Electronic Supplementary Information (ESI) for:

J-Aggregation of Protonated *meso*-Tetrakis(sulfonatothienyl)porphyrin Isomers: Morphological Selection of Self-Assembled Nanostructures from Structurally Similar Zwitterionic Porphyrins

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Preparation of aggregate suspensions

Equivalent amount of aqueous solutions of protic acids was added into aqueous solutions of the freebase forms of porphyrins followed by rapid agitating. After mixing, the solutions were left to rest in the dark at room temperature.

Preparation of deposited films of the aggregates

A drop of sample solutions (10 µl) was placed on glass cover. After one minute of immersion, the droplet was blown off quickly. Prior to use, glass covers were cleansed by immersion in H_2O_2/H_2SO_4 (1:3) for more than one hour, followed by rinsing in deionized water. For the polarized UV-vis spectral measurements, one minute of aging time for the sample solutions and one hour of immersing time were used. For clear AFM images, one minute of aging time and one minute of immersing time were used for $H_4T(5-STh)P^{2-}$, and 60 minutes of aging time and ~10 s of immersing time were used for $H_4T(4-STh)P^{2-}$.

Measurements

UV-vis absorption measurements were performed using a V-570 UV-vis spectrophotometer (Jasco). Atomic force microscopy observations were performed using a SPM-9500 (Shimadzu) operating in non-contact mode in ambient conditions. Silicon cantilevers (Nanoworld) with a resonance frequency of \sim 320 kHz were used.



Figure S1. UV-vis absorption spectra of $H_4T(5-STh)P^{2-}$ and $H_4T(4-STh)P^{2-}$ in water with HNO₃ (pH ~1), and the freebase forms of $H_4T(5-STh)P^{2-}$ and $H_4T(4-STh)P^{2-}$ in water with NaOH (pH ~10). Concentrations of the porphyrins are 1 μ M.



Figure S2. UV-vis absorption spectra of (a) $H_4T(5-STh)P^{2-}$ (100 μ M) and (b) $H_4T(4-STh)P^{2-}$ (1 mM) in water with various concentrations of HNO₃.



Figure S3. Polarized absorption spectra of the aggregates of (a) $H_4T(5-STh)P^{2-}$ and (b) $H_4T(4-STh)P^{2-}$ deposited on glass substrates from the aqueous solutions (100 μ M $H_4T(5-STh)P^{2-}$ with 0.05 M HNO₃ and 1 mM $H_4T(4-STh)P^{2-}$ with 0.1 M HNO₃, respectively). P-polarized light (broken) and s-polarized light (bold) were taken at the incident angle (θ) of 75°.



Figure S4. AFM images of $H_4T(5-STh)P^{2-}$ aggregates deposited on glass substrates from the aqueous solutions (40 µM) with various concentrations of HNO₃ .Concentrations of HNO₃ are (a) 0.01 M and (b) 0.1 M.



Figure S5. AFM images of $H_4T(4-STh)P^{2-}$ aggregates deposited on glass substrates from the aqueous solutions (1 mM) with various concentrations of HNO₃. Concentrations of HNO₃ are (a) 0.75 M and (b) 0.3 M.

(a)



(b)



Figure S6. AFM images of $H_4T(4-STh)P^{2-}$ aggregates showing (a) one-layered and (b) two-layered nanosheets with height profiles at the line AB.

(a)



(b)



(c)



Figure S7. (a) Schematic diagram depicting the exciton couplings of a one-dimensionally stacked porphyrin aggregate and the energy shifts of the J- and H-bands described by the point dipole model. (b) 1D packing model of porphyrin aggregates for the calculations of the point dipole model in exciton theory. (c) Sizes of the porphyrin core and the sulfothienyl groups used for the model, which are calculated by density functional theory (DFT) with B3LYP/6-31G(d) basis set implemented in a Gaussian-03 program package.^{s1} The values of μ and r used are 12.7 D and 0.89 nm for the H₄T(5-STh)P²⁻ aggregate, and 12.4 D and 0.83 nm for the H₄T(4-STh)P²⁻ aggregate, respectively.



Figure S8. Calculated displacements of the anionic positions of 5- and 4-sulfothienyl groups with respect to the rotational axes between the sulfothienyl groups and the porphyrin cores. The calculations were performed by density functional theory (DFT) with B3LYP/6-31G(d) basis set implemented in a Gaussian-03 program package.^{s1}

Additional References

S1 Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.