Electronic Supplementary Material (ESI) for Polymer Chemistry.


## Supplementary Information

# Tetramethylbithiophene in π-Conjugated Alternating Copolymers as Effective Structural Component for the Formation of Spherical Assemblies

Liang Tong, Soh Kushida, Junpei Kuwabara, Takaki Kanbara, Noriyuki Ishii, Akinori Saeki, Shu Seki, Seiichi Furumi and Yohei Yamamoto*

* To whom correspondence should be addressed.
E-mail: yamamoto@ims.tsukuba.ac.jp

**Supporting Figures and Table**

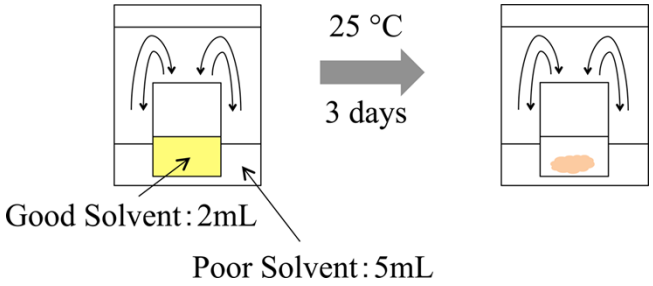


**Fig. S1** Schematic illustration of vapor diffusion method used in this study. Solution /vapor interface area and depth of the solution are 1.5 $cm^2$ and 1.3 cm, respectively.

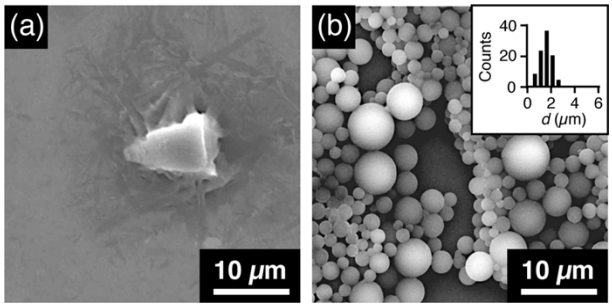


**Fig. S2** SEM micrographs of air-dried $CH_2Cl_2$/MeOH (a) and THF/MeOH (b) suspensions of the precipitates of **DOPTMT2**.

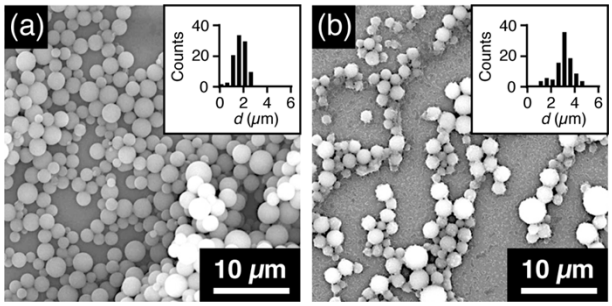


**Fig. S3** SEM micrographs of air-dried $CH_2Cl_2$/MeOH (a) and THF/MeOH (b) suspensions of the precipitates of **PTTMT2**.

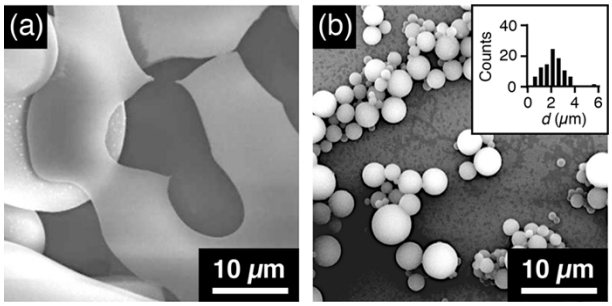


**Fig. S4** SEM micrograph of air-dried $CH_2Cl_2$/MeOH (a) and THF/MeOH (b) suspensions of the precipitates of **3,6-CTMT2**.

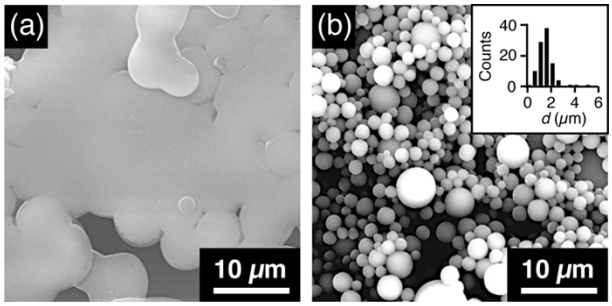


**Fig. S5** SEM micrographs of air-dried $CH_2Cl_2$/MeOH (a) and THF/MeOH (b) suspensions of the precipitates of **2,7-CTMT2**.

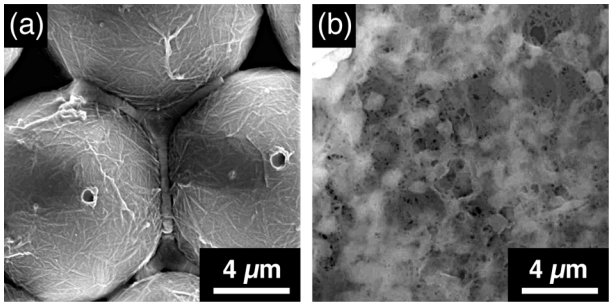


**Fig. S6** SEM micrographs of air-dried $CHCl_3$/MeOH (a) and $CH_2Cl_2$/MeOH (b) suspension of the precipitates of **DPPTMT2**.

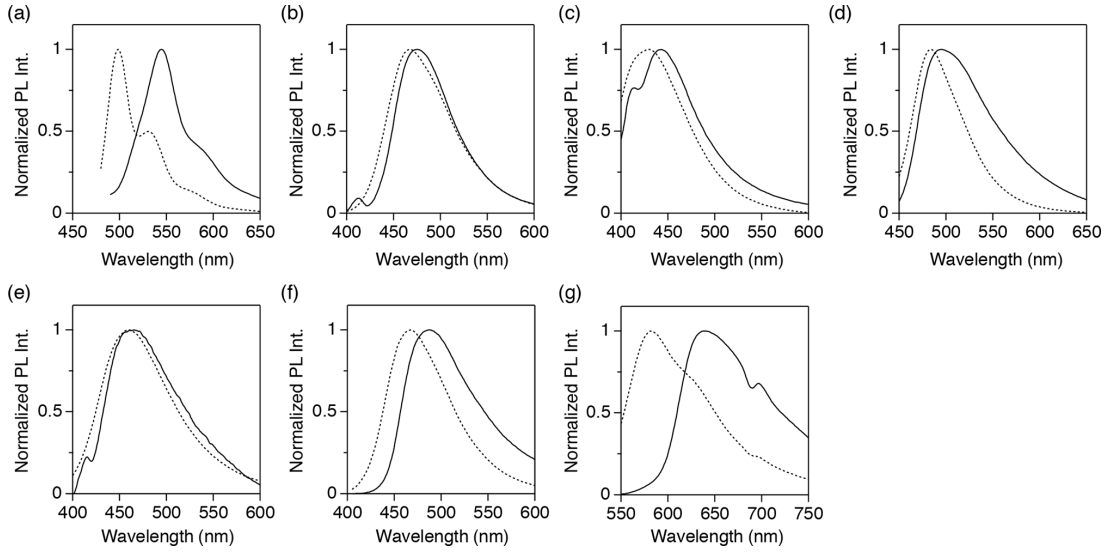


**Fig. S7** Photoluminescence spectra of (a) **F8T2** ($\lambda_{ex}$ = 457 nm), (b) **F8TMT2** ($\lambda_{ex}$ = 368 nm), (c) **DOPTMT2** ($\lambda_{ex}$ = 310 nm), (d) **PTTMT2** ($\lambda_{ex}$ = 328 nm), (e) **3,6-CTMT2** ($\lambda_{ex}$ = 319 nm), (f) **2,7-CTMT2** ($\lambda_{ex}$ = 370 nm) and **DPPTMT2** ($\lambda_{ex}$ = 421 nm) for $CHCl_3$ solutions (broken lines) and cast films from suspensions of the self-assembled spheres or aggregate (solid lines).

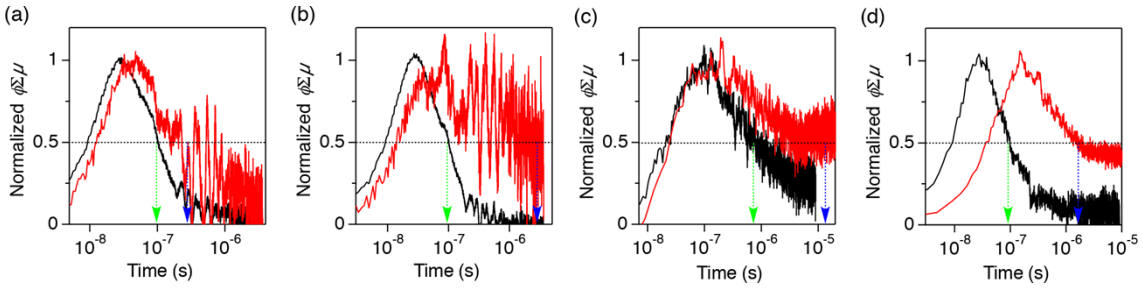


**Fig. S8** FP-TRMC profiles of thin films of self-assembled spheres or aggregates (red) and those cast from $CHCl_3$ solution (black). (a) **F8T2**,[S1] (b) **F8TMT2**,[S1] (c) **3,6-CTMT2**, and (d) **2,7-CTMT2**. The arrows indicate $\tau_{1/2}$ of thin films from solution (green) and those from suspensions of self-assembled spheres or aggregate (blue).

**Table S1** Summary of $\phi\Sigma\mu_{max}$ and $\tau_{1/2}$ for cast films from self-assembled precipitates and from solutions of $\pi$-conjugated copolymers

| | $\phi\Sigma\mu_{max}$ ($10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) | | $\tau_{1/2}$ (μs) | | |
|---|---|---|---|---|---|
| | Precipitate | Solution Cast | Precipitate | Solution Cast | Ratio[a] |
| **F8T2**[b] | 1.1 | 3.4 | 0.23 | 0.099 | 2.32 |
| **F8TMT2**[b] | 4.1 | 26 | 3.5 | 0.097 | 36.1 |
| **DOPTMT2** | 1.5 | 0.62 | 280 | 0.101 | 2770 |
| **PTTMT2** | 1.2 | 3.0 | 2000 | 0.085 | 23500 |
| **3,6-CTMT2** | 1.4 | 0.91 | 13 | 0.755 | 17.2 |
| **2,7-CTMT2** | 1.4 | 1.2 | 1.5 | 0.0952 | 15.8 |
| **DPPTMT2** | 1.5 | 0.48 | 0.453 | 0.235 | 1.92 |

[a] Ratio of $\tau_{1/2}$ for the precipitate films to that for solution-cast films

[b] Reference S1

**Table S2** Summary of $\phi_{PL}$ for cast films from self-assembled precipitates and from solutions of $\pi$-conjugated copolymers

| | $\phi_{PL}$ | |
|---|---|---|
| | Precipitate | Solution Cast |
| **F8T2** | 0.020 | 0.063 |
| **F8TMT2** | 0.024 | 0.014 |
| **DOPTMT2** | 0.007 | 0.005 |
| **PTTMT2** | 0.012 | 0.009 |
| **3,6-CTMT2** | 0.007 | 0.001 |
| **2,7-CTMT2** | 0.007 | 0.007 |
| **DPPTMT2** | 0.035 | 0.054 |

**Supporting References**


S1. T. Adachi, L. Tong, J. Kuwabara, T. Kanbara, A. Saeki, S. Seki and Y. Yamamoto, *J. Am. Chem. Soc.* 2013, **135**, 870.

S2. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. M. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.