Supporting Information

Photoswitchable Aggregation-Induced Emission of Dithienylethene-Tetraphenylethene Conjugate for Optical Memory and Super-Resolution Imaging

Chong Li^{1,2}[†], Wen-Liang Gong^{1,2}[†], Zhe Hu^{1,3}[†], Matthew P. Aldred¹[†], Guo-Feng Zhang^{1,2}, Tao Chen^{1,2}, Zhen-Li Huang^{1,3}* and Ming-Qiang Zhu^{1,2}*

¹Wuhan National Laboratory for Optoelectronics and College of Optoelectronic
Science and Technology, ²College of Chemistry and Chemical Engineering,
³Department of Biomedical Engineering, Huazhong University of Science and
Technology, Wuhan, Hubei 430074, China. †These authors contributed equally to the
practical work. *e-mail: mqzhu@hust.edu.cn; leo@mail.hust.edu.cn.

CONTENTS

- 1. Experimental:
 - (a) General Information and Instrumentation.
 - (b) Super-Resolution Microscopy Imaging.
 - (c) Synthesis Procedures.
- 2. UV-VIS Absorption Spectra of the Cycloreversion Process.
- 3. Density Functional Theory (DFT)-Calculated Orbital Plots.
- 4. Photoluminescence Intensity Changes in THF/Water Solvent Mixtures at 440 nm excitation.
- 5. Determination of Critical Irradiation Wavelength by Fluorescence Spectra.
- 6. Photoluminescence Intensity of DTE-TPE in the Open-form and Photostationary State (PSS).
- 7. Excitation Wavelength-Dependent Emission of DTE-TPE.
- 8. Dynamic Light Scattering (DLS).
- 9. X-Ray Diffraction (XRD) of DTE-TPE Powder
- 10.¹H-NMR and ¹³C-NMR Spectra.
- 11. Mass Spectra.
- 12. References.

1. Experimental:

a) General Information and Instrumentation.

Perfluorocyclypentene was purchased from Hycegas Co.Ltd (99.9 %). Thiophene was purchased from Puyang Huicheng Chemical Co. Ltd and distilled under vaccum before used. Other commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were obtained from Alladin Chemicals and Sinopharm Chemical Reagent Co.,Ltd. Chloroform was dried over CaH₂ with stirring overnight followed by distillation under reduced pressure. THF was dried using sodium wire-benzophenone system and distillation. Dimethoxyethane (DME) was bubbled with N_2 for 30 mins before use. N-Chlorosuccinimide (NCS) was recrystallized from water. 4-(1,2,2-Triphenylvinyl)phenylboronic acid was published elsewhere by our group.¹

¹H-NMR and ¹³C-NMR spectra were recorded using a 400M Bruker AV400 in CDCl₃ or CD₂Cl₂ and an internal standard of tetramethylsilane was used. Mass spectra were recorded using an Agilent 1100 LC/MSD Trap. Purification of intermediates and final products was accomplished mainly by gravity column chromatography, using silica gel (200-300 mesh). The purity of all final compounds was checked by elemental analysis (Elementar Vario Micro-cube). The UV-vis spectum was recorded using a Shimadzu UV-vis-NIR Spectrophotometer (UV-3600). The PL spectrum was recorded using Edinburgh instruments (FLSP920 spectrometers). The 365 nm UV irradiation for the "ring-closing" reaction was performed using an utraviolet transmission platform, and the visible light for the "ring-opening" reaction was obtained from a common household table lamp (25W) and a long-wavelength pass filter (490nm, Accessories of FLSP920 spectrometer). Fluorescence Microscopy: Olympus BX61. The purity of TPE-DTE and its cyclization yield were obtained on a Waters Breeze 2 HPLC with UV detector (366nm, the isobestic point of two isomers of DTE-TPE) using a 5μ m CN column and eluting with 3 % of hexane in DCM). XRD: PANalytical B.V. (X' Pert PRO). DLS: Malvern Instruments ZS90.

b) Super-Resolution Microscopy Imaging.

The optical setup for imaging was based on a home-built microscope setup consisting of an Olympus IX 71 inverted optical microscope, a 100x/NA1.49 oil immersion TIRF objective (UAPON 100XOTIRF, Olympus), two solid-state lasers (405nm, 561nm, all from CNILaser, China), and an Andor iXon 897 EMCCD camera. During super-resolution imaging, two electronic shutters (UNIBLITZ VS14, Vincent Associates) were used to control the duration of laser irradiance and a dichroic mirror (Di01-R488/561, Semrock) and a longpass filter (BLP01-561R-25, Semrock) were used to separate the collected fluorescence from scattering laser and impurity fluorescence. We use an Image J plugins written in Java by ourselves to analyze the image.

The movies were collected at a frame rate of \sim 30 Hz and all durations were 3000 frames. When the density of molecule is too low during the imaging, a weak 405 nm laser was flashed to increase the density. Repeat this cycle many times to get enough images for further super-resolution image reconstruction.



c) Synthesis Procedures.

Scheme S1. Synthetic Route for DTE-TPE.

2-Chloro-5-methylthiophene

2-Methylthiophene (9.8 g, 100 mmol), N-chlorosuccimimide (14.6 g, 110 mmol), benzene (60 mL) and acetic acid (60 mL) were added into a 25 mL two-neck round flask and refluxed at 80 0 C for 7 h. Water (200 mL) was added to the mixture and the product was extracted with hexane (100 mL ×3), then washed with water (200 mL×3). The organic phases were combined, dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by distillation (colorless oil, 11.00 g, 83 % yield, b.p. 35°C under 5 mmHg vacuum).

¹H NMR (CDCl₃, ppm): δ = 6.67 (d, 1H, J=3.6Hz, thiophene ring 4 position), 6.50 (dd, 1H, J₁=0.9Hz, J₂=3.6Hz, thiophene ring 3 position), 2.39 (d, 3H, J=0.9Hz, -CH₃).

3-Bromo-5-chloro-2-methylthiophene

To an ice-cooled solution of 2-chloro-5-methylthiophene (3.98 g, 30 mmol) in CHCl₃ (30 mL), a solution of bromine (4.80 g, 30 mmol) in CHCl₃ (10 mL) was added slowly. After addition of the bromine (4.80 g, 30 mmol), the reaction mixture was stirred for 2 h at room temperature, and subsequently poured into H₂O (60 mL). The water layer was extracted with dichloromethane (3×30 mL) and the combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was purified by distillation (3.31 g, 93 %, b.p. 35°C under 5 mmHg vacuum).

¹H NMR (CDCl₃, ppm): δ =2.31 (s, 3H, -CH₃), 6.72 (s, 1H, thiophene ring). MS (APCI, m/z): 211.5 ([M]⁺), 213.5 ([M+2]⁺)

1,2-Bis-(5-chloro-2-methyl-3-thienyl)perfluorocyclopentene(Di-Cl-DTE)

To a stirred solution of 3-bromo-5-chloro-2-methylthiophene (1.40 g, 6.6 mmol) in anhydrous THF (60 mL), a n-BuLi/hexane (2.5 M) solution (2.76 mL, 6.9 mmol) was added dropwise at -78 °C under a N_2 atmosphere. Stirring was continued for 20 mins at this low temperature, followed by the addition of a cold and anhydrous THF solution (10 ml) of perfluorocyclopentene (0.40 mL, 3 mmol). The resulting reaction mixture was stirred for 2h at that temperature and the reaction mixture was allowed to

warm overnight at room temperature. The reaction was quenched by the addition of methanol (10 ml) and the product was extracted with ether, the combined organic layers washed with water, dried (MgSO₄), filtered, and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel) using hexane as the eluent, followed by recrystallization from hexane (colorless crystals, 0.79 g, 32.3 %). The average yield of this step is usually moderate and not easy to scale up because of the volatility of perfluorocyclopentene.

¹H NMR (CDCl₃, ppm): δ =1.89 (s, 6H, -CH₃), δ 6.89 (s, 2H, thiophene ring). MS (APCI, m/z): 437.2 ([M]⁺).

1,2-Bis-{2-methyl-5-[4-(1,2,2-Triphenylvinyl)phenyl]-3-thieny}perfluorocyclopen tene (DTE-TPE)

To a 25 ml two-neck round flask, Di-Cl-DTE(0.20 g, 0.46 mmol), TPE-B(OH)₂ (0.38 g, 1.01 mmol) Na₂CO₃ (0.24 g, 2.29 mmol), water (2.5 mL) and DME (10 mL) was added under N₂ atmosphere, then the catalyst Pd(PPh₃)₄ (0.05 g, 0.05 mmol) was added under N₂ stream. The reaction mixture was refluxed at 80 0 C for 24 hours. Water (40 mL) and ether (40 mL) were added and the organic layer was washed with water (40 mL×3), dried with NaSO₄ and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel) eluting with DCM: hexane (1:9) to yield a light yellow amorphous (see XRD below) solid (0.30 g, 63.4 %).

¹H NMR (CD₂Cl₂, 400M, ppm): δ =7.21 (d, 4H, J=8.0Hz, TPE-H), 7.15 (s, 2H, thiophene ring), 6.90-7.10(m, 34H, TPE-H), 1.85 (s, 6H, -CH₃). ¹³C NMR (CD₂Cl₂, 100M, ppm):143.66, 143.63, 143.57, 143.53, 142.02, 141.49, 140.24, 131.83, 131.23, 131.15,127.81, 127.70, 127.63, 126.60, 126.53, 126.47, 125.73, 124.65, 122.21, 14.39. MS (APCI, m/z): 1029.6 ([M]⁺), HPLC purity: 99.7%, eluting with 3% DCM in hexane.

2. UV-VIS Absorption Spectra of the Cycloreversion Process.



Figure S1. Changes in UV-VIS spectra of DTE-TPE-C in THF solution (concentration= 1×10^{-5} M) upon irradiation with visible light (> 490 nm).



3. Density Functional Theory (DFT)-Calculated Orbital Plots.

Figure S2. Optimized molecular structures and the HOMO (H) and LUMO (L) electron densities of DTE-TPE-O and DTE-TPE-C.

3. Photoluminescence Intensity Changes in THF/Water Solvent Mixtures at 440 nm excitation.



Figure S3. PL spectra of TPE-DTE in THF/water mixtures with different water contents at concentration = 1×10^{-4} M, excitation wavelength = 440 nm.

4. Determination of Critical Irradiation Wavelength by

Fluorescence Spectra.



Figure S4. The change of fluorescence intensity at 530 nm of DTE-TPE (the natural state after column chromatography purification, containing small amount of DTE-TPE-C) in the solid state under excitation with various wavelengths was used to determine the critical irradiation wavelength for DTE-TPE preserving the forward and backward isomerization equilibrium.



5. Excitation Wavelength Dependent Emission of DTE-TPE

Figure S5. Excitation wavelength dependent emission in the solid-state at 400 nm, 410 nm, 420 nm, 430 nm and 480 nm.

6. Photoluminescence Intensity of TPE-DTE at the Open-form and Photostationary State (PSS).



Figure S6. PL spectra of the closed-form and PSS (After 5mins 365nm UV light irradiation) of TPE-DTE in PMMA at concentration = 3 w%, 95% water/THF mixture at concentration = 1×10^{-5} M and THF solution at concentration = 1×10^{-5} M, excitation wavelength (nm): 440 nm.

7. Dynamic Light Scattering (DLS).



Figure S7. Size distribution of TPE-DTE nanoparticles in THF/water mixture with 90% water fraction. Concentration: 1×10^{-5} mol/L. The Z-average.diameter = 243 nm, PDI=0.107

8. X-ray Diffraction of DTE-TPE Powder



Figure S8. Size distribution of TPE-DTE nanoparticles in THF/water mixture with 90% water fraction. Concentration: 1×10^{-5} mol/L.

9. ¹H-NMR and ¹³C-NMR Spectra.

5-Chloro-2-methylthiophene



3-Bromo-5-chloro-2-methylthiophene



Di-Cl-DTE



DTE-TPE (¹**H-NMR**)



DTE-TPE (¹³C-NMR)



10. Mass Spectra.

3-Bromo-5-chloro-2-methylthiophene



16

Di-Cl-DTE



DTE-TPE



11. References.

1. Matthew. P. Aldred, Chong Li, Guo-Feng Zhang, Wen-Liang Gong, Alexander. D. Q. Li, YanfengDai, Dongge Ma, Ming-Qiang Zhu. *J. Mater. Chem.*, **2012**, *22*, 7515-7528.