Electronic Supplementary Information

Controlling AIE and ACQ properties of conjugated carbazole-tetraphenylethene copolymers by ethynylene spacer

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1. Materials

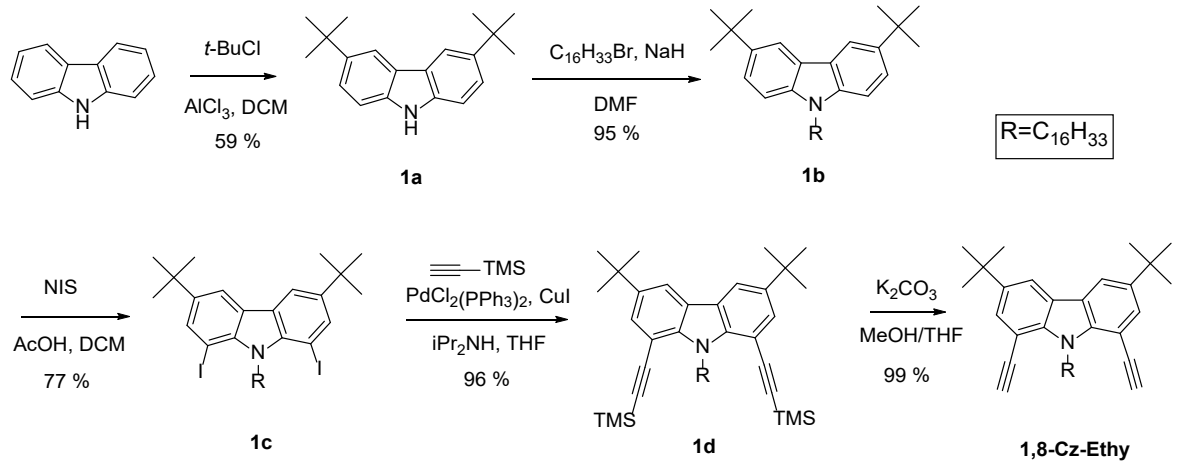
Chemicals were used as received unless otherwise indicated. Carbazole, sodium hydride (60%, dispersion in paraffin liquid), *N*-bromosuccinimide, zinc powder, bis(pinacolato)diboron, bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$), isopropylamine, and sodium *tert*-butoxide were purchased from Tokyo Chemical Industry Co., Ltd. 2-Chloro-2-methylpropane, magnesium sulfate (anhydrous), sodium chloride (NaCl), hydrochloric acid (HCl), sodium hydrogen carbonate, potassium carbonate, dichloromethane (DCM), hexane, acetic acid, ethyl acetate, methanol, toluene, chloroform, 1,4-dioxane, and dimethylformamide (DMF) were purchased from Kanto Chemical Co., Ltd. Aluminum(III) chloride, titanium(IV) chloride, and tetrahydrofuran were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. 1-Bromohexadecane, 4-bromobenzophenone, tris(dibenzylideneacetone)dipalladium(0), and triphenylphosphine were purchased from Sigma-Aldrich.

2. Synthesis

2.1 Monomer synthesis

2.1.1 Synthesis of 1,8-Cz-Ethy

The Cz-Ethy monomers were synthesized as reported literature.[S1,S2]



Scheme S1. Synthesis of 1,8-Cz-Ethy.

3,6-Di-*tert*-butyl-9*H*-carbazole (1a). Carbazole (1.0 g, 6.0 mmol) and aluminum(III) chloride (0.80 g, 6.0 mmol) were dissolved in 20 mL of DCM in an ice bath with argon protection for 1 hour. 2-Chloro-2-methylpropane (1.16 g, 1.25 mmol) in DCM (4 mL) was then added to the mixture, and the solution was stirred at room temperature for 16 h. The reaction was quenched by dropping HCl solution, and the organic phase was extracted with DCM and washed by saturated NaCl aqueous solution. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator and the crude product was purified by recrystallization using hexane, yielding 0.99 g (3.5 mmol, 59 %) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.08 (s, 2H), 7.86 (s, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 1.25 (s, 18H).

3,6-Di-*tert*-butyl-9-hexadecyl-9*H*-carbazole (1b). 1a (0.95 g, 3.4 mmol) and sodium hydride (0.20 g, 5.1 mmol) were dissolved in 12 mL of DMF via stirring at room temperature for 30 mins. 1-Bromohexadecane (1.56 g, 5.10 mmol) was then added and the mixture was stirred overnight at room temperature. After water was added, the organic phase was extracted with DCM and washed by saturated NaCl aqueous solution. After drying over anhydrous sodium sulfate, the solution was concentrated by an evaporator and was purified by silica gel column chromatography (hexane/DCM = 10/1), yielding 1.62 g (3.23 mmol, 95 %) of the target compound as clear colorless liquid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.10 (s, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.23 (t, J = 7.3 Hz, 2H), 1.84 (t, J = 8.1 Hz, 2H), 1.46 (s, 18H), 1.25 (s, 26H), 0.88 (t, J = 6.2 Hz, 3H).

3,6-Di-*tert*-butyl-9-hexadecyl-1,8-diiodo-9*H*-carbazole (1c). 1b (1.60 g, 3.18 mmol), *N*-iodosuccinimide (1.67 g, 7.43 mmol), 5 mL of DCM and 5 mL of acetic acid were mixed via stirring overnight at room temperature. After the addition of sodium thiosulfate and stirring for 15 mins, DCM

was added. The organic phase was washed by sodium bicarbonate and saturated NaCl aqueous solutions. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator and the crude product was purified by silica gel column chromatography (hexane), yielding 1.80 g (2.38 mmol, 77 %) of the target compound as clear colorless liquid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.99 (s, 2H), 7.97 (s, 2H), 5.07 (t, *J* = 8.1 Hz, 2H), 1.64 (t, *J* = 1.8 Hz, 2H), 1.41 (s, 18H), 1.25 (s, 26H), 0.88 (t, *J* = 6.8 Hz, 3H).

3,6-Di-*tert*-butyl-9-hexadecyl-1,8-bis((trimethylsilyl)ethynyl)-9*H*-carbazole (1d). 1c (1.80 g, 2.38 mmol) and copper(I) iodide (22 mg, 0.12 mmol) were mixed in diisopropylamine (8 mL) and THF (8 mL) under Ar. The mixture was then ultra-sonicated for 30 mins. After $PdCl_2(PPh_3)_2$ (0.064 g, 0.12 mmol) and trimethylsilylacetylene (1.4 g, 14 mmol) were added, the mixture was stirred at room temperature for 16 h. The solvent was removed by an evaporator. The organic phase was extracted with DCM and washed by a saturated NaCl aqueous solution. After drying over anhydrous sodium sulfate, the solution was concentrated by an evaporator and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 30/1), yielding 1.58 g (2.27 mmol, 96 %) of the target compound as clear yellow liquid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.04 (s, 2H), 7.61 (s, 2H), 5.31 (t, *J* = 7.7 Hz, 2H), 1.79 (t, *J* = 5.3 Hz, 2H), 1.43 (s, 18H), 1.25 (s, 26H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.32 (s, 18H).

3,6-Di-*tert*-butyl-1,8-diethynyl-9-hexadecyl-9*H*-carbazole (1,8-Cz-Ethy). 1d (1.58 g, 2.27 mmol) and potassium carbonate (0.63 g, 4.6 mmol) were mixed in THF (30 mL) and methanol (30 mL) and it was stirred at room temperature for 2 h. The organic phase was extracted with DCM and washed by pure water. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator

and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate= 30/1), yielding 1.24 g (2.29 mmol, 99 %) of the target compound as a yellow solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.07 (s, 2H), 7.66 (s, 2H), 5.19 (t, J = 8.2 Hz, 2H), 3.36 (s, 2H), 1.93 (t, J = 7.1 Hz, 2H), 1.43 (s, 18H), 1.25 (s, 26H), 0.88 (t, J = 7.1 Hz, 3H).

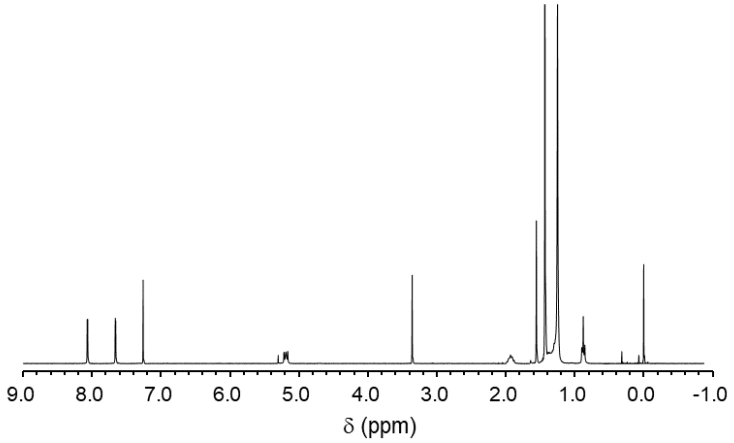
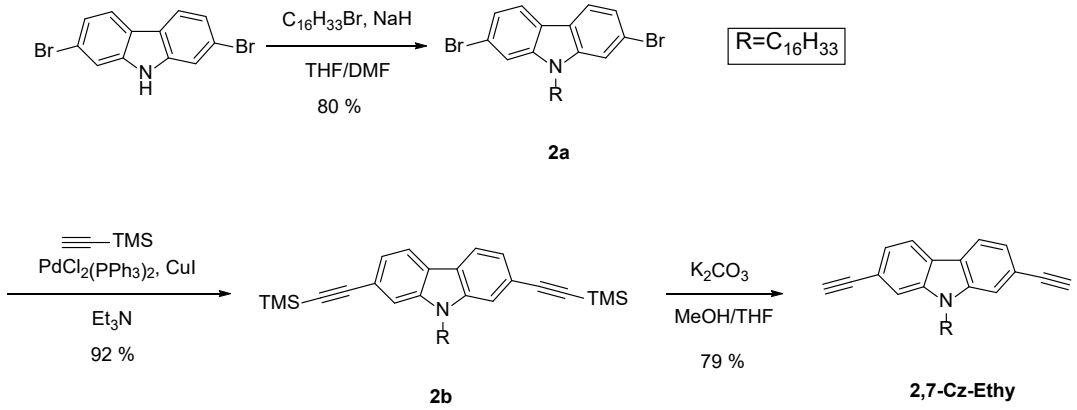


Fig. S1. ^{1}H-NMR spectrum of 1,8-Cz-Ethy in $CDCl_3$.

2.1.2 Synthesis of 2,7-Cz-Ethy[S1]



Scheme S2. Synthesis of 2,7-Cz-Ethy.

2,7-Dibromo-9-hexadecyl-9*H*-carbazole (2a). 2,7-Dibromo-9*H*-carbazole (0.5 g, 1.5 mmol) and sodium hydride (0.055 g, 2.3 mmol) were mixed in THF (4 mL) and DMF (2 mL) and it was stirred at room temperature for 30 mins. 1-Bromohexadecane (0.71 g, 2.3 mmol) was then added and the mixture was stirred at room temperature for 4 h. Water was added dropwise until no bubbles were generated, and the organic phase was extracted with DCM and washed by water. After drying over

anhydrous sodium sulfate, the solution was concentrated by an evaporator and the crude product was purified by recrystallization from hexane and silica gel column chromatography (hexane), yielding 0.67 g (1.2 mmol, 80%) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.89 (d, *J* = 8.1 Hz, 2H), 7.53 (s, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 1.84 (t, *J* = 6.8 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.8 Hz, 3H).

9-Hexadecyl-2,7-bis((trimethylsilyl)ethynyl)-9*H*-carbazole (2b). 2a (0.55 g, 1.0 mmol) and copper(I) iodide (10 mg, 0.05 mmol) were added to triethylamine (10 mL) and the mixture was ultra-sonicated for 30 mins under Ar. After $PdCl_2(PPh_3)_2$ (0.056 g, 0.08 mmol) and trimethylsilylacetylene (0.39 g, 4.0 mmol) were added, the mixture was stirred at 70 ℃ for 16 h. The mixture was then cooled to room temperature, and the insoluble fraction was filtered off. The organic phase was extracted with DCM and washed by brine. After drying over anhydrous sodium sulfate, the solution was concentrated by an evaporator and the crude product was purified by silica gel column chromatography (hexane), yielding 0.54 g (0.92 mmol, 92 %) of the target compound as the orange solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.96 (d, *J* = 7.7 Hz, 2H), 7.50 (s, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 4.23 (t, *J* = 7.3 Hz, 2H), 1.84 (t, *J* = 6.8 Hz, 2H), 1.25 (s, 26H), 0.87 (t, *J* = 6.2 Hz, 3H), 0.29 (s, 18H).

2,7-Diethynyl-9-hexadecyl-9*H*-carbazole (2,7-Cz-Ethy). 2b (0.50 g, 0.80 mmol) and potassium carbonate (0.21 g, 1.6 mmol) were added to THF (15 mL) and methanol (15 mL), are the mixture was stirred at room temperature for 2 h. The organic phase was extracted with DCM and washed by water. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator and the crude product was purified by silica gel column chromatography (hexane/DCM = 1/5), yielding 0.28 g (0.63 mmol, 79 %) of the target compound as the orange solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.22 (s, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.27 (t, *J* = 7.0 Hz, 2H), 3.08 (s, 2H), 1.85 (t, *J* = 7.0 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.6 Hz, 3H).

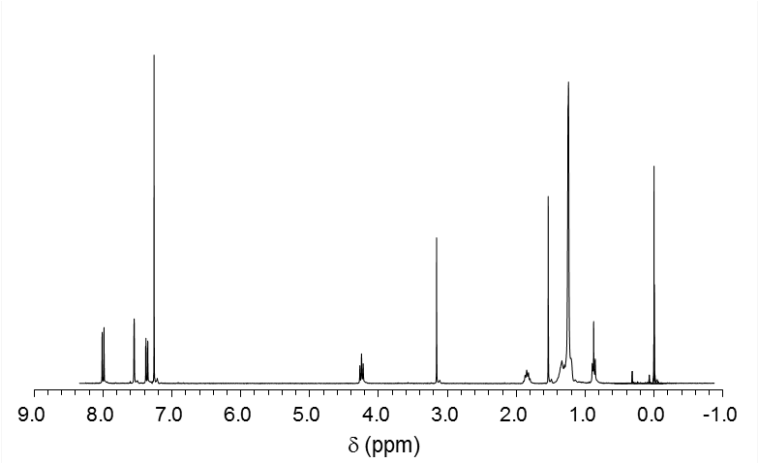
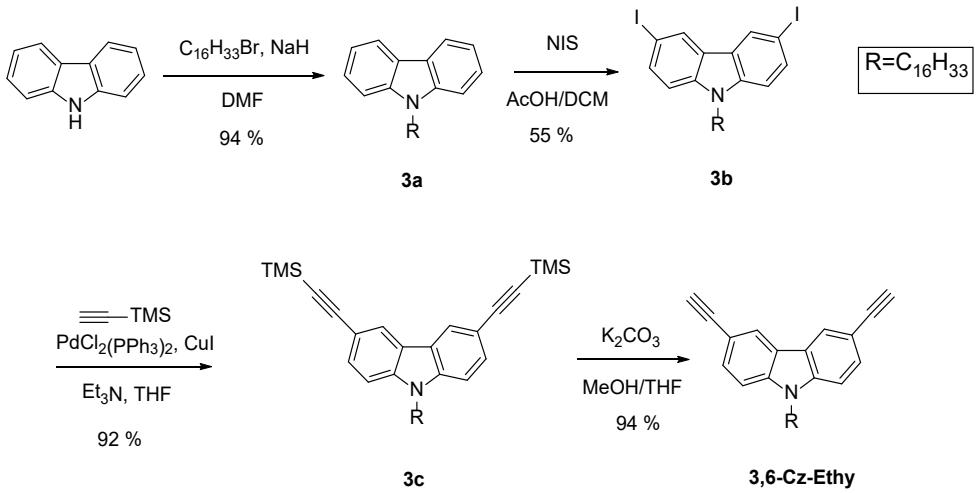


Fig. S2. ^{1}H-NMR spectrum of 2,7-Cz-Ethy in $CDCl_3$.

2.1.3 Synthesis of 3,6-Cz-Ethy[S1]



Scheme S3. Synthesis of 3,6-Cz-Ethy.

9-Hexadecyl-9*H*-carbazole (3a). Carbazole (2.0 g, 12 mmol) and sodium hydride (0.72 g, 18 mmol) were added to DMF (24 mL) and the mixture was stirred at room temperature for 30 mins. 1-Bromohexadecane (1.56 g, 5.10 mmol) was then added and the mixture was stirred at room temperature overnight. Water was added, and the organic phase was extracted with DCM and washed by brine. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator and

the crude product was purified by silica gel column chromatography (hexane/DCM = 1/4), yielding 4.44 g (11.3 mmol, 94 %) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.10 (d, *J* = 7.0 Hz, 2H), 7.49-7.39 (m, 4H), 7.21 (d, *J* = 7.0 Hz, 2H), 4.29 (t, *J* = 7.1 Hz, 2H), 1.87 (t, *J* = 7.3 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.4 Hz, 3H).

9-Hexadecyl-3,6-diiodo-9*H*-carbazole (3b). 3a (1.5 g, 3.80 mmol) and *N*-iodosuccinimide (1.8 g, 7.9 mmol) were added to DCM (30 mL) and acetic acid (18 mL), and the mixture was stirred at room temperature overnight. After sodium thiosulfate was added, the mixture was stirred for 15 mins. DCM was added and the organic phase was washed by sodium bicarbonate solution and brine. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator and the crude product was purified by recrystallization, yielding 1.35 g (2.10 mmol, 55 %) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.33 (d, *J* = 1.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 4H), 7.17 (d, *J* = 8.8 Hz, 2H), 4.22 (t, *J* = 7.1 Hz, 2H), 1.81 (t, *J* = 7.0 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.6 Hz, 3H).

9-Hexadecyl-3,6-bis((trimethylsilyl)ethynyl)-9*H*-carbazole (3c). 3b (0.64 g, 1.0 mmol) and copper(I) iodide (10 mg, 0.050 mmol) were added to triethylamine (10 mL) and THF (3 mL) under Ar. The mixture was then ultra-sonicated for 30 mins. After $PdCl_2(PPh_3)_2$ (0.056 g, 0.080 mmol) and trimethylsilylacetylene (0.39 g, 4.0 mmol) were added, the mixture was stirred at room temperature for 16 h. After the insoluble fraction was filtered off, the filtrate was concentrated by an evaporator and the organic phase was extracted with DCM and washed by brine. After drying over anhydrous sodium sulfate, the solution was concentrated by an evaporator and the crude product was purified by silica gel column chromatography (hexane/DCM= 1/4), yielding 0.54 g (0.92 mmol, 92 %) of the target compound as clear orange liquid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.19 (s, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 9.9 Hz, 2H), 4.25 (t, *J* = 7.1 Hz, 2H), 1.83 (t, *J* = 6.6 Hz, 2H), 1.26 (s, 26H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.28 (s, 18H).

3,6-Diethynyl-9-hexadecyl-9*H*-carbazole (3,6-Cz-Ethy). 3c (0.50 g, 0.86 mmol) and potassium carbonate (0.23 g, 1.7 mmol) were added to THF (15 mL) and methanol (15 mL) and the mixture was stirred at room temperature for 2 h. The organic phase was extracted with DCM and washed by pure water. After drying over anhydrous sodium sulfate, the solvent was removed by an evaporator and the crude product was purified by silica gel column chromatography (hexane/DCM= 1/4), yielding 0.36 g (0.81 mmol, 94 %) of the target compound as the orange solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.22 (s, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.27 (t, *J* = 7.0 Hz, 2H), 3.08 (s, 2H), 1.85 (t, *J* = 7.0 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.6 Hz, 3H).

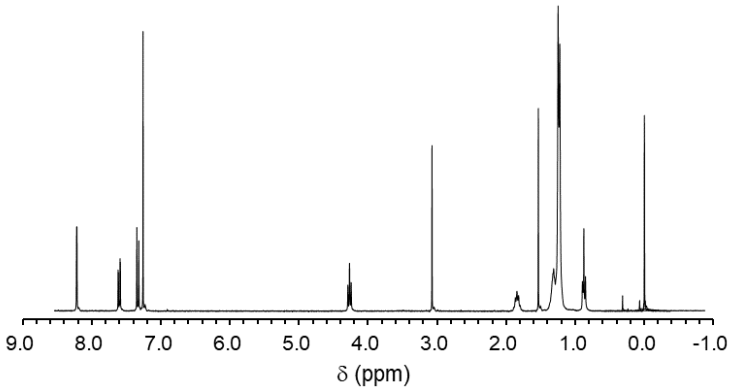
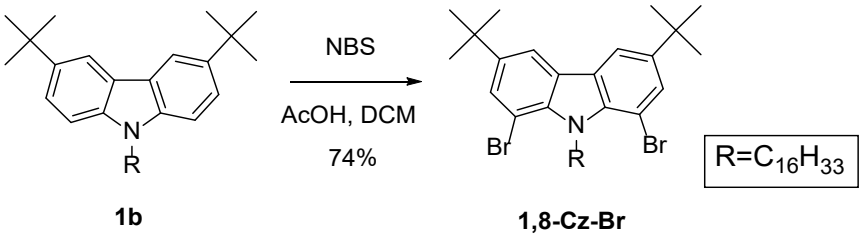


Fig. S3. ^{1}H-NMR spectrum of 3,6-Cz-Ethy in $CDCl_3$.

2.1.4 Synthesis of 1,8-Cz-Br[S1]



Scheme S4. Synthesis of 1,8-Cz-Br.

1b (0.93g, 1.85 mmol) and *N*-bromosuccinimide (0.84 g, 4.72 mmol) were added to DCM (20 mL) and acetic acid (10 mL) and the mixture was stirred at room temperature overnight. The organic phase was extracted with DCM and was washed by sodium carbonate and sodium hydroxide solutions. After drying over anhydrous magnesium sulfate, the solvent was removed by an evaporator and the crude product was purified by silica gel column chromatography (hexane), yielding 0.90 g (1.36 mmol, 74%) of the target compound as colorless liquid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.95 (s, 2H), 7.63 (s, 2H), 5.08 (t, *J* = 6.8 Hz, 2H), 1.77 (t, *J* = 6.8 Hz, 2H), 1.41 (s, 18H), 1.23 (s, 26H), 0.86 (t, *J* = 6.2Hz, 3H).

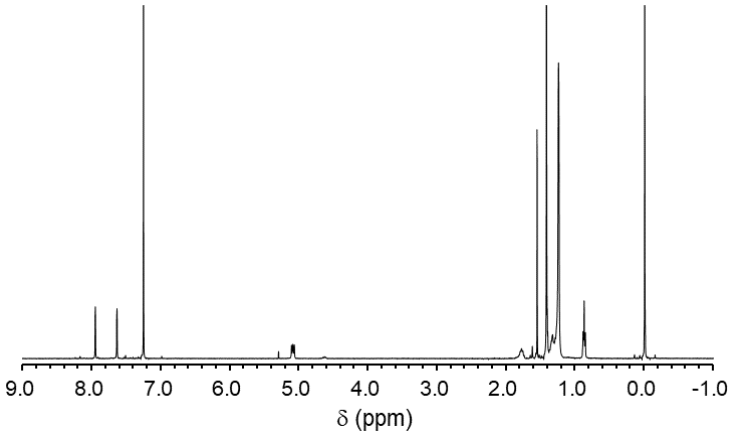
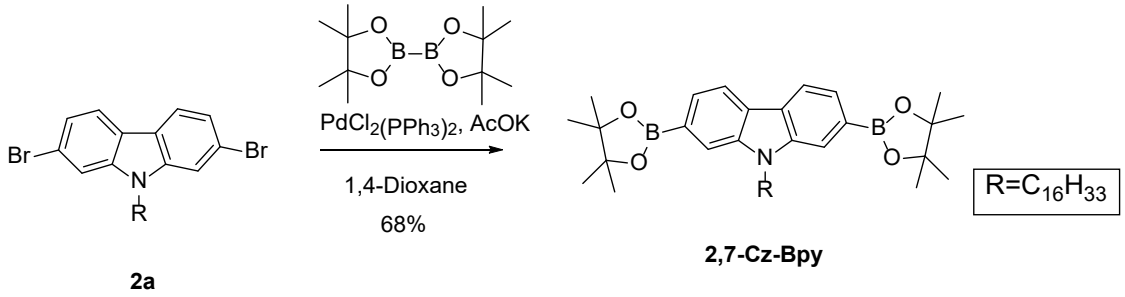


Fig. S4. ^{1}H-NMR spectrum of 1,8-Cz-Br in $CDCl_3$.

2.1.5 Synthesis of 2,7-Cz-Bpy[S3]



Scheme S5. Synthesis of 2,7-Cz-Bpy.

2a (0.55 g, 1.0 mmol), 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,3,2-dioxaborolane (0.56 g, 2.2 mmol), potassium acetate (0.58 g, 6.0 mmol), and $PdCl_2(PPh_3)_2$ (0.056 g,

0.08 mmol) were added to 1,4-dioxane (7 mL) and the mixture was refluxed at 90 ℃ under Ar for 12 h. The mixture was cooled to room temperature, and the organic phase was extracted with DCM and washed by a saturated NaCl aqueous solution. After drying over anhydrous magnesium sulfate, the solvent was removed by an evaporator and the crude product was purified by silica gel column chromatography (DCM), yielding 0.44 g (0.68 mmol, 68%) of the target compound as the yellow solid. ^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.12 (d, J = 7.3 Hz, 2H), 7.88 (s, 2H), 7.68 (d, J = 7.3 Hz, 2H), 4.37 (t, J = 6.2 Hz, 2H), 1.88 (t, J = 7.0 Hz, 2H), 1.40 (s, 24H), 1.25 (s, 26H), 0.87 (t, J = 6.8 Hz, 3H).

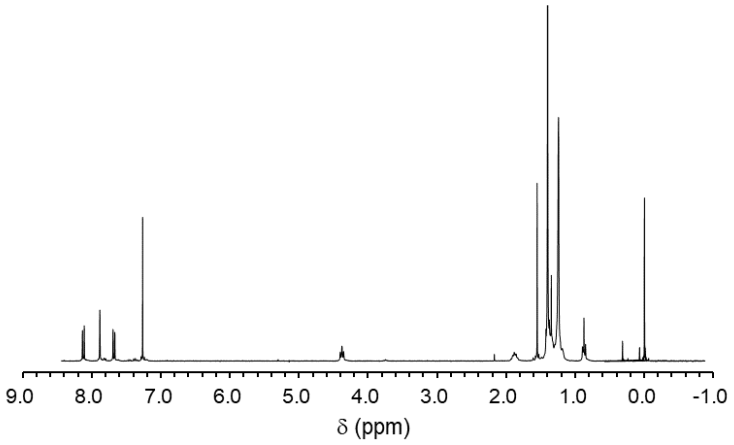
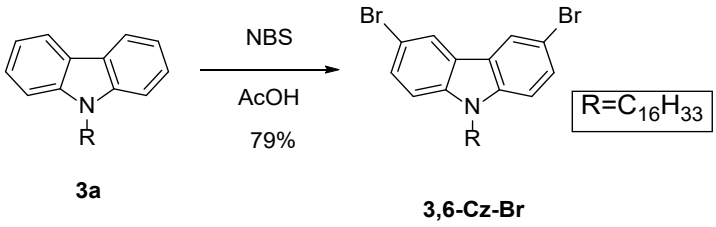


Fig. S5. ^{1}H-NMR spectrum of 2,7-Cz-Bpy in $CDCl_3$.

2.1.6 Synthesis of 3,6-Cz-Br[S4]



Scheme S6. Synthesis of 3,6-Cz-Br.

9-Hexadecylcarbazole (0.25 g, 0.64 mmol) and *N*-bromosuccinimide (0.27 g, 1.56 mmol) were added to acetic acid (18 mL) and the mixture was stirred at room temperature overnight. The organic phase was extracted with ethyl acetate and washed by sodium hydrogen carbonate and sodium hydroxide solutions. After drying over anhydrous magnesium sulfate, the solvent was removed by an evaporator,

and the crude product was purified by silica gel column chromatography (hexane), yielding 0.28 g (0.50 mmol, 79%) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.15 (s, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 7.5 Hz, 2H), 4.25 (t, J = 6.9 Hz, 2H), 1.83 (t, J = 6.9 Hz, 2H), 1.25 (s, 26H), 0.88 (t, J = 6.6 Hz, 3H).

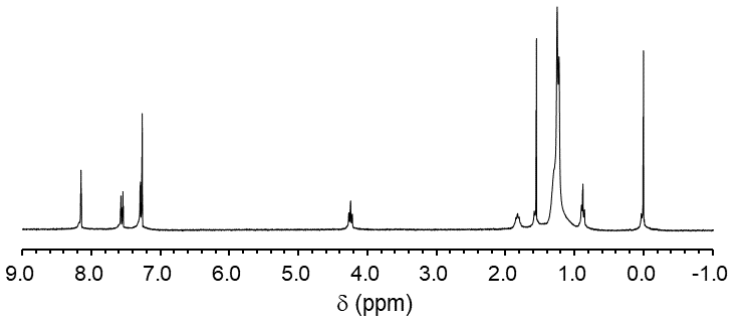
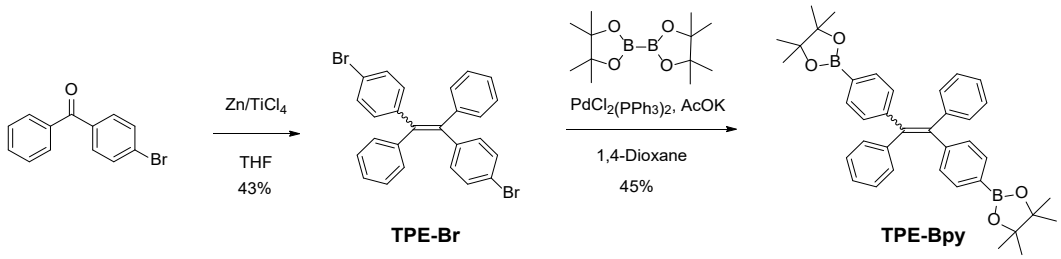


Fig. S6. ^{1}H-NMR spectrum of 3,6-Cz-Br in $CDCl_3$.

2.1.7 Synthesis of TPE-Bpy [S5]



Scheme S7. Synthesis of TPE-Bpy.

Synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (TPE-Br). Zinc powder (2.5 g, 38 mmol) was added to THF (48 mL) under Ar. Titanium(IV) chloride (6.9 g, 36 mmol) was slowly added in an ice bath, and the mixture was refluxed at 90 ℃ for 4 h. After bromobenzophenone (2.0 g, 7.7 mmol) in THF (4 mL) was slowly added at room temperature, the mixture was refluxed at 90 ℃ overnight. After cooling to room temperature, sodium bicarbonate solution was added until no bubbles were generated. DCM was then added and the mixture was stirred for 5 h. After filtration of celite, the organic phase was extracted with DCM and washed by brine. The solvent was removed by an

evaporator and the crude product was purified by silica gel column chromatography (hexane/DCM= 1/5) and recrystallized from toluene/ethanol=2/3, yielding 0.80 g (16 mmol, 43 %) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.25-7.21 (m, 4H), 7.12-7.10 (m, 6H), 7.00-6.97 (m, 4H), 6.89-6.86 (m, 4H).

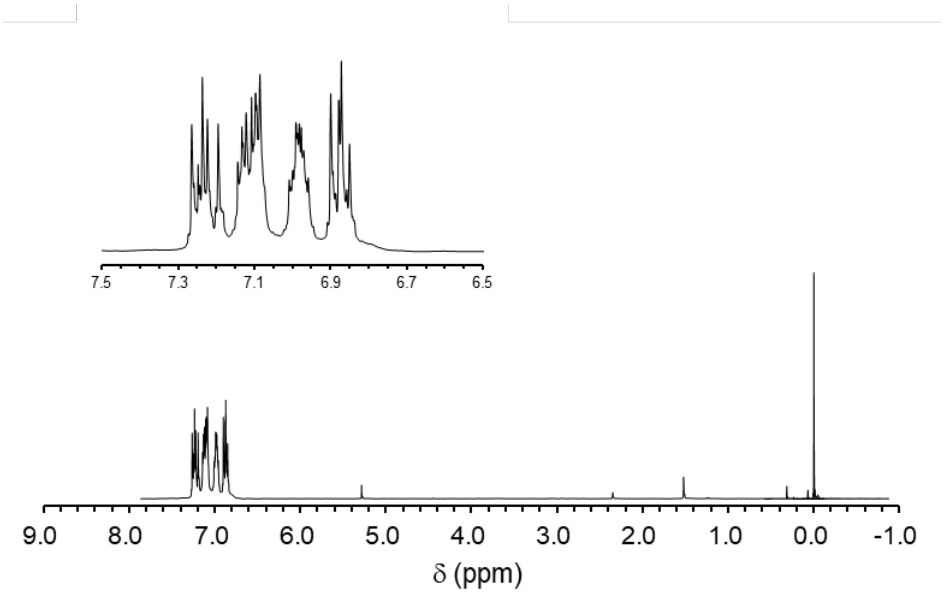


Fig. S7. ^{1}H-NMR spectrum of **TPE-Br** in $CDCl_3$.

Synthesis of 1,2-diphenyl-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (TPE-Bpy). TPE-Br (0.60 g, 1.22 mmol), 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,3,2-dioxaborolane (0.68 g, 2.78 mmol), potassium acetate (0.72 g, 7.32 mmol), and $PdCl_2(PPh_3)_2$ (0.051 g, 0.073 mmol) were added to 1,4-dioxane (24 mL) and the mixture was refluxed overnight under Ar. After cooling to room temperature, the insoluble fraction was filtered off. The filtrate was concentrated by an evaporator. The organic phase was extracted with DCM and washed by brine. After drying over anhydrous magnesium sulfate, the solvent was removed by an evaporator and the crude product was purified by silica gel column chromatography (chloroform). Recrystallization from acetone/ethanol yielded 0.32 g (0.55 mmol, 45 %) of the target compound as the white solid.

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.55-7.52 (m, 4H), 7.12-7.10 (m, 6H), 7.00-6.97 (m, 4H), 6.89-6.86 (m, 4H).

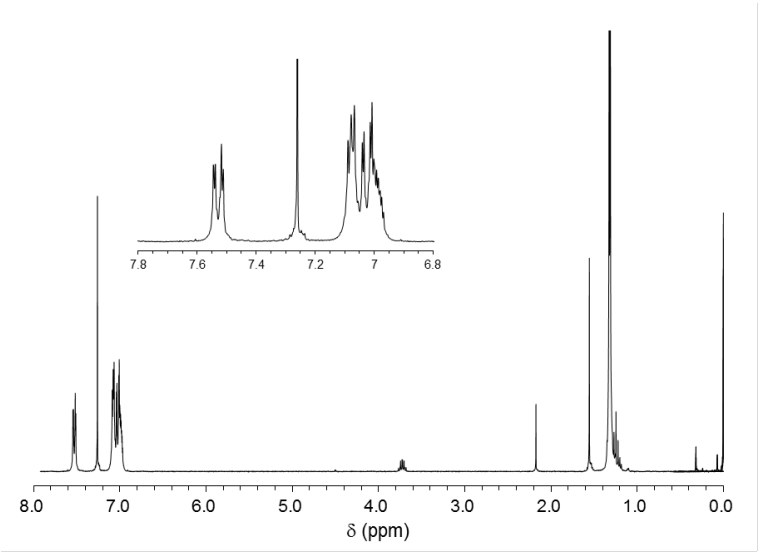
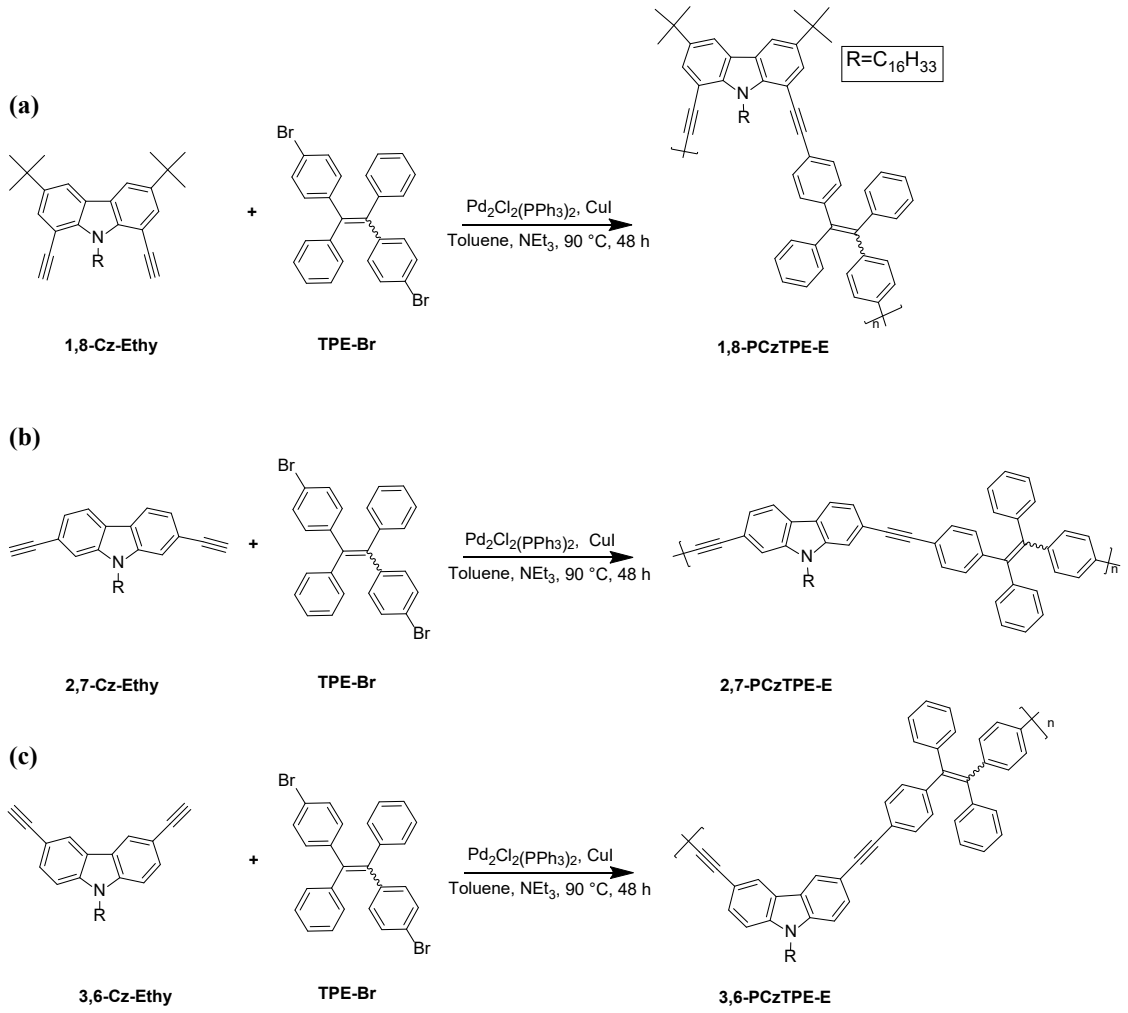


Fig. S8. ^{1}H-NMR spectrum of **TPE-Bpy** in $CDCl_3$.

2.2 Polymer synthesis

PCzTPE-E polymers were synthesized by the modified conditions of Sonogashira polycondensation.[S6]



Scheme S8. Synthesis of (a) 1,8-PCzTPE-E, (b) 2,7-PCzTPE-E, and (c) 3,6-PCzTPE-E.

To synthesize PCzTPE-E polymers, 0.20 mmol of Cz-Ethy monomer, 0.20 mmol of TPE-Br, 0.01 mmol of copper iodide, and 0.01 mmol of $PdCl_2(PPh_3)_2$ were dissolved in triethylamine (1 mL) and toluene (3 mL) under Ar. The mixture was then refluxed at 90 ℃ for 48 h. After cooling to room temperature, methanol (100 mL) was added and the mixture was stirred for 30 mins. The precipitates were collected by vacuum suction filtration. They were subjected to Soxhlet washing with methanol to remove the low molecular weight fractions, yielding 35.6 mg of 1,8-PCzTPE-E (0.0404 mmol,

20%), 12 mg of 2,7-PCzTPE-E (0.015 mmol, 7.8%), and 108 mg of 3,6-PCzTPE-E (0.141 mmol, 70%).

1,8-PCzTPE-E. ^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.08 (br, Ar-H), 7.69 (br, Ar-H), 7.32-7.00 (br, Ar-H), 5.20 (br, N-CH_2-R), 2.10 (br, N-C-CH_2-R), 1.73 (br, N-C-CH_2-R), 1.43 (br, Ar-C-CH_3), 1.12 (br, R-CH_2-R), 0.88 (br, R-CH_3). IR: ν (cm^{-1}) = 2920, 2852 (stretching of C-H), 2133 (stretching of C≡C). GPC (THF): M_n = 15400 g mol^{-1}, M_w = 19300 g mol^{-1}, M_w/M_n = 1.29.

2,7-PCzTPE-E. ^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 7.99 (br, Ar-H), 7.54-6.91 (br, Ar-H), 4.26 (br, N-CH_2-R), 1.86 (br, N-C-CH_2-R), 1.73 (br, N-C-CH_2-R), 1.25 (br, R-CH_2-R), 0.88 (br, R-CH_3). IR: ν (cm^{-1}) = 2919, 2851 (stretching of C-H), 2135 (stretching of C≡C). GPC (THF): M_n = 6870 g mol^{-1}, M_w = 13400 g mol^{-1}, M_w/M_n = 1.95.

3,6-PCzTPE-E. ^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.19 (br s, Ar-H), 7.62 (br s, Ar-H), 7.52-7.00 (m, Ar-H), 4.30 (br, N-CH_2-R), 1.87 (br, N-C-CH_2-R), 1.28 (m, R-CH_2-R), 0.82 (s, R-CH_3). IR: ν (cm^{-1}) = 2918, 2849 (stretching of C-H), 2134 (stretching of C≡C). GPC (THF): M_n = 12500 g mol^{-1}, M_w = 15700 g mol^{-1}, M_w/M_n = 1.26.

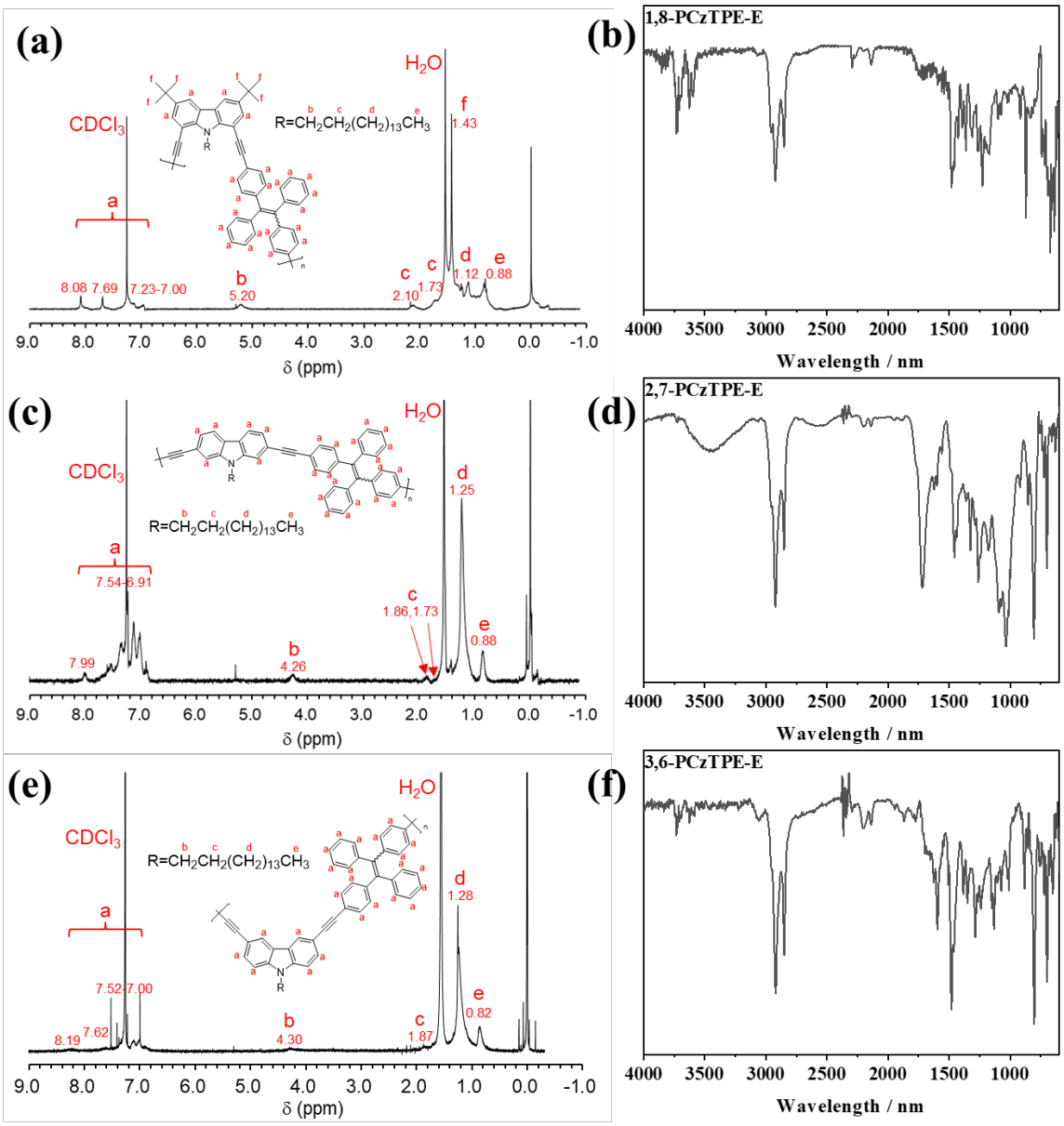
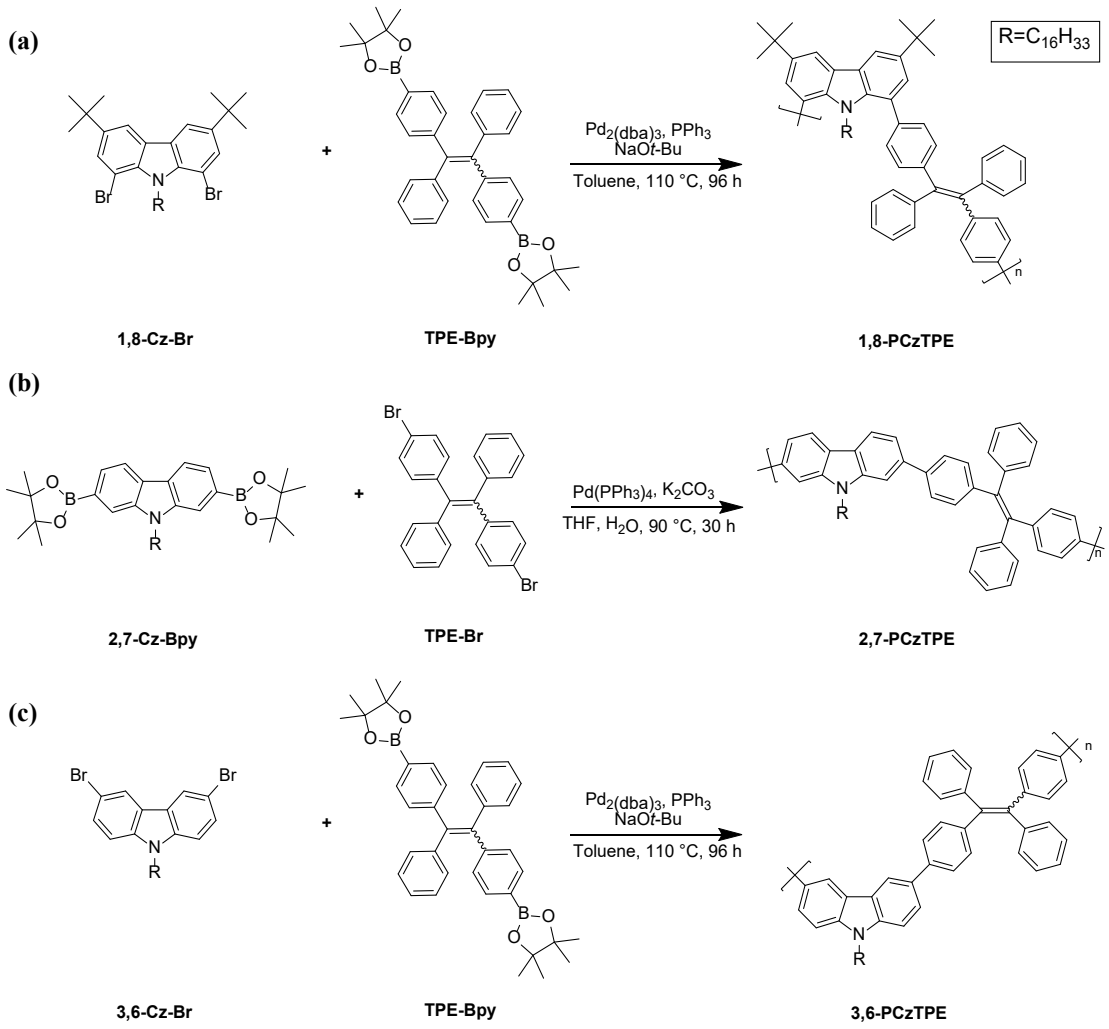


Fig. S9. ^{1}H-NMR spectra of (a) 1,8-PCzTPE-E, (c) 2,7-PCzTPE-E, and (e) 3,6-PCzTPE-E in $CDCl_3$; FT-IR spectra of (b) 1,8-PCzTPE-E, (d) 2,7-PCzTPE-E, and (f) 3,6-PCzTPE-E.



Scheme S9. Synthesis of (a) 1,8-PCzTPE, (b) 2,7-PCzTPE, and (c) 3,6-PCzTPE.

1,8-PCzTPE and 3,6-PCzTPE were synthesized by Suzuki polycondensation between dibromocarbazole and tetraphenylethenediboronic acid bis(pinacol) ester, while 2,7-PCzTPE was synthesized from carbazolediboronic acid bis(pinacol) ester and dibromotetraphenylethene.

1,8-PCzTPE. 0.1590 mmol of 1,8-Cz-Br, 0.1586 mmol of TPE-Bpy, 0.01699 mmol of $Pd_2(dba)_3$, 0.0680 mmol of PPh_3, and 0.1696 mmol of sodium *tert*-butoxide were added to toluene (20 mL) under Ar. The mixture was then heated to 105 ℃ for 72 h. After cooling to room temperature, methanol (100 mL) was added and the mixture was stirred for 30 mins. After the precipitates were collected by vacuum suction filtration, they were subjected to Soxhlet washing with methanol to remove the low molecular weight fractions, yielding 90.6 mg of 1,8-PCzTPE (0.105 mmol, 65%).

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.02 (br, Ar-H), 7.53-6.98 (br, Ar-H), 4.17 (br, N-CH_2-R), 1.88 (br, N-C-CH_2-R), 1.42 (br, Ar-C(CH_3)$_3$), 1.22 (R-CH_2-R), 0.84 (br, R-CH_3). IR: ν (cm^{-1}) = 2924, 2851 (stretching of C-H), 1599, 1508 (stretching of C=C), 1466, 1396, 1364 (bending of C-H), 1021, 910, 735, 700. GPC (THF): M_n = 2200 g mol^{-1}, M_w = 2700 g mol^{-1}, M_w/M_n = 1.23.

2,7-PCzTPE. 0.161 mmol of 2,7-PCzTPE, 0.161 mmol of Cz-Bpy, 0.161 mmol of K_2CO_3, and 0.0043 mmol of $Pd(PPh_3)_4$ were added to THF (6 mL) and water (1 mL) under Ar. The mixture was then refluxed at 90 °C for 30 h. After cooling to room temperature, methanol (100 mL) was added and the mixture was stirred for 30 mins. After the precipitates were collected by vacuum suction filtration, they were subjected to Soxhlet washing with methanol to remove the low molecular weight fractions, yielding 53.5 mg of 2,7-PCzTPE (0.0742 mmol, 46%).

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.09 (br, Ar-H), 7.86 (br, Ar-H), 7.66 (br, Ar-H), 7.56 (br, Ar-H), 7.28-6.91 (br, Ar-H), 4.34 (br, N-CH_2-R), 1.88 (br, N-C-CH_2-R), 1.41-1.16 (br, R-CH_2-R), 1.44-1.16 (br, R-CH_2-R), 0.88 (br, R-CH_3). IR: ν (cm^{-1}) = 2919, 2851 (stretching of C-H). GPC (THF): M_n = 1820 g mol^{-1}, M_w = 2360 g mol^{-1}, M_w/M_n = 1.29.

3,6-PCzTPE. 0.3919 mmol of 3,6-Cz-Br, 0.4017 mmol of TPE-Bpy, 0.0085 mmol of $Pd_2(dba)_3$, 0.0339 mmol of PPh_3, and 0.1696 mmol of sodium *tert*-butoxide were added to toluene (20 mL) under Ar. The mixture was then heated to 105 °C for 72 h. After cooling to room temperature, methanol (100 mL) was added and the mixture was stirred for 30 mins. After the precipitates were collected by vacuum suction filtration, they were subjected to Soxhlet washing with methanol to remove the low molecular weight fractions, yielding 233.3 mg of 3,6-PCzTPE (0.3231 mmol, 83%).

^{1}H-NMR ($CDCl_3$, 293 K): δ [ppm] = 8.28 (br s, Ar-H), 7.65 (br s, Ar-H), 7.45-7.39 (m, Ar-H), 7.28-6.98 (m, Ar-H), 4.28 (br, N-CH_2-R), 1.85 (br, N-C-CH_2-R), 1.22 (m, R-CH_2-R), 0.84 (s, R-CH_3). IR: ν (cm^{-1}) = 2922, 2851 (stretching of C-H), 1640, 1600 (stretching of C=C), 1479, 1261 (bending of C-H), 1100, 1028, 801, 700. GPC (THF): M_n = 4400 g mol^{-1}, M_w = 6600 g mol^{-1}, M_w/M_n = 1.45.

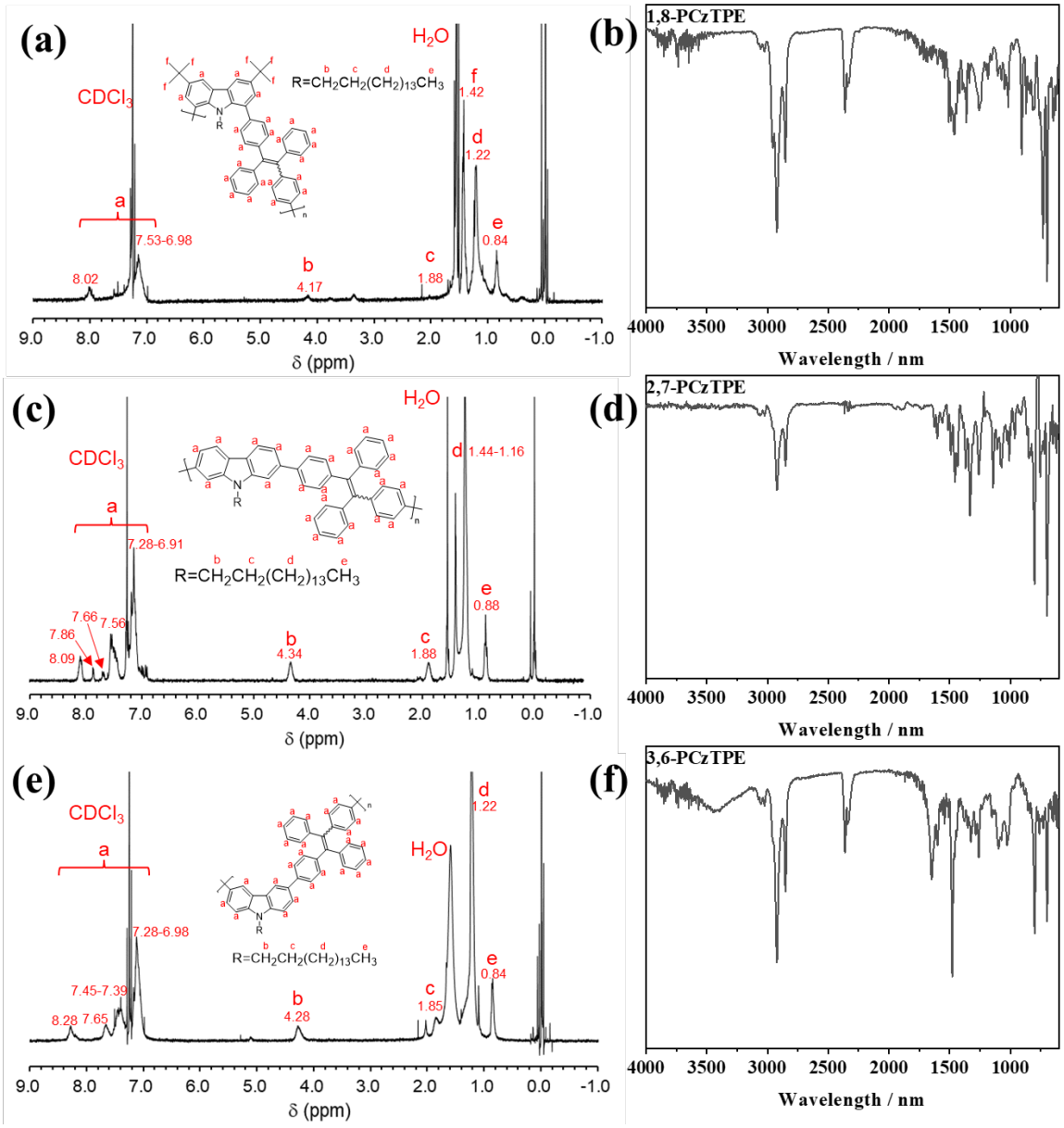


Fig. S10. ^{1}H-NMR spectra of (a) 1,8-PCzTPE, (c) 2,7-PCzTPE, and (e) 3,6-PCzTPE in $CDCl_3$; FT-IR spectra of (b) 1,8-PCzTPE, (d) 2,7-PCzTPE, and (f) 3,6-PCzTPE.

Table S1. Elemental Analysis Results of the PCzTPE Series Polymers

Sample		H (%)	C (%)	N (%)
1,8-PCzTPE	Anal. Calcd	8.84	89.48	1.68
	Found	9.24	88.94	1.82
2,7-PCzTPE	Anal. Calcd	7.98	90.08	1.95
	Found	8.39	89.70	1.91
3,6-PCzTPE	Anal. Calcd	7.98	90.08	1.95
	Found	8.23	89.62	2.15

2.3 Fabrication of Pdots

Conjugated polymer nanoparticles or polymer dots (Pdots) were fabricated by a reprecipitation method.[S7] The PCzTPE (or PCzTPE-E) /THF solutions (0.06 mg·mL^{-1}) were prepared and filtered through PTFE disposable membrane filter. 2 mL of the filtered solution was rapidly injected into 12 mL of pure water (Milli-Q), and the mixture was sonicated in an ultrasonic bath at 283 K for 30 mins. This was followed by a continuous flow of compressed dry air for 1 h to evaporate water. The obtained colloidal suspension was further concentrated in a water bath at 30 ℃ with air flow for 2 h. The final volume of the concentrated suspension was 5 mL, which was further filtered through PTFE disposable membrane filter to yield Pdots suspension.

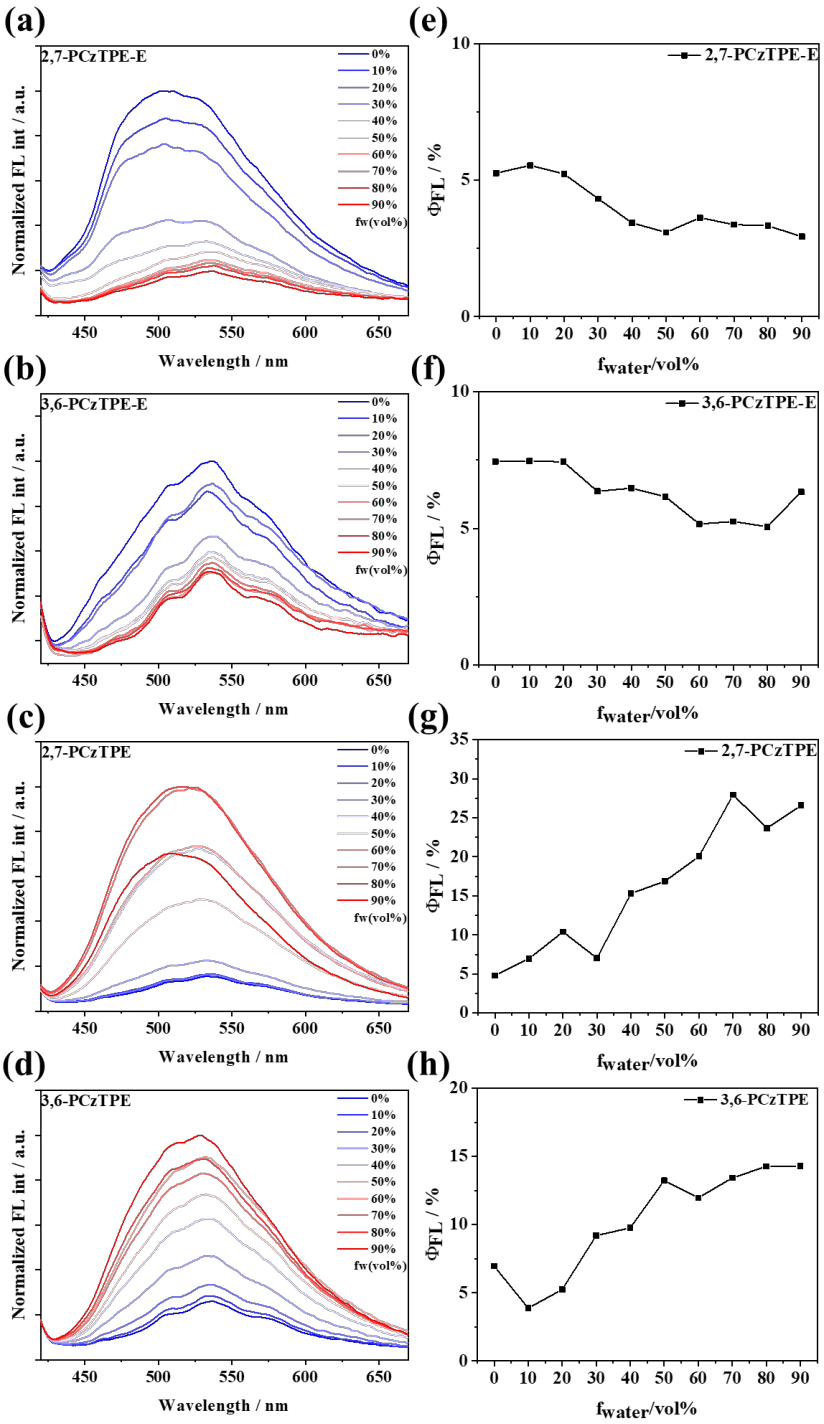


Fig. S11. Fluorescence spectra of (a) 2,7-PCzTPE-E, (b) 3,6-PCzTPE-E, (c) 2,7-PCzTPE, and (d) 3,6-PCzTPE in THF/water mixtures with different water volume fractions (f_{water}). The corresponding fluorescence quantum yields of (e) 2,7-PCzTPE-E, (f) 3,6-PCzTPE-E, (g) 2,7-PCzTPE, and (h) 3,6-PCzTPE in THF/water mixtures.

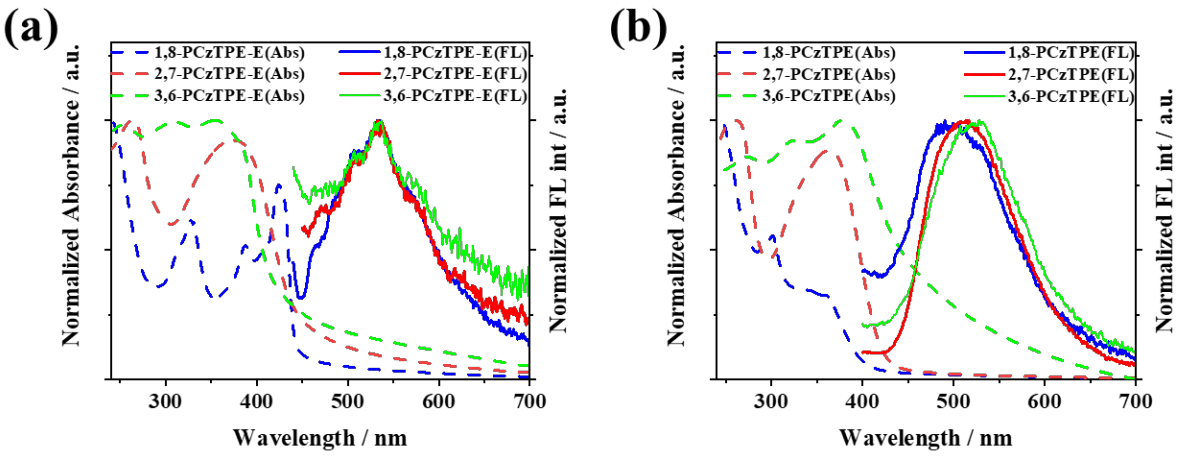


Fig. S12. Steady-state absorption and fluorescence spectra of the PCzTPE-E and PCzTPE films.

Table S2. Spectroscopic and Photophysical Properties of the PCzTPE-E and PCzTPE films [a]

Polymer film	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Φ (%)
1,8-PCzTPE-E	424	424	535	7.9
2,7-PCzTPE-E	375	375	533	4.8
3,6-PCzTPE-E	354	354	537	5.5
1,8-PCzTPE	357	357	490	18.5
2,7-PCzTPE	363	363	513	36.1
3,6-PCzTPE	378	378	528	16.8

[a] λ_{abs}, peak absorption wavelength; λ_{ex}, peak excitation wavelength; λ_{em}, peak fluorescence wavelength; Φ, fluorescence quantum yield.

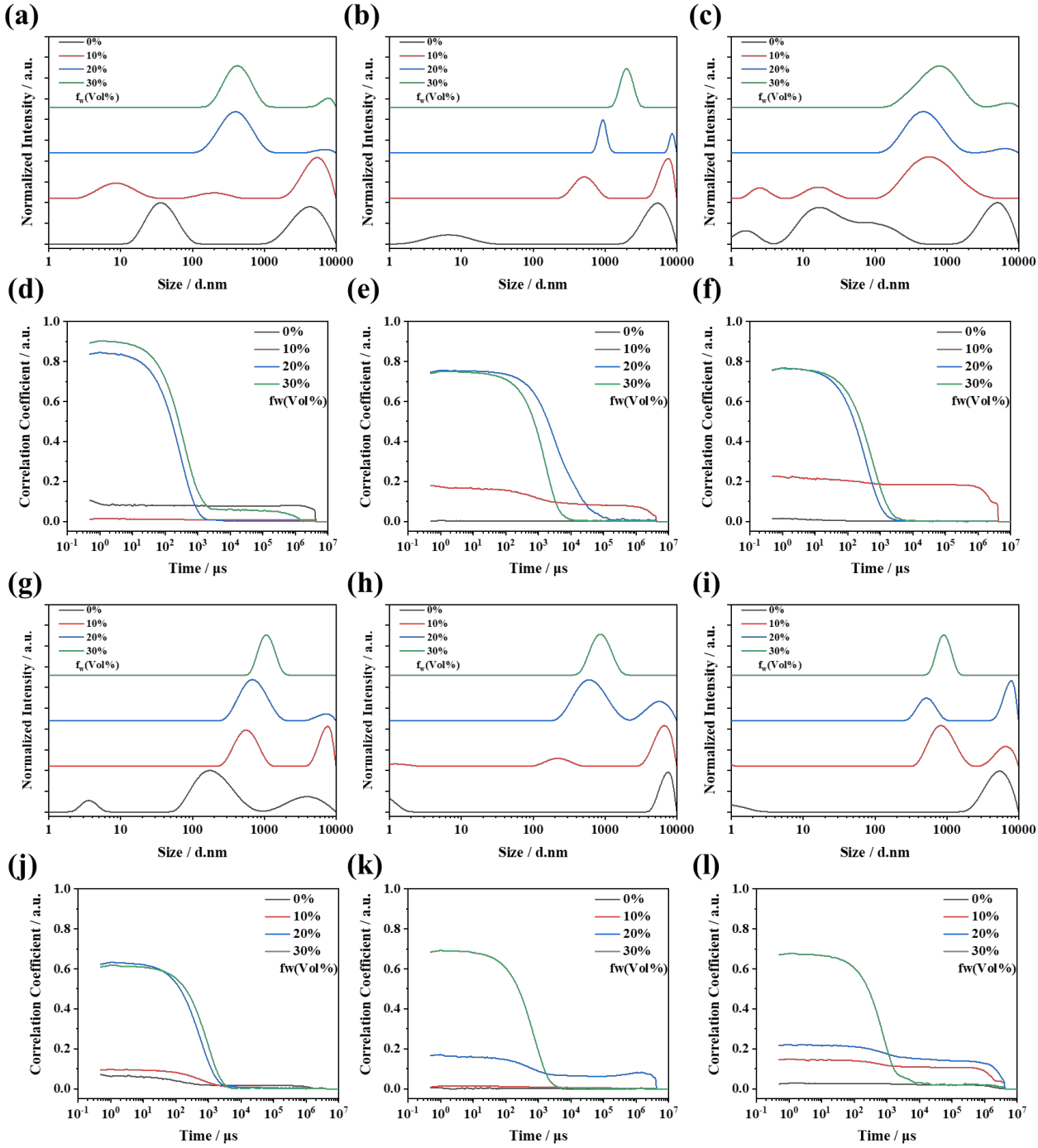


Fig. S13. Dispersion sizes of (a) 1,8-PCzTPE-E, (b) 2,7-PCzTPE-E, (c) 3,6-PCzTPE-E, (g) 1,8-PCzTPE, (h) 2,7-PCzTPE, and (i) 3,6-PCzTPE in THF/water mixtures with different f_{water}. The corresponding correlation coefficient curves of (d) 1,8-PCzTPE-E, (e) 2,7-PCzTPE-E, (f) 3,6-PCzTPE-E, (j) 1,8-PCzTPE, (k) 2,7-PCzTPE, and (l) 3,6-PCzTPE.

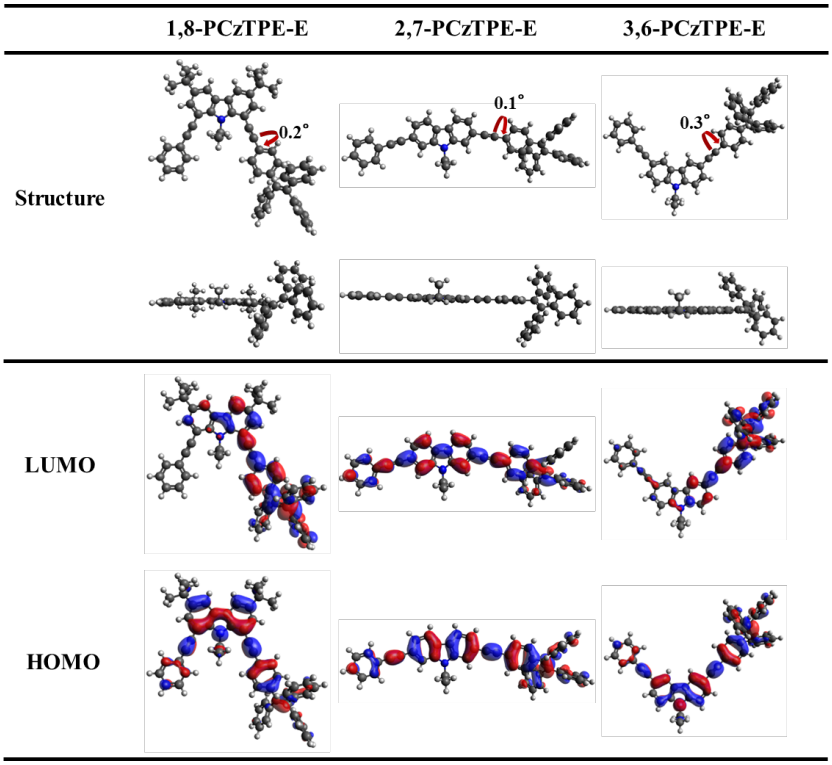


Fig. S14. Frontier molecular orbital plots of 1,8-PCzTPE-E, 2,7-PCzTPE-E, and 3,6-PCzTPE-E estimated by DFT calculations at the B3LYP/6-311G(d,p) level.

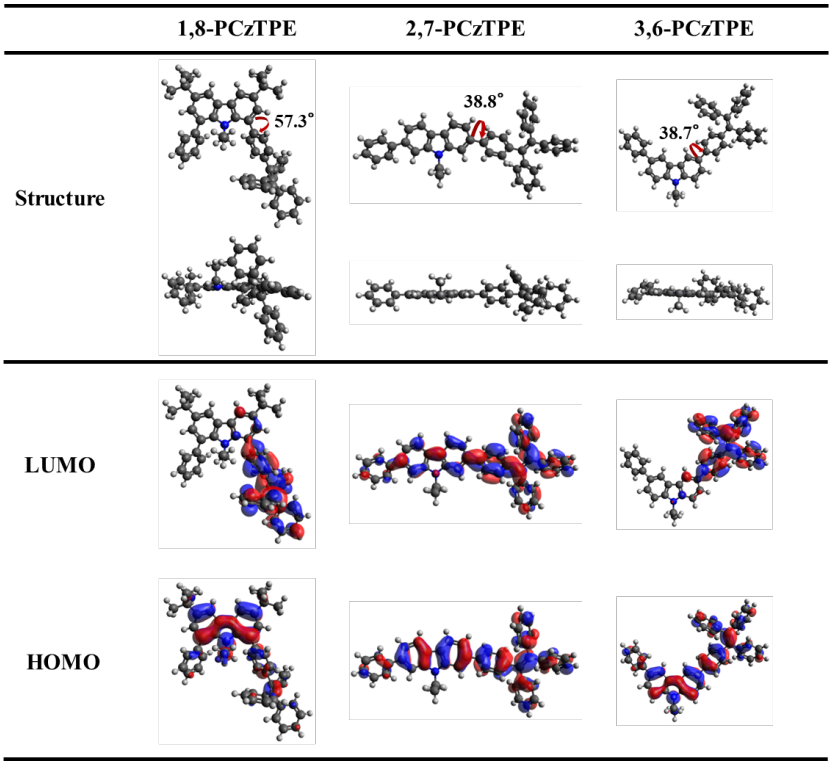


Fig. S15. Frontier molecular orbital plots of 1,8-PCzTPE, 2,7-PCzTPE, and 3,6-PCzTPE estimated by DFT calculations at the B3LYP/6-311G(d,p) level.

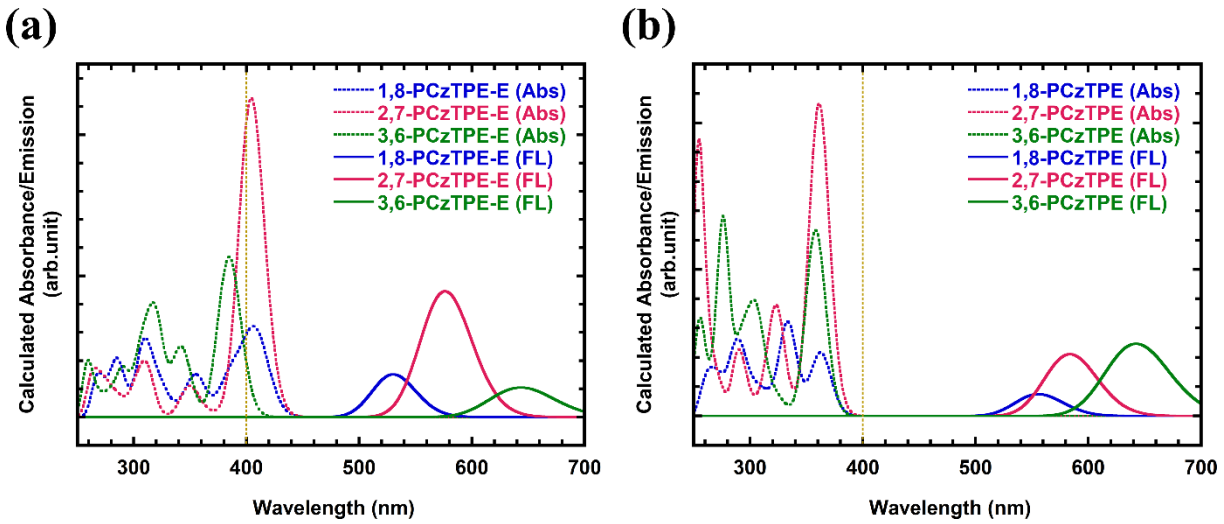


Fig. S16. Calculated optical absorption and fluorescent emission spectra of (a) 1,8-PCzTPE-E, 2,7-PCzTPE-E, and 3,6-PCzTPE-E and (b) 1,8-PCzTPE, 2,7-PCzTPE, and 3,6-PCzTPE by DFT at the B3LYP/6-311++G(d,p) level.[S8-S10]

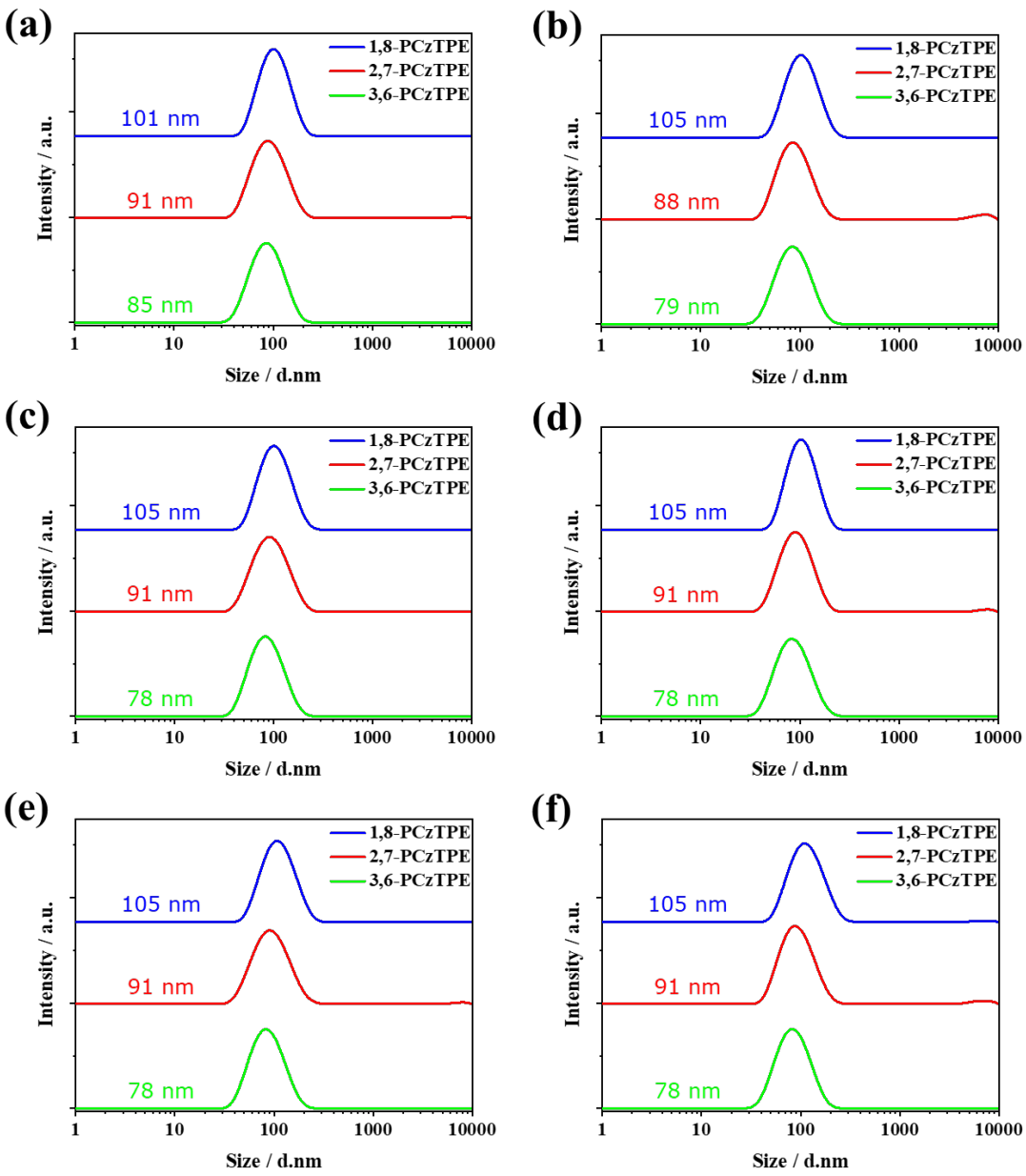


Fig. S17. The size dispersion of the PCzTPE-based Pdots in aqueous solutions measured by DLS after being stored for (a) 1 week, (b) 2 weeks, (c) 3 weeks, (d) 4 weeks, (e) 6 weeks, and (f) 8 weeks.

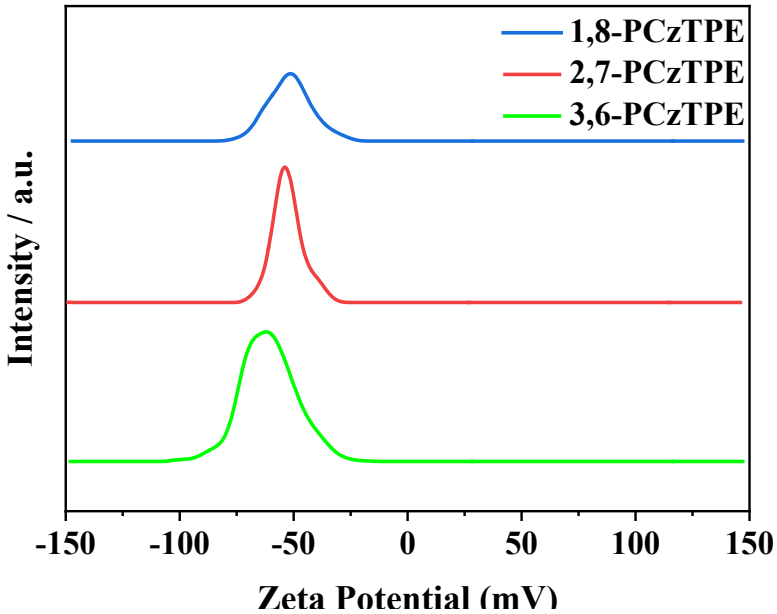


Fig. S18. The zeta potentials of the Pdot dispersion in aqueous solutions.

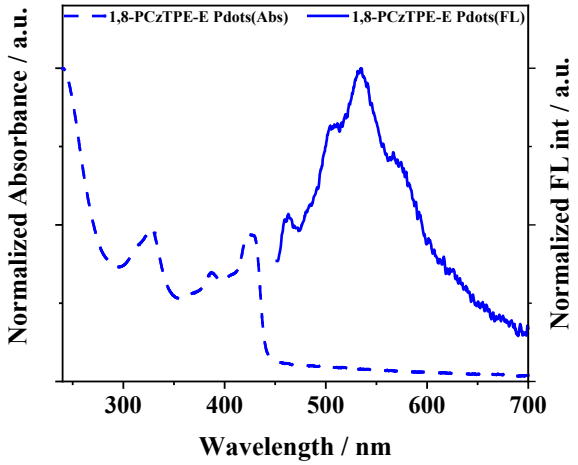


Fig. S19. Steady-state absorption and fluorescence spectra of the 1,8-PCzTPE-E-based Pdots in aqueous solutions.

Table S3. Spectroscopic and Photophysical Properties of the 1,8-PCzTPE-E-based Pdots in aqueous solutions[a]

Pdots	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Φ (%)	ζ (mV)
1,8-PCzTPE-E	423	423	534	3.9	-42

[a] λ_{abs}, peak absorption wavelength; λ_{ex}, peak excitation wavelength; λ_{em}, peak fluorescence wavelength; Φ, fluorescence quantum yield; ζ, zeta potential.

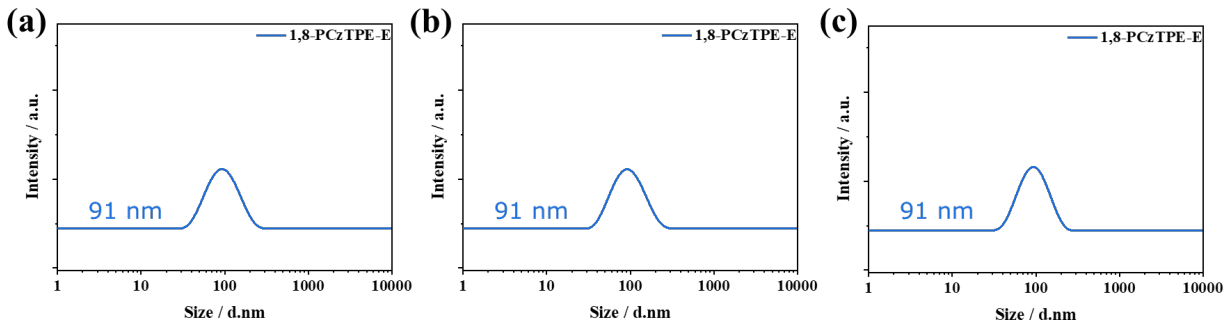


Fig. S20. The size dispersion of (a) freshly prepared 1,8-PCzTPE-E-based Pdots, and 1,8-PCzTPE-E-based Pdots after being stored for (b) 1 week and (c) 2 weeks.

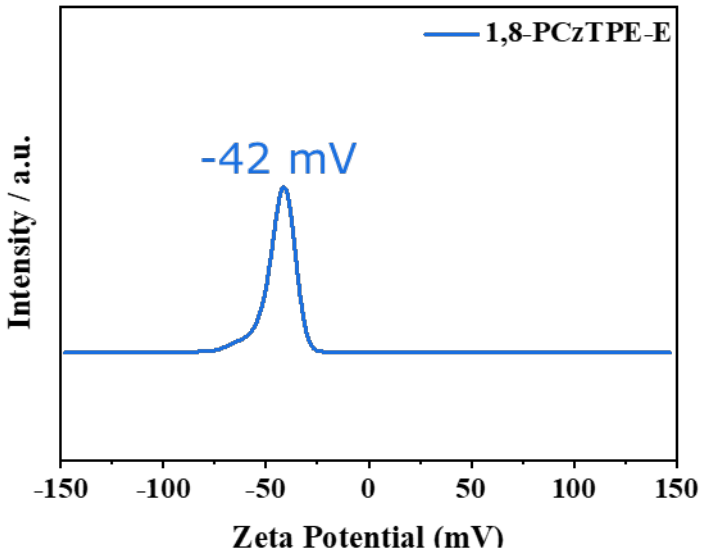
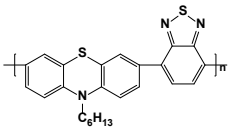
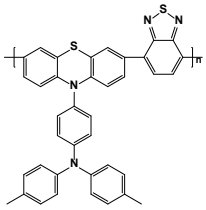
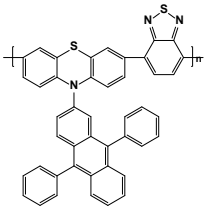
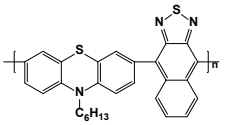
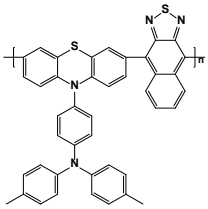
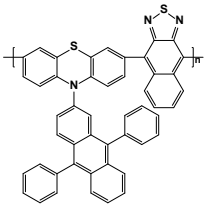
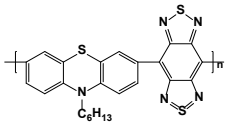
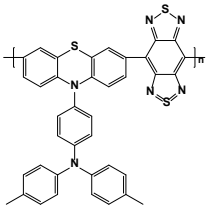
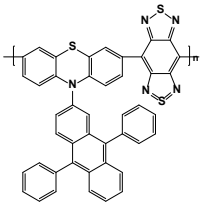
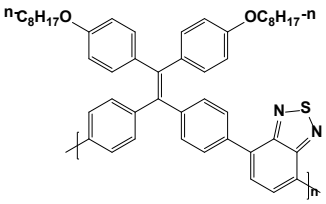
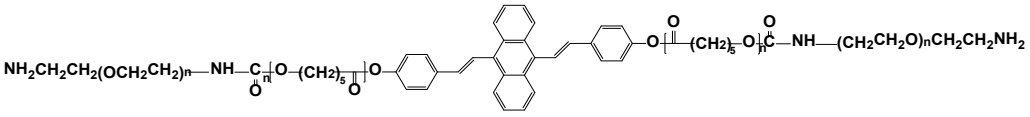
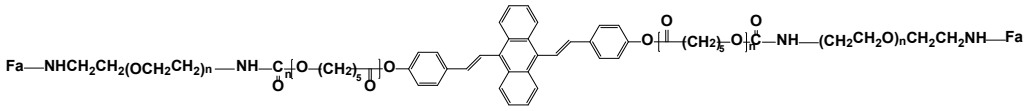


Fig. S21. The zeta potential of the 1,8-PCzTPE-E-based Pdot dispersion in an aqueous solution.

Table S4. The Φ values of some reported Pdots fabricated by polymers with AIE properties

Pdots	Polymer structure	Φ (%)	Ref.
P1a		23	S11
P1b		25	S11
P1c		25	S11
P2a		11	S11
P2b		17	S11
P2c		19	S11

P3a		0.1	S11
P3b		0.6	S11
P3c		1.7	S11
Pdots		25.43	S12
P3		15.8	S13
P4		17.0	S13

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