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Supplementary Information for

Cruciform *p-n* Diblock Conjugated Oligomers for Electroluminescent Applications

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Experiment Section.

Materials and instruments

Chemicals were reagent grades and purchased from Aldrich, Acros, and Lancaster Chemical Co. Toluene and tetrahydrofuran (THF) were distilled to keep anhydrous before use. The NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. Molecular masses were determined by laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MASS). UV-vis spectra were recorded on a Shimadzu 3150 PC spectrophotometer. The concentration of the oligomer solution was adjusted to ~0.001 mmol L^{-1}. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 °C min^{-1} under N_2. Elemental microanalyses were carried out on a Vario EL III CHNOS Elementar analyzer. Cyclic voltammetry (CV) was performed at a scanning rate of 200 mV s^{-1} on an AUTOLAB.PGSTAT30 potentiostat/galvanostat system (Ecochemie, Netherlands), which was equipped with a three-electrode cell. Pt wires were used as the counter electrode and the working electrode, and an Ag/Ag^+ was used as a reference electrode. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) was used as a supporting electrolyte. The reduction and oxidation behavior of the oligomers are measured in the solution of THF and CH_2Cl_2 (1×10^{-3} mol L^{-1}), respectively. According to de Leeuw et al., the ionization potential (E_{HOMO}) and electron affinity (E_{LUMO}) are approximately equal to the onset oxidation potential and the onset reduction potential (vs Ag/Ag^+) plus 4.7 eV, respectively.

Fluorescence quantum yields (Φ_f) of the oligomers in cyclohexane solution were measured by using 9,10-diphenylanthracene ($\Phi_f = 0.95$ in cyclohexane) as standards. Values are calculated according to Eq. 1, where Φ_{unk} is the fluorescence quantum yield of the sample, Φstd is the fluorescence quantum yield of the standard, I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, Aunk and Astd are the absorbance of the sample and the standard at the excitation wavelength, respectively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).

$$\Phi_{unk} = \Phi_{std} (I_{unk}/A_{unk}) (A_{std}/I_{std}) (\eta_{unk}/\eta_{std})^2 \qquad \text{Eq. 1}$$

Synthesis.

2,5-Dibromoterephthalic acid diethyl ester (2).
To a mixture of 2,5-dibromo-*p*-xylene (**1**) (13.2 g, 50 mmol), sodium hydroxide (18.0 g, 450 mmol) in water (350 mL), potassium permanganate (35.0 g, 222 mmol) was added, and the mixture was heated to reflux for 12 h. After cooling and precipitation, the filtrate was acidified with concentrated HCl to give crude 2,5-dibromo-terephthalic acid 4.8 g (25%). The crude product was dissolved in $SOCl_2$ (50 mL) and heated to reflux for 4 h. Most of $SOCl_2$ was removed at reduced pressure, and then absolute ethanol (50 mL) was put into the residue. The resulting mixture was heated to reflux for another 4 h. Finally, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane and ethyl acetate to afford **2** 2.1 g (80%) as a white solid. Mp: 126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.22 (2H, s, Ar-H), 4.44–4.36 (4H, q, CH_2), 1.43–1.37 (6H, t, CH_3).

2,5-Dibromoterephthaloyldihydrazides (3).
Hydrazine monohydrate (99%) (1.88 mL, 30 mmol) was added to a solution of ethyl-2,5-dibromoterephthalate (**2**) (1.9 g, 5 mmol) in methanol (50 mL), and then the mixture was refluxed overnight under a nitrogen atmosphere. After the reaction was completed, the product was poured into water and recrystallized from methanol to give **3** 1.67 g (95%) as a white solid. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 9.69 (2H, s, NH), 7.58 (2H, s, Ar-H),4.51 (4H, s, NH_2).

Compound 4.
4-tert-butylbenzoyl (0.59 g, 3.02 mmol) chloride was added into a solution containing 2,5-Dibromoterephthaloyldihydrazides (3) (0.53 g, 1.51 mmol) in pyridine (10 mL). The reaction mixture was stirred for 12 h and then poured into water. The product was filtered and crystallized from methanol to give 4 0.74 g (73%) as a white solid. ^{1}H NMR (DMSO-d_6, 400MHz, ppm): 10.74 (2H, d, NH), 10.63 (2H, d, NH), 7.93 (4H, d, Ar-H), 7.79 (2H, s, Ar-H), 7.58 (4H, d, Ar-H), 1.38 (18H, s, CH_3).

2-(4-Tert-butylphenyl)-5-(2,5-dibromo-4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)phenyl)-1,3,4-oxadiazole (5).
4 (0.8 g, 1.02 mmol) was dissolved in $POCl_3$ (20 mL). The reaction mixture was heated to 90 ^{o}C overnight and then cooled to room temperature. Most $POCl_3$ in reaction mixture was removed at reduced pressure and the resulting precipitates were poured into water. The product was filtered and crystallized from methanol and chloroform several times to give **5** 0.53 g (70%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.52 (2H, s, Ar-H), 8.11 (4H, d, Ar-H), 7.57 (4H, d, Ar-H), 1.38 (18H, t, CH_3). ^{13}C NMR ($CDCl_3$, 400 MHz, ppm): 166.03, 161.65, 156.33, 137.01, 128.64, 127.34, 126.47, 120.68, 120.13, 35.41, 31.32.

2-(4-Tert-butylphenyl)-5-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)-2,5-bis(9,9-didodecyl-9H-fluoren-2-yl)phenyl)-1,3,4-oxadiazole (Oligomer 1).
A mixture of 9,9-didodecyl-9H-fluoren-2-ylboronic acid (1.09 g, 2 mmol), oxadiazole monomer (**5**) (0.636 g, 1 mmol) and tetrakis(triphenylphosphine)palladium (1.0 mol%) was added in a degassed mixture of toluene ([monomer] = 0.2 M) and 2 M aqueous potassium carbonate (3:2 in volume). The mixture was vigorously stirred and reacted at 85-90 ^{o}C for two days. After the mixture was cooled to room temperature, methylene chloride was added. The organic layer was separated and washed with brine for drying over $MgSO_4$. Upon evaporating off the solvent in the reduced pressure, the residue was purified with column chromatography on silica gel with acetic ester /methylene chloride to yield oligomer **1** 1.08 g (73%) as white solids. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.39 (2H, s, Ar-H), 7.7-7.8 (4H, t, Ar-H), 7.4-7.5 (4H, d, Ar-H), 7.34-7.4 (10H, m, Ar-H), 7.2 (2H, d, Ar-H), 1.8-2.0 (8H, m, CH_2), 0.6-1.4 (92H, m, CH_2, CH_3). Anal. Calcd for $C_{104}H_{142}N_4O_2$: C, 84.38; H, 9.67; N, 3.78; O, 2.16. Found: C, 83.95; H, 9.76; N, 3.98; O, 2.31. MASS (MALDI-TOF): 1481.4 (M^+ +1, 100%).

2-(4-Tert-butylphenyl)-5-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)-2,5-bis(7-(9,9-didodecyl-9H-fluoren-2-yl)-9,9-didodecyl-9H-fluoren-2-yl)phenyl)-1,3,4-oxadiazole (Oligomer 2).
The procedure for oligomer **1** was followed to prepare oligomer **2** as pale yellow solids (67%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.42 (2H, s, Ar-H), 7.77-7.85 (16H, m, Ar-H), 7.6 (4H, d, Ar-H), 7.3-7.4 (10H, m, Ar-H), 7.2 (4H, d, Ar-H), 1.8-2.0 (16H, m, CH_2), 0.6-1.4 (184H, m, CH_2, CH_3). Anal. Calcd for $C_{178}H_{254}N_4O_2$: C, 86.14; H, 10.32; N, 2.26; O, 1.29. Found: C, 85.73; H, 10.46; N, 2.44; O, 1.37. MASS (MALDI-TOF): 2481.7 (M^+, 100%).

2-(4-Tert-butylphenyl)-5-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)-2,5-bis(7-(7-(9,9-didodecyl-9H-fluoren-2-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9,9-didodecyl-9H-fluoren-2-yl)phenyl)-1,3,4-oxadiazole (Oligomer 3).
The procedure for oligomer **1** was followed to prepare oligomer **3** as pale yellow solids (61%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.43 (2H, s, Ar-H), 7.62-7.84 (28H, m, Ar-H), 7.54 (4H, d, Ar-H), 7.26-7.42 (10H, m, Ar-H), 7.2 (4H, d, Ar-H), 1.8-2.0 (24H, m, CH_2), 0.6-1.4 (276H, m, CH_2, CH_3). Anal. Calcd for $C_{252}H_{366}N_4O_2$: C, 86.88; H, 10.59; N, 1.61; O, 0.92. Found: C, 86.41; H, 10.72; N, 1.83; O, 1.04. MASS (MALDI-TOF): 3482.3 (M^+, 100%).

The ^{1}H NMR spectra is depicted in Figure S1. Among them, the spectrum of oligomer **1** displays the simplest resonance pattern for the aromatic protons. The peaks at 7.2 (doublet), 7.6 (doublet), and 8.42 (singlet) can be assigned to the protons e, c, and a of the oxadiazole segment, while peaks at 7.3-7.4 and 7.77-7.85 (protons b and d) are attributed to the protons of the fluorene unit. The spectra of oligomers **2** and **3** exhibited very similar patterns, but the peaks of protons b and d display a complicated mode due to the longer fluorene branch.

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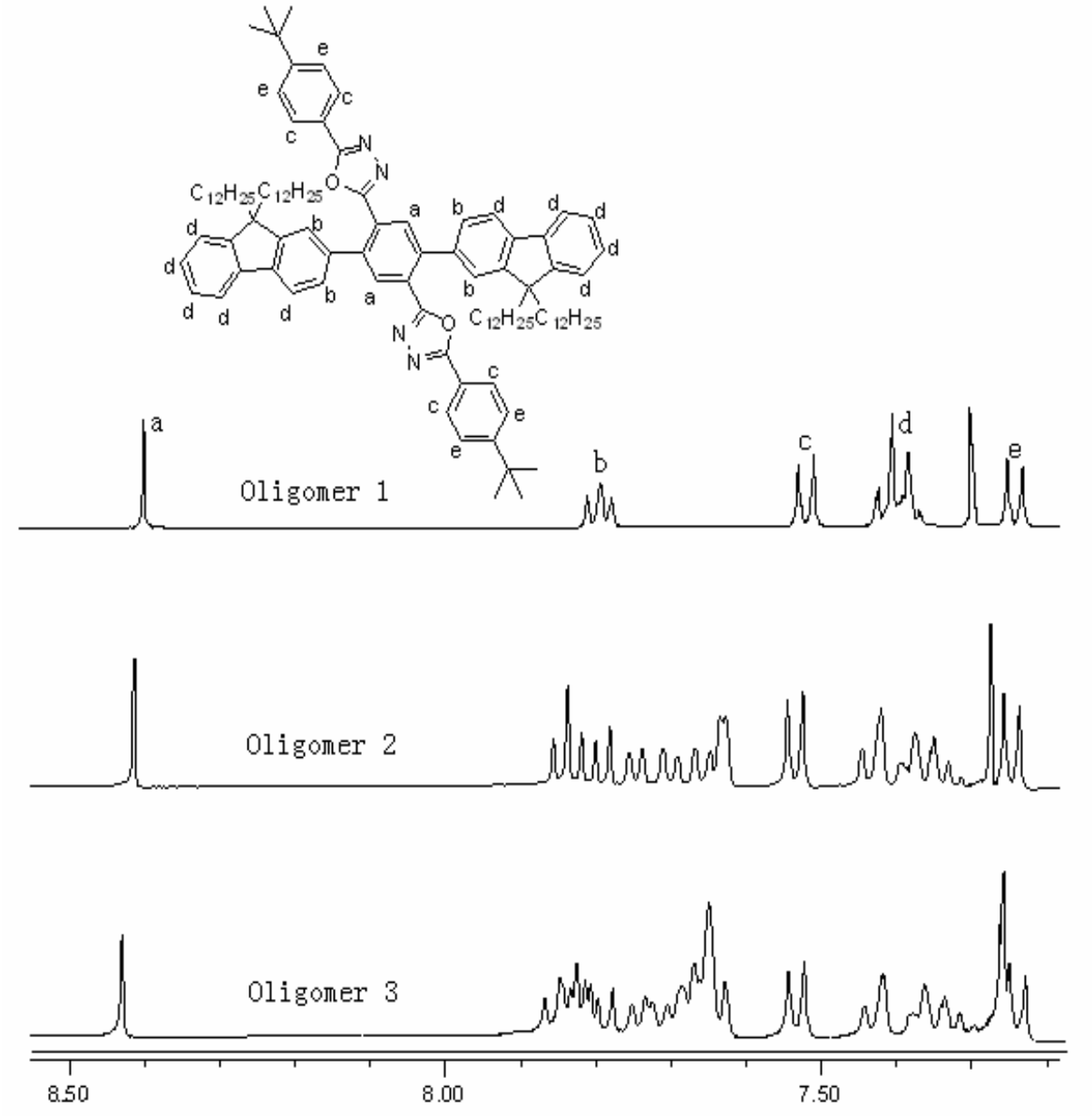

Fig. S1 ^{1}H NMR spectra of the oligomers in $CDCl_3$