## **Electronic Supplementary Information**

Formation and decay of charge carriers in aggregate nanofibers consisting of poly(3-hexylthiophene)-coated gold nanoparticles

Dongki Lee,<sup>a</sup> Jaewon Lee,<sup>a</sup> Ki-Hee Song,<sup>b</sup> Hanju Rhee,<sup>b</sup> and Du-Jeon Jang<sup>a, \*</sup>

<sup>a</sup>Department of Chemistry, Seoul National University, Seoul 08826, Korea <sup>b</sup>Space-Time Resolved Molecular Imaging Team, Korea Basic Science Institute, Seoul 02841, Korea



Fig. S1 Proposed formation mechanisms of thin and thick NFs.



Fig. S2 AFM images of thin (left) and thick NFs (right).



Fig. S3 Absorption spectra (circles) of thin (a) and thick NFs (b). While Gaussian-fitted curves 1 (violet) and 2 (blue) are attributed to the  $S_0$ - $S_1$  transition of free chains, curves 3 (green), 4 (yellow), and 5 (red) are attributed to the 0-2, the 0-1, and the 0-0 transitions of aggregated chains, respectively. Black curves represent the sum of the five fitted curves. The exact locations and the absorbance percentages of the five fitted curves are outlined in Table S1.

TABLE S1. Spectral Positions of Five Gaussian Curves Fitted to Each Absorption Spectrum of NFs Dispersed in Cyclohexanone

sample	curve 1 (nm)	curve 2 (nm)	curve 3 (nm)	curve 4 (nm)	curve 5 (nm)
thin NFs	443±93 (54%) <sup>a</sup>	485±44 (12%)	524±31 (14%)	559±17 (6%)	603±27 (14%)
thick NFs	453±91 (56%)	486±33 (8%)	522±25 (12%)	559±19 (11%)	605±25 (13%)
pristine NFs	422±58 (27%)	479±36 (26%)	515±26 (19%)	555±22 (16%)	603±23 (12%)

<sup>a</sup>Absorbance percentage of each curve.



Fig. S4 Absorption spectra of pristine NFs (blue), thin NFs (green), and thick NFs (red).



Fig. S5 Emission spectra of pristine NFs (green) and thin NFs (red) in cyclohexanone with excitation at 430 nm.



Fig. S6 Emission spectra (circles) of thin (a) and thick NFs (b) in cyclohexanone with excitation at 532 nm, fitted with three Gaussian curves  $\lambda_1$  (blue),  $\lambda_2$  (green), and  $\lambda_3$  (red); black curves represent the sum of the three fitted curves.



Fig. S7 Picosecond transient-absorption kinetic profiles of thin NFs (green) and thick NFs (red) excited at 355 nm and probed at 660 (a), 740 (b), 820 (c), 1000 (d), and 1200 nm (e) observed in time windows of 50 ps. NFs were dispersed in cyclohexanone, and solid lines are best-fitted curves to extract kinetic constants.

sample	$\lambda_{\rm pr}~({\rm nm})$	$A_0^a (10^{-3})$	decay time (ps)
thin NFs	660	5.38	0.7 (76%) + 14 (24%)
	740	2.42	1.7 (46%) + 44 (54%)
	820	3.42	1.3 (58%) + 16 (42%)
	1000	11.1	1.7 (57%) + 26 (43%)
	1200	3.71	1.2 (68%) + 17 (32%)
thick NFs	660	4.61	0.6 (69%) + 16 (31%)
	740	2.69	1.2 (25%) + 18 (75%)
	820	3.13	1.4 (47%) + 25 (53%)
	1000	9.95	2.0 (43%) + 29 (57%)
	1200	3.99	1.1 (60%) + 16 (40%)
pristine NFs	660	2.80	1.0 (71%) + 24 (29%)
	740	1.99	1.6 (31%) + 63 (69%)
	820	3.60	1.5 (40%) + 90 (60%)
	1000	10.4	1.3 (34%) + 18 (66%)
	1200	4.09	1.7 (38%) + 38 (62%)

Table S2. Transient-Absorption Kinetic Constants of NFs Dispersed in Cyclohexanone with Excitation at 355 nm, Observed in Time Windows of 50 ps

<sup>a</sup> Initial transient absorbance