## **Electronic Supplementary Information**

# Broadband absorption and light-energy transfer in a phenyl-core thiophene dendrimer with multiple $\pi$ -conjugations

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### §1. Quantum calculations of the Ph-(7T)<sub>3</sub> moieties



**Figure S1.** (a) Chemical structures of  $\pi$ -conjugation patterns included in Ph-(7T)<sub>3</sub>. (b) Simulated wavelength-dissolved molar-absorption-coefficient spectra of the molecules shown in panel a. The spectra are normalized by the peak-top values. Absolute coefficient values and molecular orbital mappings are provided in Table S1 and Fig. S2.

**Table S1.** Computationally calculated wavelengths of absorption peaks and molar absorption coefficients of thiophene and phenylthiophene derivatives that comprise Ph-(7T)<sub>3</sub> dendrimer. Absorption peak with longest wavelength was observed in Ph-3T (442 nm) although largest number of thiophene rings was observed in Ph-(7T)<sub>2</sub> (436 nm). It appears that the  $\alpha$ - $\alpha$  bonds between thiophene rings contribute to the conjugation while  $\alpha$ - $\beta$  bonds cannot expand conjugation; conjugation in Ph-(7T)<sub>3</sub> may be disconnected by existence of  $\alpha$ - $\beta$  bonds so that absorption peaks are shorter than expected.

Molecules	$\lambda_{\max}^{a}(\mathbf{nm})$	$arepsilon^b$ at $\lambda_{ m max}$ (L mol <sup>-1</sup> cm <sup>-1</sup>
1T	215	7967
2Τ (α/α)	321	16860
2Τ (α/β)	293	14308
3T (α/α)	397	31200
3T (α/β)	338	8311
4T	382	21575
5T	341	29436
Ph-1T	297	18390
Ph-(1T) <sub>2</sub>	300	35640
Ph-2T	378	32081
Ph-3T	442	44476
Ph-3T ( $\alpha/\beta$ )	308	16739
Ph-4T	361	16303
Ph-7T	437	17013
Ph-(7T) <sub>2</sub>	436	20887

 ${}^{a}\lambda_{\max}$ : Wavelength of absorption peak.  ${}^{b}\varepsilon$ : Molar absorption coefficient.



LUMO





**Figure S2.** Molecular structures and molecular orbital mappings of the thiophene and phenylthiophene derivatives that compose the Ph- $(7T)_3$  dendrimer. Each orbital contributes to the absorption peak displayed in Table S1 (*i.e.*, each maximum absorption peak is due to a transition from HOMO–*n* to LUMO+*n*);  $\pm n$  indicates that the orbitals are energetically deeper or shallower than the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) by *n*, respectively. The white, gray, and yellow balls indicate hydrogen, carbon, and sulfur atoms, respectively. The blue and light purple clouds in the molecular mappings indicate negative and positive phases of the orbitals, respectively.



**Figure S3.** Computationally calculated energy diagrams of thiophene and phenylthiophene derivatives that comprise  $Ph-(7T)_3$  dendrimer. Each chemical structure is shown in Fig. S2.

Molecules	HOMO (eV)	LUMO (eV)	Band Gap (eV)
1T	-6.3328	-0.2106	6.1222
2Τ (α/α)	-5.4741	-1.2480	4.2262
$2T(\alpha/\beta)$	-5.5999	-0.9931	4.6068
3T (α/α)	-5.1325	-1.6900	3.4425
3T (α/β)	-5.4801	-0.2712	4.2037
4T	-5.2429	-1.5701	3.6728
5T	-5.1910	-1.6172	3.5738
Ph-1T	-5.6584	-1.0794	4.5790
Ph-(1T) <sub>2</sub>	-5.8403	-1.6325	4.2078
Ph-2T	-5.2186	-1.5919	3.6268
Ph-3T	-4.9789	-1.8720	3.1070
Ph-3T( $\alpha/\beta$ )	-5.5480	-1.8152	3.7328
Ph-4T	-5.2854	-1.4344	3.8511
Ph-7T	-5.0990	-1.8513	3.2476
Ph-(7T) <sub>2</sub>	-5.1530	-1.9354	3.2177

**Table S2.** Computationally calculated energy level of HOMO and LUMO of thiophene and phenylthiophene derivatives that comprise  $Ph-(7T)_3$  dendrimer. Band gap was calculated from difference between HOMO and LUMO.

#### §2. Absorption and photoluminescence spectra



**Figure S4.** Photoluminescence (PL) spectra of CHCl<sub>3</sub> solutions of Ph- $(7T)_3$  recorded with excitation wavelengths of 265, 308, 350, and 400 nm. Spectra represented by green line is shown in Fig. 3a of main manuscript. Although PL intensity differs according to excitation wavelength, peak positions (514 nm) are almost identical for all excitation conditions. Difference of intensity due to excitation wavelength would be caused by difference of absorption-to-emission efficiency according to excitation light.



**Figure S5.** (a) Absorption and (b) photoluminescence (PL) spectra of  $Ph-(7T)_3$  solutions. Red, yellow, green, blue, and purple solid lines indicate spectra recorded for CHCl<sub>3</sub>, hexane, NMP, THF, and toluene solutions of  $Ph-(7T)_3$ , respectively.

## §3. Fluorescence quantum yields

solvents	$\phi_{\mathrm{F}^{a}}(\%)$
CHCl <sub>3</sub>	$4.5\pm0.02$
Hexane	3.6 ± 0.01
Toluene	$5.3\pm0.02$
THF	$3.2\pm0.01$
NMP	$4.4\pm0.01$

Table S3. Fluorescence quantum yields of  $Ph-(7T)_3$  in each solvent excited at 350 nm.

<sup>*a*</sup> $\phi_{\rm F}$ : Florescence quantum yield.