Supporting Information

Functional Covalent Layer-by-Layer Thin Films by [2+2] Cycloaddition–Retroelectrocyclization

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Materials

All reagents were used without further purification. 4-(4'-*N*,*N*-Dihexylaminophenylethynyl)styrene[1] and TCNQ polyester[2] (**P2**) (M_n (GPC, THF) 4600; M_w/M_n 1.56; $T_{d5\%}$ 324 ^oC) were prepared according to the reported procedure.

General measurements

NMR spectra were recorded on a JEOL model AL300 spectrometer at 20 ^oC. Deuterated chloroform was used as a solvent. Chemical shifts are reported in ppm (parts per million) using either tetramethylsilane (TMS) or residual solvent signals as an internal reference. The resonance multiplicity is described as s (singlet) and m (multiplet). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer in the range from 4000 to 600 cm^{-1}. Gel permeation chromatography (GPC) was measured on a JASCO system (PU-2080, CO-2065, RI-2031, and AS-2055) equipped with polystyrene gel column (Shodex KF-804L) using THF as an eluent at the flow rate of 1.0 mL min^{-1} after calibration with standard polystyrenes. UV-vis-near IR absorption spectra were recorded on an Agilent HP8453 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Rigaku TG8120 under nitrogen flow at the heating rate of 10 ^oC min^{-1}. Water contact angle measurements were made on a Surface & Electro-Optics Phoenix 150/300 Contact Angle Analyzer with 1 drop of de-ionized water. Film thicknesses were determined by a KLA Tencor Alpha-Step D-100 stylus profiler. Electrochemistry measurements were carried out on a BAS electrochemical analyzer model 612C at 20 ^oC in a classical three-electrode cell. The working, reference, and auxiliary electrodes were an ITO electrode, $Ag/AgNO_3/CH_3CN/(nC_4H_9)_4NClO_4$, and a Pt wire, respectively. All potentials are referenced to the ferrocene/ferricinium (Fc/Fc^+) couple used as an internal standard. Atomic force microscope (AFM) images were taken by using a Seiko Instruments Nanocute.

Synthesis

P1: To an ampoule tube, 4-(4'-*N*,*N*-dihexylaminophenylethynyl)styrene (1.708 g, 4.409 mmol), a solution of 2,2'-azobis(isobutyronitrile) in benzene (0.11 M, 0.40 mL), and benzene (4.41 mL) were added. The tube was attached to a vacuum line, freeze pump thaw 10 times, sealed off, and then heated to 60 ^oC for 60 h. After cooling to room temperature, the mixture was poured into a large excess of methanol. The precipitate was dissolved in dichloromethane (20 mL) and poured into methanol again. The precipitate was collected as yellow solid (1.461 g, 85.5 %). ^1H NMR (300 MHz, $CDCl_3$, δ): 0.87 (br m, 6n H), 1.27 (m, 14n H), 1.52 (m, 5n H), 3.20 (br m, 4n H), 6.48 (br s, 4n H), 7.34 (br s, 4n H); IR (neat): ν = 2954, 2924, 2854, 2208, 2163, 1601, 1520, 1464, 1399, 1366, 1294,

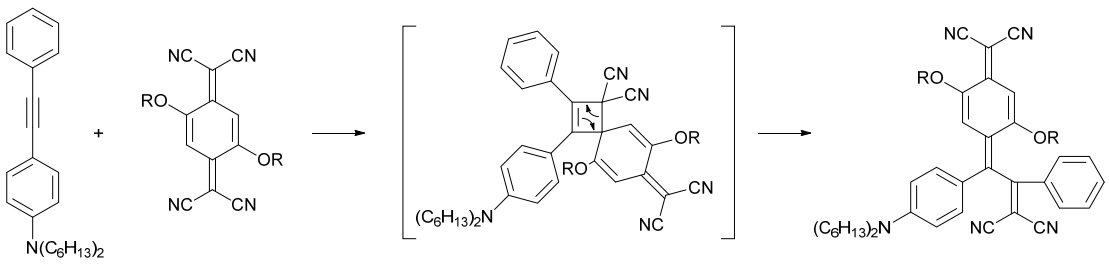
1276, 1254, 1227, 1195, 1135, 1106, 1017, 984, 934, 889, 828, 811, 757, 677, 664, 644, 629, 617, 604 cm^{-1}. (M_n (GPC, THF) 51000; M_w/M_n 2.45; $T_{d5\%}$ 385 ^oC).

Fabrication of Layer-by-Layer Films

Polymer solutions (10 mM repeat $unit^{-1}$) were prepared by dissolving polystyrene derivative (**P1**) into toluene and TCNQ polyester (**P2**) into THF. LbL assembly was performed by sequentially spin-coating **P1** and **P2** solutions on a cleaned ITO substrate at 1000 rpm for 60 s followed by heating to 100 ^oC for 10 min and washing with THF to remove unreacted polymers.

Ag^+ Ion Recognition

After the multilayer film (6 layers) was soaked into a 0.2 mM CF_3SO_3Ag solution in 1,2-dichloroethane for 1 min, it was thoroughly washed with 1,2-dichloroethane. The Ag^+ recognition was investigated by the UV-vis-near IR absorption spectra. Next, this film was soaked into triethylamine for 1 min and thoroughly washed with 1,2-dichloroethane. The Ag^+ release was investigated by the UV-vis-near IR absorption spectra. A series of the procedure was repeated 5 times.



Scheme S1. Reaction mechanism of the [2+2] CA–RE between *N*,*N*-dihexylaniline-substituted alkyne and 7,7,8,8-tetracyanoquinodimethane (TCNQ).

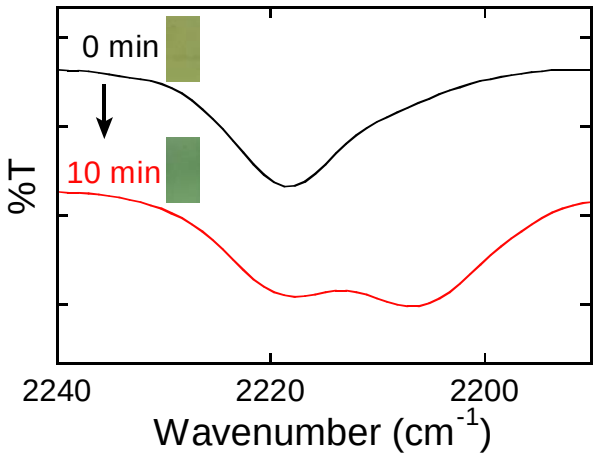


Figure S1. IR spectral change and images of the mixed film on the ITO substrate before and after heating at 100 °C for 10 min.

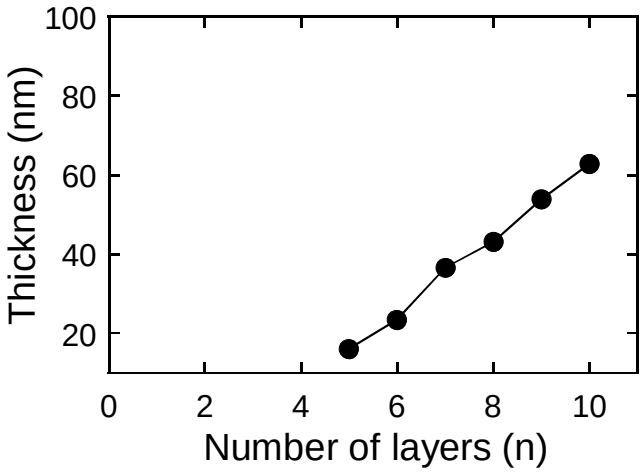


Figure S2. Plots of the thickness and layer number during the LbL assembling process of **P1** and **P2**. The thickness of <20 nm could not be reliably determined due to instrumental limitations.

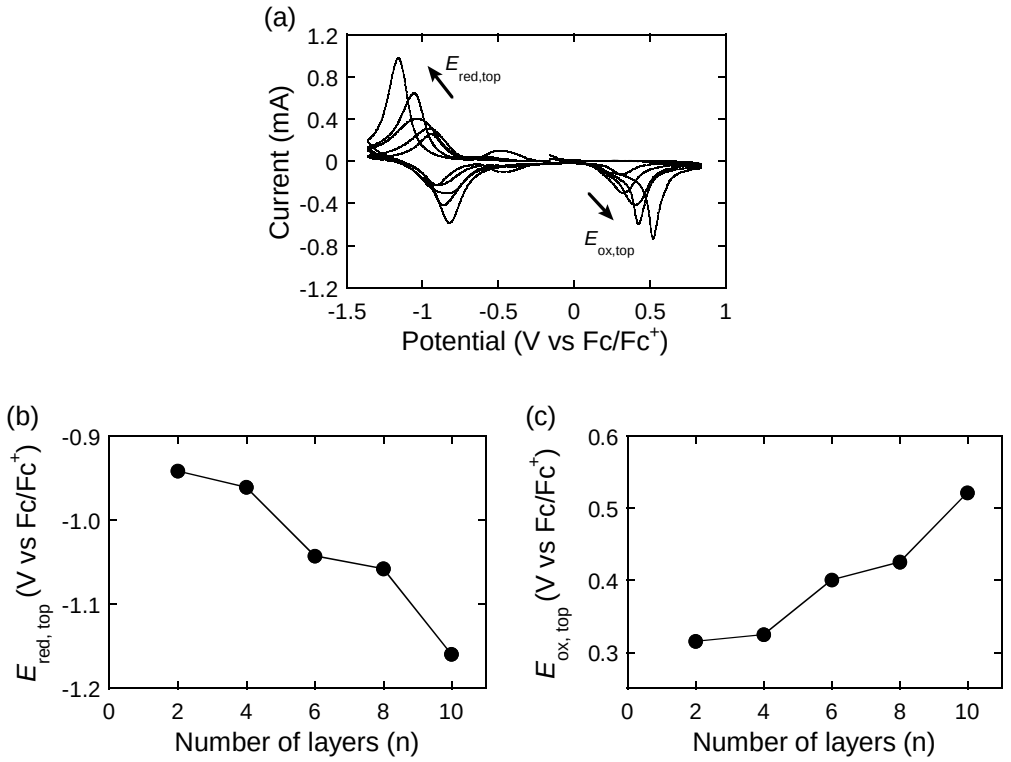


Figure S3. (a) CVs of multilayer films on an ITO electrode measured in CH_3CN with 0.1 M $(nC_4H_9)_4NClO_4$ at 20 ^oC and the scan rate of 0.1 Vs^{-1}, and the dependence of the layer number on (b) the $E_{red,top}$ and (c) $E_{ox,top}$ values.

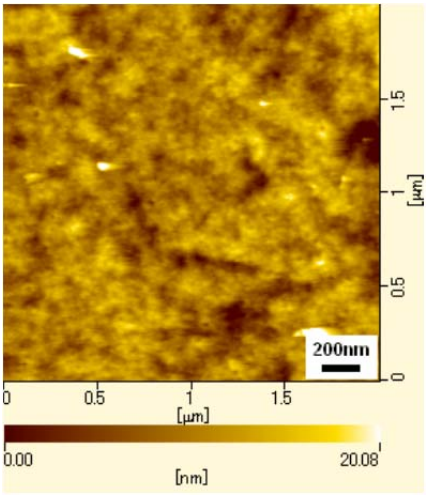


Figure S4. AFM (topo) image of 6 layer film.

References

1 Fujita, H.; Michinobu, T.; Tokita, M.; Ueda, M.; Higashihara, T. Synthesis and postfunctionalization of rod-coil diblock and coil-rod-coil triblock copolymers composed of poly(3-hexylthiophene)and poly(4-(4’‐*N*,*N*‐dihexylaminophenylethynyl)styrene) segments. *Macromolecules* **2012**, *45* (24), 9643-9656.

2 Washino, Y.; Murata, K.; Ashizawa, M.; Kawauchi, S.; Michinobu, T. Creation of persistent charge-transfer interactions in TCNQ polyester. *Polym. J.* **2011**, *43* (4), 364-369.