at RT. Reference spectra for individual components and the mixed solution used for micelle preparation were obtained in THF at RT.



Figure S14: UV/vis spectra of **TeM[5]**, co-assembled with TAA in water at RT. Reference spectra for individual components and the mixed solution used for micelle preparation were obtained in THF at RT.



Figure S15: UV/vis spectra of **TeM[25]**, co-assembled with TCNQ in water at RT. Reference spectra for individual components and the mixed solution used for micelle preparation were obtained in THF at RT.

After completion of a given assembly procedure, 3 mL of each aqueous micelle mixture was drawn and used without further dilution for particle size analysis. DLS measurements of self-assembled **TeM[n]** reveal the formation of monodisperse particles, with average diameters ranging from approx. 70 to 180 nm (Table S7). These particles were found to adopt spherical micelle morphologies by TEM. A faint corona can be observed surrounding a darker micelle core at higher magnification (Figure S17).

	Dopant	Toluene?	Diameter (nm)	Polydispersity Index
		N	71	0.092
1 ew1[5]	-	Y	153	0.109
TeM[10]	-	N	85	0.064
TeM[15]	-	N	129	0.064
T.M[25]		N	135	0.095
1 elv1[25]	-	Y	181	0.172
	50/ Day	N	83	0.075
	5% Pen	Y	97	0.206
T.M(5)	10% Pen 1 equiv. TAA	N	132	0.098
1 ew1[5]		Y	173	0.132
		N	96	0.111
		Y	96	0.120
	5% Don	Ν	103	0.037
	570 F Ch	Y	113	0.102
	100/ Dam	N	119	0.082
T.M[25]	10% Fell	Y	166	0.119
1 elv1[25]		Ν	147	0.109
		Y	102	0.088
	1 equiv.	N	134	.256
	TCNQ	Y	131	.280

Table S7: Particle size and polydispersity data of various **TeM[n]** micelles.



Figure S16: Representative DLS measurements of pristine TeM[n] micelles in water at 25° C.



Figure S17: TEM imaging of TeM[25]

### **III.** Synthetic methods

#### General methods

Chemicals were purchased from Ambeed Inc, Sigma-Aldrich, Strem, TCI America, and Thermo Fisher Scientific, and were used as received without further purification. Anhydrous tetrahydrofuran (THF), dichloromethane (DCM) and N,N-dimethylformamide (DMF) were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Deionized water was degassed with argon for a minimum of 30 minutes when used as a reaction solvent. All reactions were conducted in oven-dried glassware under argon atmosphere. 2-bromo-6,11-bis(n-octyldiisopropylsilyl-ethynyl)tetracene (1)<sup>5</sup> and *rel*-3a*R*,4*R*,7*S*,7a*S*)-1,3,3a,4,7,7a-hexahydro-1,3-dioxo-4,7-methano-2*H*-isoindole-2-octanoic acid (3)<sup>6</sup> were synthesized according to literature procedures. The polymerization catalyst (IMesH<sub>2</sub>)(Cl)<sub>2</sub>(CsH<sub>5</sub>N)<sub>2</sub>Ru=CHPh (Grubbs III)<sup>7</sup> was synthesized according to literature procedure. Small molecule dopants 6,13-bis(triisopropylsilylethynyl)-pentacene (Pen)<sup>8</sup> and 4-[Bis(4-methoxyphenyl)amino]phenol (TAA)<sup>9</sup> were synthesized according to literature procedure.

### Instrumentation

<sup>1</sup>H-NMR spectra were recorded on Bruker 400 MHz and 500 MHz spectrometers. <sup>13</sup>C-NMR were recorded on a Bruker 125 MHz spectrometer. Chemical shifts are reported as  $\delta$  ppm, along with the corresponding integration values. Coupling constants (J) are reported in hertz (Hz). Standard multiplicity abbreviations were used as follows: s (singlet), d (doublet), t (triplet), dd (double doublet), td (triple doublet), m (multiplet).

Mass spectral data were obtained using a XEVO G2-XS Waters equipped with a QTOF detector with multiple inlet and ionization capabilities including electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric solids analysis probe (ASAP).



Figure S18: Synthetic scheme

Synthesis of 2

To a flask containing **1** (1.93 mmol, 1.56 g, 1 equiv.), 4-hydroxyphenylboronic acid pinacol ester (2.89 mmol, 636 mg, 1.5 equiv.),  $K_2CO_3$  (19.3 mmol, 2.67 g, 10 equiv.), and  $Pd(dppf)Cl_2 \cdot CH_2Cl_2$  (96 µmol, 78 mg, 0.05 equiv.) was added dry THF (36 mL) and degassed  $H_2O$  (4 mL). The reaction mixture was stirred for 20 hours at 65°C. Upon cooling to room temperature, the mixture was diluted with  $H_2O$  and extracted with CHCl<sub>3</sub>. Combined organics were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification on silica (25 to 75% hexanes/DCM) afforded the desired product **2** as a viscous red oil (1.2 g, 76% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 9.30 - 9.27 (m, 2H), 8.62 (m, 2H), 8.12 (s, 1H), 8.08 (d, J = 9 Hz, 1H), 7.73 - 7.68 (m, 3H), 7.54 (m, 2H), 7.00 (m, 2H), 4.82 (s, 1H), 1.72 - 1.68 (m, 4H), 1.53 - 1.45 (m, 5H), 1.33 - 1.21 (42H), 0.93 - 0.86 (m, 5H), 0.86 - 0.80 (m, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ ppm): 155.40, 137.85, 133.69, 132.72, 132.54, 132.43, 131.22, 130.66, 130.32, 129.17, 128.64, 127.43, 126.70, 126.61, 126.28, 126.24, 126.06, 124.86, 118.65, 118.40, 115.89, 106.19, 106.13, 103.81, 103.76, 34.00, 33.97, 31.97, 31.92, 29.44, 29.41, 29.37, 29.34, 24.91, 24.86, 22.67, 18.68, 18.66, 18.40, 14.12, 14.09, 12.08, 10.39.

MS (ESI): Calculated ([M+H]<sup>+</sup>): 821.5513; Observed: 821.5508

# Synthesis of TeNo

To a solution of **2** (1.46 mmol, 1.2 g, 1 equiv.), **3** (1.75 mmol, 534 mg, 1.2 equiv.), and 4dimethylaminopyridine (DMAP) (15  $\mu$ mol, 2 mg, 0.01 equiv.) in dry THF (30 mL) was added pivalic anhydride (1.75 mmol, 355  $\mu$ L, 1.2 equiv.). The reaction mixture was stirred for 20 hours at 60°C. Upon cooling to room temperature, the reaction was quenched by the addition of H<sub>2</sub>O (2 mL), then diluted with DCM. Organics were washed 3X with saturated sodium bicarbonate and 1X with brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification on silica (75 to 100% hexanes/DCM) afforded the desired product **TeNo** as a sticky red solid (1.3 g, 80% yield).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 9.36 (s, 1H), 9.33 (s, 1H), 8.65 (m, 2H), 8.19 (s, 1H), 8.13 (d, J = 9 Hz, 1H), 7.81 (m, 2H), 7.75 (dd, J = 9, 1.75 Hz, 1H), 7.57 (m, 2H), 7.27 (m, 2H), 6.29 (m, 2H), 3.51 (m, 2H), 3.29 (m, 2H), 2.68 (s, 2H), 2.62 (t, J = 7.5 Hz, 2H), 1.84-1.76 (m, 2H), 1.76 - 1.69 (m, 4H), 1.64 - 1.58 (m, 2H), 1.55 - 1.22 (m, 56H), 0.96-0.91 (m, 4H), 0.88 - 0.82 (m, 6H).

 $^{13}$ C NMR (126 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 178.06, 172.21, 150.50, 138.55, 137.83, 137.60, 132.79, 132.67, 132.30, 131.34, 130.69, 130.48, 129.33, 128.34, 127.47, 126.76, 126.71, 126.61, 126.22, 126.16, 125.89, 122.11, 118.71, 118.55, 106.35, 106.24, 103.80, 103.78, 47.84, 45.20, 42.75, 38.66, 34.37, 33.98, 33.97, 31.99, 31.94, 29.44, 29.37, 29.36, 28.94, 28.78, 27.73, 26.79, 24.91, 24.88, 24.85, 22.69, 22.67, 18.70, 18.68, 18.43, 18.41, 14.13, 14.09, 12.12, 10.41.

MS (ESI): Calculated ([M]<sup>+</sup>): 1107.6956; Observed: 1107.6913

Synthesis of 4

A solution of triethylene glycol monomethyl ether (42.6 mmol, 7 g, 1 equiv.) and NaOH (76.7 mmol, 3 g, 1.8 equiv.) in THF (15 mL) and H<sub>2</sub>O (12 mL) was stirred at 0°C in an ice bath for 30 minutes. A solution of TsCl (44.7 mmol, 8.5 g, 1.05 equiv.) in THF (9 mL) was then added dropwise via cannula. The reaction mixture was allowed to warm to room temperature while stirring for 4 hours. The mixture was diluted with H<sub>2</sub>O, then extracted 3X with DCM. Combined organics were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford the desired product 4 as a colorless oil (13.3 g, 98% yield), which was used without further purification.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.80 (m, 2H), 7.34 (dd, *J* = 8.6, 0.7 Hz, 2H), 4.16 (m, 2H), 3.69 (m, 2H), 3.64 - 3.57 (m, 6H), 3.55 - 3.50 (m, 2H), 3.37 (s, 3H), 2.45 (s, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ ppm): 144.77, 133.09, 129.81, 127.99, 71.92, 70.76, 70.58, 70.56, 69.22, 68.69, 59.02, 21.63.

MS (ESI): Calculated ([M+H]<sup>+</sup>): 319.1215; Observed: 319.1212

# Synthesis of TEGNo

To a suspension of NaH (60% in mineral oil, 37.6 mmol, 1.5 g, 1.5 equiv.) in dry DMF (40 mL) was added 5-norbornene-2-methanol (25.1 mmol, 3 mL, 1 equiv.) dropwise. The reaction mixture was stirred for 10 minutes at room temperature, then for 1 hour at 60°C. The mixture was allowed to cool to room temperature, then a solution of 4 (40.2 mmol, 12.8 g, 1.6 equiv.) in dry DMF (10 mL) was added. The reaction mixture was stirred for 10 minutes at room temperature, then 20 hours at 60°C. Upon cooling to room temperature, the mixture was diluted with  $H_2O$ , then extracted 3X with DCM. Combined organics were washed 3X with saturated sodium bicarbonate and 3X with brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification on silica (25% hexanes/EtOAc) afforded the desired product **TEGNo** (3 g, 44% yield) as a pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 6.11 (td, J = 6, 3 Hz, 1H), 6.05 (dd, J = 6, 3 Hz, 0.4H), 5.92 (dd, J = 6, 3 Hz, 0.6H), 3.70 - 3.49 (m, 12H), 3.40 - 3.34 (m, 3.6H), 3.19 (m, 0.6H), 3.07 (t, J = 9 Hz, 0.6H), 2.90 (s, 0.6H), 2.81 - 2.73 (m, 1.4H), 2.35 (m, 0.6H), 1.80 (m, 0.6H), 1.73 - 1.65 (m, 0.6H), 1.41 (m, 0.6H), 1.30 (m, 0.8H), 1.26 - 1.19 (m, 1H), 1.13 - 1.06 (m, 0.4H), 0.48 (m, 0.6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ ppm): 137.10, 136.63, 136.61, 132.49, 76.06, 75.09, 71.97, 70.67, 70.63, 70.60, 70.55, 70.28, 70.24fz, 59.04, 49.41, 44.99, 43.96, 43.65, 42.20, 41.54, 38.79, 38.71, 29.71, 29.16.

MS (ESI): Calculated ([M+Na]<sup>+</sup>): 293.1729; Observed: 293.1718

# Synthesis of TEGPNo40-b-TePNo[n]

To a stock solution of TEGNo (40 equiv.) in dry DCM was added a solution of Grubbs III (1 equiv.) in dry DCM, for a final concentration of 0.025 M. The reaction mixture was stirred for 2 hours, then 4 aliquots were drawn and transferred to clean reaction vessels. Varying amounts of TeNo (see Table S8) in DCM (1 mL) were added to each aliquot, and the reaction mixtures were stirred for an additional 2 hours. Polymerizations were quenched by the addition of ethyl vinyl ether (1 mL). Solvent was evaporated, and the polymers precipitated 3X from minimal DCM into cold MeOH. Filtration afforded **TEGPNo40-***b***-TePNo[n]** as red solids.

	TEGNo input	TeNo input	TeNo input	Yield
	(mmol monomer)	(mmol)	(mg)	(mg)
TEGPNo40-b-TePNo5	0.2	.025	28	28
TEGPNo40-b-TePNo10	0.2	.05	55	87
TEGPNo40-b-TePNo15	0.2	.075	83	82
TEGPNo40-b-TePNo25	0.2	.125	139	139

Table S8: Monomer inputs and yields for synthesis of TEGPNo40-b-TePNo[n]

General procedure for the preparation of TeM[n] micelles

Polymer was dissolved in anhydrous THF to a concentration of 2 mg/mL. An aliquot (600  $\mu$ L) was drawn via syringe, and rapidly injected into degassed H<sub>2</sub>O (6 mL) with vigorous stirring. Stirring was maintained for 30 minutes to allow the mixture to clarify.

General procedure for the preparation of **sTeM[n]** swollen micelles

Water (6 mL) and toluene (75  $\mu$ L) were added to a vial and briefly vortexed to mix, then degassed with argon. Polymer was dissolved in anhydrous THF to a concentration of 2 mg/mL. An aliquot (600  $\mu$ L) was drawn via syringe, and rapidly injected into the H<sub>2</sub>O/toluene mixture with vigorous stirring. Stirring was maintained for 30 minutes to allow the mixture to clarify.

General procedure for the preparation of doped **TeM[n]** micelles

A stock solution of polymer (2 mg/mL) and dopant (relative to TeNo concentration) was prepared in anhydrous THF. An aliquot (600  $\mu$ L) was drawn via syringe, and rapidly injected into degassed H<sub>2</sub>O (6 mL) with vigorous stirring. Stirring was maintained for 30 minutes to allow the mixture to clarify.

# IV. NMR spectra



Figure S19: <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2



Figure S20: <sup>1</sup>H and <sup>13</sup>C NMR spectra of TeNo



Figure S21: <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4



Figure S22: <sup>1</sup>H and <sup>13</sup>C NMR spectra of TEGNo



Figure S23: <sup>1</sup>H NMR spectra of TEGPNo40-b-TePNo5



Figure S24: <sup>1</sup>H NMR spectra of TEGPNo40-b-TePNo10



Figure S25: <sup>1</sup>H NMR spectra of **TEGPNo40-***b***-TePNo15** 



Figure S26: <sup>1</sup>H NMR spectra of **TEGPNo40-***b***-TePNo25** 

#### V. References

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