Electronic Supplementary Information

Poly(arylene ether)s Based on Platinum(II) Acetylide Complexes: Synthesis, Photophysical, and Nonlinear Absorption Properties

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Experimental Section

Materials and Synthesis

Anhydrous dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), toluene, tetrahydrofuran (THF), and trimethylamine (TEA) were dried and distilled according to standard procedure prior to use, *trans*-dichlorobis(triphenylphosphine)palladium (II) (*trans*-$PdCl_2(PPh_3)_2$) was provided by TCI Shanghai development Co. Ltd., China, other chemicals were obtained from Aldrich and used as received unless otherwise mentioned. *trans*-$PtCl_2(PBu_3)_2$ was synthesized according to previously reported literature.[1]

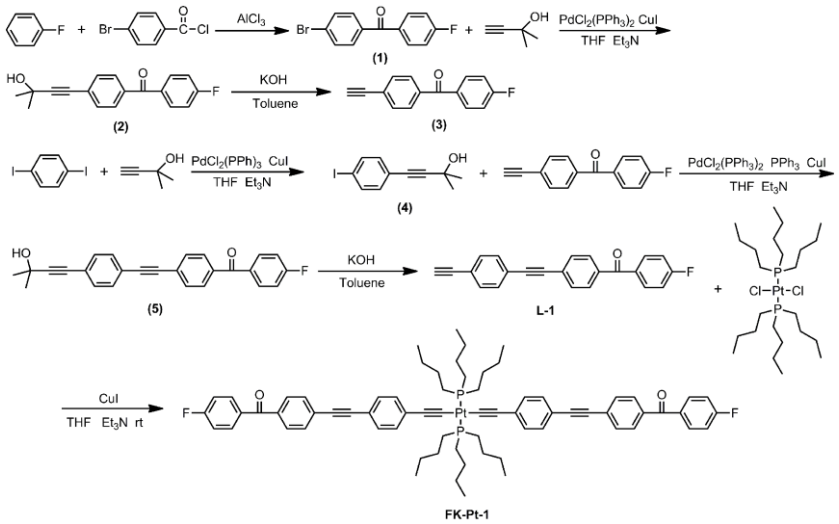

Fig. S1 Synthetic route of platinum acetylide monomer FK-Pt-1.

4-Bromo-4’-fluorobenzophenone (1)

To a 250 mL three-neck flask were added 4-bromobenzoyl chloride (22 g, 0.100 mol) and fluorobenzene (80 mL) under nitrogen. Anhydrous aluminum chloride (17 g, 0.128 mol) was added slowly after the solution was cooled down to 0 ^{o}C, the mixture was stirred for 2 h at room temperature and then heated to reflux for 6 h. The mixture was allowed to cool down and added 30 mL water, heating the mixture to reflux to remove the fluorobenzene through a Dean-Stark trap equipped with a condenser. The mixture was poured into ice water to precipitate, filtered, and washed with 0.5 M NaOH solution and water two times. The product was further recrystallized in ethanol to afford white crystals (21.20 g), yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.77-7.72 (m, 4H), 7.09 (t, J = 8.5 Hz, 4H). MALDI-TOF-MS: Calcd. for $C_{13}H_8BrFO$: 279.1. Found: 280.2 ($[M+H]^+$).

4-(3-Hydroxyl-3-methyl-1-butynyl)-4’-fluorobenzophenone (2)

4-Bromo-4’-fluorobenzophenone (11.16 g, 40 mmol), 2-methyl-3-butyn-2-ol (5.04 g, 60 mmol), $PdCl_2(PPh_3)_2$ (1.4 g, 2 mmol), CuI (380 mg, 2 mmol), and triphenylphosphine (390 mg, 1.5 mmol) were dissolved in degassed THF (120 mL) and trimethylamine (120 mL) under argon. The reaction was kept at 80 ^{o}C for 12 h, then allowed to cool down to room temperature and filtered to remove the insoluble salt.[2]

The filtrate was washed with 1 M HCl and water successively, followed by drying over anhydrous magnesium sulfate. The product was purified by silica-gel chromatography eluting with dichloromethane and ethyl acetate (9:1, v/v) to give a brown solid (10.38 g), yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.85-7.80 (m, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 8.9 Hz, 2H), 1.49 (s, 6H). MALDI-TOF-MS: Calcd. for $C_{18}H_{15}FO_2$: 282.3. Found: 283.3 ($[M+H]^+$).

4-Ethynyl-4'-fluorobenzophenone (3)

To a three-neck round bottom flask equipped with a Dean-Stark trap were added 4-(3-Hydroxyl-3-methyl-1-butynyl)-4'-fluorobenzophenone (8.47 g, 30 mmol) and a suspension of potassium hydroxide (5.04 g, 90 mmol) in 120 mL toluene under argon. The reaction was heated to 130 ^{o}C to reflux and kept for 1 h. After cooling down, the mixture was diluted with water and chloroform, transferred to a separation funnel, the organic phase was separated and washed with water, followed by drying over anhydrous $MgSO_4$. The product obtained by removing the solvent was further washed with cold n-hexane to afford 4-ethynyl-4'-fluorobenzophenone as a brown solid (5.86 g), yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.85-7.80 (m, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.40 (t, J = 8.9 Hz, 2H), 3.33 (s, 1H). MALDI-TOF-MS: Calcd. for $C_{15}H_9FO$: 224.2. Found: 225.2 ($[M+H]^+$). Anal. Calcd. for $C_{15}H_9FO$: C, 80.35, H, 4.05. Found: C, 80.42, H, 4.19.

4-(4-Iodophenyl)-2-methyl-3-butyne-2-ol (4)

In a 250 mL round bottom flask, *p*-diiodobenzene (9.9 g, 30 mmol), $PdCl_2(PPh_3)_2$ (1.05 g, 1.5 mmol), CuI (285 mg, 1.5 mmol), and triphenylphosphine (390 mg, 1.5 mmol) were dissolved in degassed THF (80 mL) and trimethylamine (80 mL) under argon. 2-Methyl-3-butyn-2-ol (2.52 g, 30 mmol) was dropwise added. The reaction was stirred at room temperature for 8 h, the precipitates were filtered and washed with more trimethylamine.[3] The deep orange filtrate was washed with 1 M HCl and water, then dried over anhydrous $MgSO_4$, the solution was concentrated and subjected to silica-gel chromatography eluting with dichloromethane and hexane (8:2, v/v) to obtain a white

solid (4.25 g), yield: 49.4%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.73 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 2.50 (s, 1H), 1.45 (s, 6H). MALDI-TOF-MS: Calcd. for $C_{11}H_{11}IO$: 286.1. Found: 287.2 ($[M+H]^+$). Anal. Calcd. for $C_{11}H_{11}IO$: C, 46.18, H, 3.88. Found: C, 46.42, H, 3.95.

4-[4-[2-[4-(4-Fluorobenzoyl)phenyl]ethyl]phenyl]-2-methyl-3-butyne-2-ol (5)

To a 250 mL round bottom flask were added 4-Ethynyl-4'-fluorobenzophenone (6.73 g, 30 mmol), 4-(4-Iodophenyl)-2-methyl-3-butyne-2-ol (8.58 g, 30 mmol), $PdCl_2(PPh_3)_2$ (1.05 g, 1.5 mmol), and CuI (457 mg, 2.4 mmol). The mixture was dissolved in degassed THF (150 mL) and TEA (150 mL) under argon, and stirred at room temperature for 12 h. The precipitates were filtered and washed with trimethylamine. The filtrate was washed with diluted HCl and water successively, then dried over anhydrous $MgSO_4$. The crude product was purified through silica-gel chromatography to obtain a brown solid (8.95 g), yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.87-7.82 (m, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.18 (t, J = 8.5 Hz, 2H), 1.63 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 194.3, 167.2, 163.8, 136.8, 133.5, 132.4, 131.6, 129.9, 127.3, 123.1, 122.4, 115.7, 91.7, 83.1, 79.2, 77.3, 76.5. 65.4, 31.3. MALDI-TOF-MS: Calcd. for $C_{26}H_{19}FO_2$: 382.4. Found: 383.4 ($[M+H]^+$). Anal. Calcd. for $C_{26}H_{19}FO_2$: C, 81.66, H, 5.01. Found: C, 81.42, H, 5.15.

4-(4-Ethynyl)phenyl-4'-fluorobenzophenone (L-1)

The deprotection of compound 5 was performed using the same method of compound 3. Potassium hydroxide powder (3.36 g, 60 mmol) was suspended in a toluene solution of 5 (7.65g, 20 mmol) under a nitrogen atmosphere. The reaction was heated to reflux and stirred for 1 h, then the mixture was diluted with chloroform and washed with water, after which the aqueous phase was extracted with chloroform two times, the organic phase was combined and dried over anhydrous $MgSO_4$. The crude product was further purified through a short silica-gel chromatography to afford compound L-1 as a pale

yellow solid (5.32 g), yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.87-7.83 (m, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.54-7.48 (m, 4H), 7.19 (t, J = 8.6 Hz, 2H), 3.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 194.3, 167.1, 163.7, 136.8, 133.5, 132.3, 131.6, 129.9, 127.2, 122.8, 115.7, 91.8, 90.4, 83.1, 79.2, 77.2, 76.5. MALDI-TOF-MS: Calcd. for $C_{23}H_{13}FO$: 324.4. Found: 325.7 ($[M+H]^+$). Anal. Calcd. for $C_{26}H_{19}FO_2$: C, 85.17, H, 4.04. Found: C, 85.32, H, 4.15.

Synthesis of FK-Pt-1

Under a nitrogen atmosphere, *trans*-$[PtCl_2(PBu_3)_2]$ (1.48 g, 2.2 mmol), L-1 (1.43 g, 4.4 mmol), and a trace amount of CuI (42 mg, 0.22 mmol) was dissolved in a mixture of THF/TEA (60 mL, 1:1, v/v), the reaction was stirred at room temperature overnight, followed by filtration to remove the precipitates and CuI. The product in filtrate was concentrated and purified by column chromatography with dichloromethane/hexane (1:2) as eluent. The final monomer labeled as FK-Pt-1 was obtained as a yellow crystalline solid (2.36 g), yield: 86%. T_m: 168.0 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.88-7.85 (m, 4H), 7.78 (d, J = 8.2 Hz, 4H), 7.63 (d, J = 8.2 Hz, 4H), 7.43 (d, J = 8.1 Hz, 4H), 7.27 (d, J = 8.4 Hz, 4H), 7.20 (t, J = 8.5 Hz, 4H), 2.17-2.14 (m, 12H), 1.65-1.62 (m, 12H), 1.51-1.46 (m, 12H), 0.96 (t, J = 7.3 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 194.4, 166.5, 164.4, 136.4, 133.8, 132.6, 131.4, 130.8, 129.9, 128.1, 118.6, 115.6, 112.7, 109.5, 93.5, 89.1, 77.0, 26.4, 24.4, 24.0, 13.8. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 3.26 ($J_{P\text{-}Pt}$ = 2343 Hz). MALDI-TOF-MS: Calcd. for $C_{70}H_{79}F_2O_2P_2Pt$: 1246.4. Found: 1246.6. Anal. Calcd. for $C_{70}H_{79}F_2O_2P_2Pt$: C, 67.40, H,6.38. Found: C, 67.31, H, 6.36.

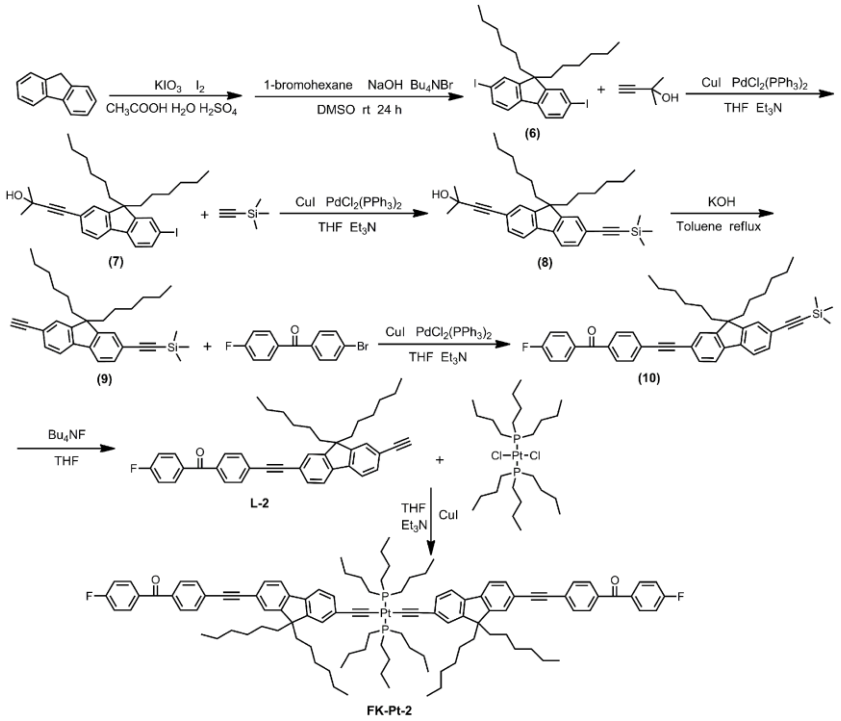

Fig. S2 Synthetic route of platinum acetylide monomer FK-Pt-2.

2,7-Diiodo-9,9-dihexylfluorene (6)

First 2,7-diiodofluorene was synthesized by dissolving fluorene solution in a mixture of $CH_3COOH/H_2O/H_2SO_4$ (100/20/3), followed by the addition of KIO_3 and iodine by stirring at 80 ^oC for 10 h according to the procedure in the literature.[4,5] 2,7-Diiodo-9,9-dihexylfluorene was subsequently obtained by adding tetra-n-butylammonium bromide (3.6 g), 50% aqueous NaOH (27 mL) and 1-bromohexane (36 g, 216 mmol) to a DMSO solution of 2,7-diiodofluorene (25 g, 72 mmol) in a 500 mL three-neck flask. The reaction was stirred at room temperature for 24 h, poured into a mixture of hexane and water, then transferred to a separation funnel, the organic phase was collected. Aqueous phase was further extracted with hexane (2 × 100 mL) and the hexane solution was combined together. After washing with 0.1 M HCl and water, the product was purified through silica gel column chromatography eluting with hexane and dichloromethane (9:1) to afford white solid (34.2 g), yield: 81%. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.63 (d, J = 8.4 Hz, 2H), 7.61 (s, 2H), 7.37 (d, J = 8.6 Hz, 2H), 1.89-1.83 (m, 4H), 1.13-1.00 (m, 12H), 0.75 (t, J = 6.8 Hz, 6H), 0.59-0.50 (m, 4H). MALDI-TOF-MS: Calcd. for $C_{25}H_{32}I_2$: 586.3. Found: 587.3 ($[M+H]^+$). Anal. Calcd. for

$C_{25}H_{32}I_2$: C, 51.21, H, 5.50. Found: C, 51.21, H, 5.61.

2-(3-Hydroxy-3-methylbutynyl)-7-iodo-9,9-dihexylfluorene (7)

CuI (476 mg, 2.5 mmol) and $Pd(PPh_3)_2Cl_2$ (640 mg, 0.9 mmol) were added in a degassed THF/TEA solution of 2,7-Diiodo-9,9-dihexylfluorene (30 g, 51 mmol). Subsequently, 2-Methyl-3-butyn-2-ol (4.2 g, 50 mmol) was dropwise added. The reaction was stirred at room temperature for 12 h, the precipitates were filtered and washed with more trimethylamine. Then the filtrate was washed with diluted HCl and water, dried over anhydrous $MgSO_4$, the crude product was purified by silica-gel chromatography eluting with hexane and dichloromethane (5:1) to give an orange oil, yield: 53%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.65 (s, 1H), 7.64 (d, J = 4.7 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.41-7.36 (m, 3H), 1.84-1.88 (m, 4H), 1.66 (s, 6H), 1.15-1.03 (m, 12H), 0.77 (t, J = 6.7 Hz, 6H), 0.61-0.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 153.2, 150.0, 140.5, 140.2, 136.3, 132.6, 131.0, 126.3, 122.0, 121.8, 119.9, 99.4, 93.7, 83.6, 66.1, 55.3, 40.3, 31.5, 29.7, 23.7, 22.6, 13.9. MALDI-TOF-MS: Calcd. for $C_{30}H_{39}IO$: 542.5. Found: 543.5 ($[M+H]^+$). Anal. Calcd. for $C_{30}H_{39}IO$: C, 66.41, H, 7.25. Found: C, 66.21, H, 7.16.

2-(3-Hydroxy-3-methylbutynyl)-7-trimethylsilyl-9,9-dihexylfluorene (8)

Compound 7 (16.8 g, 31 mmol), trimethylsilylacetylene (4.52 g, 46 mmol), CuI (285 mg, 1.5 mmol), and $Pd(PPh_3)_2Cl_2$ (1.05 g, 1.5 mmol) were dissolved in degassed THF/TEA. The mixture was stirred at room temperature for 10 h, followed by filtration to remove the salt. The orange filtrate was further washed with diluted HCl and water, then concentrated and subjected to a flash column chromatography eluting with dichloromethane to afford an amber oil, yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.58 (d, J = 7.8 Hz, 2H), 7.46-7.36 (m, 4H), 1.95-1.90 (m, 4H), 1.65 (s, 6H), 1.14-1.00 (m, 12H), 0.76 (t, J = 6.8 Hz, 6H), 0.58-0.48 (m, 4H), 0.28 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 153.2, 150.0, 140.4, 140.2, 136.2, 132.6, 131.1, 126.1, 122.0, 121.6, 120.0, 106.1, 99.4, 93.7, 83.6, 77.1, 76.6, 66.1, 55.3, 40.3, 31.5, 29.7, 23.7, 22.6, 13.9. MALDI-TOF-MS: Calcd. for $C_{35}H_{48}OSi$: 512.8. Found: 513.9 ($[M+H]^+$). Anal.

Calcd. for $C_{35}H_{48}OSi$: C, 81.97, H, 9.43. Found: C, 82.12, H, 9.34.

2-Ethynyl-7-trimethylsilyl-9,9-dihexylfluorene (9)

To a round-bottom flask were added compound 8 (15.4 g, 30 mmol), potassium hydroxide (5.04 g, 90 mmol), and toluene (150 mL) under a nitrogen atmosphere. The mixture was heated to 130 ^{o}C and reflux for 1 h. After the reaction, the mixture was diluted with chloroform, and washed with water three times, followed by drying over anhydrous $MgSO_4$. The solution was concentrated and purified through silica-gel chromatography using CH_2Cl_2/hexane (1:5) as elute to afford an amber oil (12.5 g), yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.66-7.60 (m, 2H), 7.53-7.44 (m, 4H), 3.15 (s, 1H), 1.97-1.92 (m, 4H), 1.15-1.02 (m, 12H), 0.78 (t, J = 6.8 Hz, 6H), 0.61-0.52 (m, 4H), 0.30 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 151.1, 141.1, 140.7, 131.3, 126.6, 126.3, 122.0, 120.8, 119.9, 106.1, 94.3, 84.6, 77.2, 76.6, 55.3, 40.3, 31.5, 29.7, 23.7, 22.6, 13.9. MALDI-TOF-MS: Calcd. for $C_{32}H_{42}Si$: 454.7. Found: 455.8 ($[M+H]^+$). Anal. Calcd. for $C_{32}H_{42}Si$: C, 84.52, H, 9.31. Found: C, 84.29, H, 9.53.

2-[2-[4-(4-Fluorobenzoyl)phenyl]ethynyl]-7-trimethylsilyl-9,9-dihexylfluorene (10)

4-Bromo-4'-fluorobenzophenone (6.14 g, 22 mmol), CuI (190 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (250 mg, 0.35 mmol), and compound 9 (10 g, 22 mmol) were dissolved in 180 mL degassed THF/TEA (1:1). The mixture was heat to 80 ^{o}C and stirred for 8 h. The precipitates were filtered and washed with trimethylamine, after which, the filtrate was extracted with diluted HCl and water, then dried over anhydrous $MgSO_4$. When completed, the product was purified using chromatography on silica eluting with CH_2Cl_2/hexane (2:5) to obtain a dark red solid (11.3 g), yield: 79%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.87-7.83 (m, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.68-7.61 (m, 4H), 7.55-7.52 (m, 2H), 7.49-7.45 (m, 2H), 7.18 (t, J = 8.6 Hz, 2H), 1.99-1.94 (m, 4H), 1.15-0.95 (m, 12H), 0.77 (t, J = 6.8 Hz, 6H), 0.63-0.51 (m, 4H), 0.29 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 194.3, 167.1, 163.8, 151.1, 141.2, 140.7, 136.6, 132.6, 131.7, 131.4, 131.0, 129.9, 127.9, 126.2, 122.0, 121.4, 119.9, 115.6, 106.1, 94.4, 93.7, 88.9, 77.2, 76.6, 55.3, 40.3, 31.5, 29.7, 23.7, 22.6, 13.9. MALDI-TOF-MS: Calcd. for

$C_{45}H_{49}FOSi$: 653.3. Found: 654.2 ($[M+H]^+$). Anal. Calcd. for $C_{45}H_{49}FOSi$: C, 82.77, H, 7.56. Found: C, 83.07, H, 7.75.

2-[2-[4-(4-Fluorobenzoyl)phenyl]ethynyl]-7-ethynyl-9,9-dihexylfluorene (L-2)

To a 250 mL round-bottom flask, compound 10 (11 g, 16.5 mmol) was dissolved in 120 mL THF and 25 mL methanol. Subsequently, tetrabutylammonium fluoride (1 M in THF, 22 mL), the mixture was sealed under argon and stirred at room temperature for 8 h. The solvent was evaporated and the crude product was purified on silica-gel column chromatography to afford a dark red solid (9.8 g), yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.87-7.83 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.69-7.63 (m, 4H), 7.56-7.53 (m, 2H), 7.50-7.48 (m, 2H), 7.18 (t, J = 8.6 Hz, 2H), 3.16 (s, 1H), 2.00-1.95 (m, 4H), 1.15-1.04 (m, 12H), 0.77 (t, J = 6.7 Hz, 6H), 0.66-0.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 194.3, 167.1, 163.8, 151.2, 141.0, 136.7, 133.8, 132.5, 131.5, 131.2, 129.9, 127.8, 126.6, 126.1, 121.5, 121.0, 119.9, 115.6, 93.7, 89.0, 84.5, 77.2, 76.6, 55.3, 40.3, 31.5, 29.6, 23.7, 22.6, 13.9. MALDI-TOF-MS: Calcd. for $C_{42}H_{41}FO$: 580.8. Found: 581.8 ($[M+H]^+$). Anal. Calcd. for $C_{42}H_{41}FO$: C, 86.86, H, 7.12. Found: C, 86.97, H, 7.05.

Synthesis of FK-Pt-2

L-2 (8.60 g, 14.8 mmol), *trans*-$[PtCl_2(PBu_3)_2]$ (4.96 g, 7.4 mmol), and CuI (140 mg, 0.74 mmol) was dissolved in a mixture of THF/TEA (160 mL, 1:1, v/v), the mixture was stirred at room temperature overnight, followed by filtration to remove the precipitates and the solid residues. The filtrate was concentrated and purified by column chromatography eluting with EtOAc/hexane (1:9). The monomer labeled as FK-Pt-2 was obtained as an orange red crystalline solid (8.42 g), yield: 64.7 %. T_m: 109.7 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.89-7.87 (m, 4H), 7.81 (d, J = 8.1 Hz, 4H), 7.70-7.64 (m, 6H), 7.58-7.53 (m, 6H), 7.31-7.29 (d, J = 8.1, 4H), 7.21 (t, J = 8.5 Hz, 4H), 2.25-2.22 (m, 12H), 1.99-1.94 (m, 8H), 1.72-1.69 (m, 12H), 1.54-1.48 (m, 12H), 1.16-1.07 (m, 24H), 0.99 (t, J = 7.3 Hz, 18H), 0.80 (t, J = 7.1 Hz, 12H), 0.71-0.59 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 194.5, 166.5, 164.4, 150.9, 142.3, 137.3, 136.4, 133.8, 132.6, 131.4, 130.9, 130.0, 128.3, 126.0, 125.2, 120.3, 119.6, 115.6, 94.2, 88.6, 77.3, 77.0, 76.8, 55.0, 40.6, 31.6, 29.8, 26.5, 24.5, 24.2, 23.8, 22.7, 14.0, 13.9. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 2.99 ($J_{P\text{-}Pt}$ = 2358 Hz). MALDI-TOF-MS: Calcd. for $C_{108}H_{134}F_2O_2P_2Pt$: 1759.3. Found: 1759.5. Anal. Calcd. for $C_{108}H_{134}F_2O_2P_2Pt$: C, 73.73, H, 7.68. Found: C, 73.61, H, 7.47.

Synthesis of poly(arylene ether)-platinum acetylide copolymer (CP-1)

Typically the copolymerization procedure of poly(arylene ether)s with platinum acetylide chromophores was carried out as follows: *Bis*(4-fluorophenyl) sulfone (3.89 g, 17 mmol), 4,4'-(hexafluoroisopropylidene) diphenol (5.72 g, 15.3 mmol), FK-Pt-1 (2.12 g, 1.7 mmol), and anhydrous potassium carbonate (2.82 g, 20 mmol) were dissolved in DMAc (40 mL) and toluene (20 mL) in a three-neck flask equipped with a mechanical stirrer and a Dean-Stark trap with a condenser. The mixture was heated to reflux under argon at 130 ^{o}C for 3 h to remove the resulting water, and then continued to stir at 135-140 ^{o}C at a higher speed for 3 h until the solution became viscous. The solution was poured into 1000 mL water to precipitate as a robust yellow threadlike polymer, which was pulverized into powders, washed with hot water and ethanol 5 times, respectively. The product was dried at 80 ^{o}C under vacuum overnight to afford 10.06 g (yield: 91%) CP-1. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 3.25 ($J_{P\text{-}Pt}$ = 2351 Hz). M_n: 188 kDa, M_w: 425 kDa, PDI: 2.26. T_g: 187.2 ^{o}C.

Synthesis of poly(arylene ether)-platinum acetylide copolymer (CP-2)

To a three-neck flask equipped with a mechanical stirrer and a Dean-Stark trap with a condenser were added *bis*(4-fluorophenyl) sulfone (3.43 g, 13.5 mmol), 4,4'-(hexafluoroisopropylidene) diphenol (5.04 g, 15 mmol), FK-Pt-2 (2.64 g, 1.5 mmol), and anhydrous potassium carbonate (2.48 g, 18 mmol). The mixture were dissolved in 48 mL DMAc and 25 mL toluene, then heated to reflux under argon at 130 ^{o}C for 3 h and continued to stir at 135-140 ^{o}C at a higher speed for 3 h. After the reaction, the viscous polymer solution was poured into water to precipitate as yellow robust fibers,

followed by pulverization into powders. The resulting polymer was then washed with hot water and ethanol, then dried at 80 ^{o}C under vacuum to give 9.17 g (yield: 87 %) CP-2. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 2.98 ($J_{P\text{-}Pt}$ = 2354 Hz). M_n: 221 kDa, M_w: 471 kDa, PDI: 2.13. T_g: 171.6 ^{o}C.

Synthesis of 6F-PAES

The pristine 6F-PAES was synthesized by a similar procedure as previously reported using *bis*(4-fluorophenyl) sulfone (11.44 g, 45 mmol) and 4,4'-(hexafluoroisopropylidene) diphenol (15.13 g, 45 mmol) as monomers (1:1) to afford white 6F-PAES polymer solid 23.6 g (yield: 93%). M_n: 478 kDa, M_w: 673 kDa, PDI: 1.41. T_g: 202.5 ^{o}C.

Synthesis of MPt-1 and MPt-2

The model compound MPt-1 and MPt-2 were synthesized according to literatures using a modified procedure.[6,7] MPt-1: yellow crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.54-7.51 (m, 4H), 7.40-7.33 (m, 10H), 7.25 (t, J = 6.8 Hz, 4H), 2.18-2.10 (m, 12H), 1.63-1.56 (m, 12H), 1.51-1.39 (m, 12H), 0.93 (t, J = 7.2 Hz, 18H). MALDI-TOF-MS: Calcd. for $C_{56}H_{72}P_2Pt$: 1002.2. Found: 1002.2. MPt-2: orange crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.61-7.47 (m, 12 H), 7.41-7.32 (m, 6H), 7.26 (m, 4H), 2.23-2.17 (m, 12H), 1.98-1.86 (m, 8H), 1.68-1.63 (m, 12H), 1.52-1.42 (m, 12H), 1.16-1.03 (m, 24H), 0.95 (t, J = 7.2 Hz, 18H), 0.77 (t, J = 6.7 Hz, 12H), 0.69-0.54 (m, 8H). MALDI-TOF-MS: Calcd. for $C_{94}H_{128}P_2Pt$: 1515.1. Found: 1515.1.

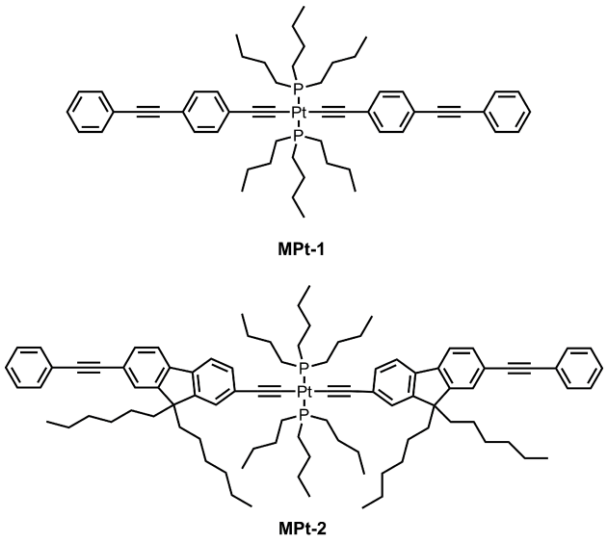

Fig. S3 Structure of model compounds MPt-1 and MPt-2.

Membrane and Monolith Fabrication

The membrane samples of the polymers were fabricated for measuring their mechanical properties. A 1 g/mL solution of the polymer in DMAc (10 mL) was stirred overnight to obtain a homogenous viscous solution, the glass plate (8 × 8 cm) was rinsed with acetone before drying. The solution was filtered and poured onto the glass plate and allow for flowing and covering the entire glass plate, then the film was dried initially at 80 ^{o}C for 24 h, 100 ^{o}C for 24 h, and 120 ^{o}C for 24 h, finally held at this temperature under vacuum 24 h, after which the membrane could be easily peeled off. The polymer monolith was prepared by pouring 40 mL DMAc solution of the copolymers CP-1/6F-PAES (1:1 w/w) or CP-2/6F-PAES (1:1 w/w) into a Teflon mode, and placed in oven at 100 ^{o}C for a week. For comparison, the monolith of 6F-PAES blend with MPt-1 or MPt-2, namely, MPt-1/6F-PAES (2:19 w/w) and MPt-2/6F-PAES (2:13 w/w) were fabricated by the same procedure, in which the concentration of Pt(II) acetylide chromophores are identical to their polymer monoliths counterparts

Characterization

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance III (300 MHz) spectrometer, whereas ^{31}P NMR (202 MHz) spectrum was

recorded on a Bruker 510 NMR spectrometer (500 MHz) in $CDCl_3$ with tetramethylsilane (TMS) as a reference. Mass spectra (MS) were performed on AXIMA-CFR laser desorption ionization flying time spectrometer. IR spectra were carried out on a Nicolet Impact 410 Fourier transform infrared spectrophotometer. Thermogravimetric analysis (TGA) was measured using a Netzch Sta 449 thermal analyser system at a heating rate of 10 $^oC\ min^{-1}$ in a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821e instruments at a heating rate of 20 $^oC\ min^{-1}$ under nitrogen. The molecular weight of the polymers were recorded on a Gel permeation chromatograms (GPC) PL-GPC 220 with DMF as an eluent at 80 ^oC at a flow rate of 1.00 mL min^{-1}. UV-vis Absorption spectra was carried out on UV2501-PC spectrophotometer. Fluorescence and Phosphorescence emission spectra were performed at 298 K and 77 K on a FLS 920 steady-transient spectrophotometer, fluorescence quantum yields were determined using quinine sulfate in 1.0 M H_2SO_4 as the standard. The mechanical properties were evaluated on a Shimadzu AG-I Universal Tester at a strain rate of 10 mm min^{-1}, the polymer membrane samples of 45.0 (length) × 5.0 (width) × 0.1 (thickness) mm^3 were casted from DMAc solution onto the glass plate, each sample was measured for 5 times at least in parallel, from which the mean values were extracted.

Q-switched Nd:YAG laser of 6 ns pulses (532 nm) with a repetition of 10 Hz was employed for nonlinear optical measurements using an open aperture z-scan technique. The beam was focused on a 15 cm focus lens and the spot diameter was determined to be ~ 20 μm. With an identical linear transmittance of 85%, all the samples were dissolved in THF in a 5 mm × 10 mm quartz cuvette and moved along the *z* direction. The transmitted and reference pulse energy were monitored by two photo detectors with high precision.

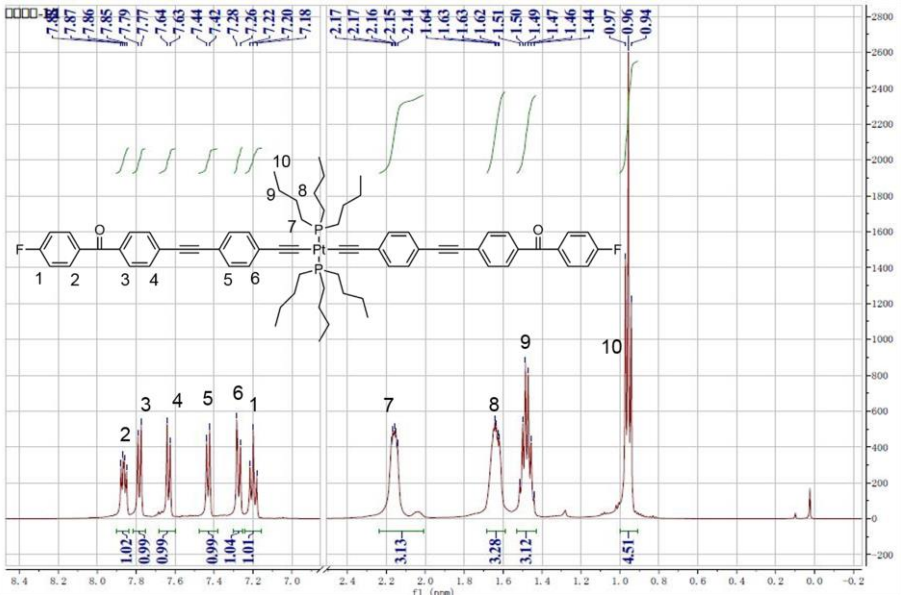

Fig. S4 ^{1}H NMR spectrum of FK-Pt-1.

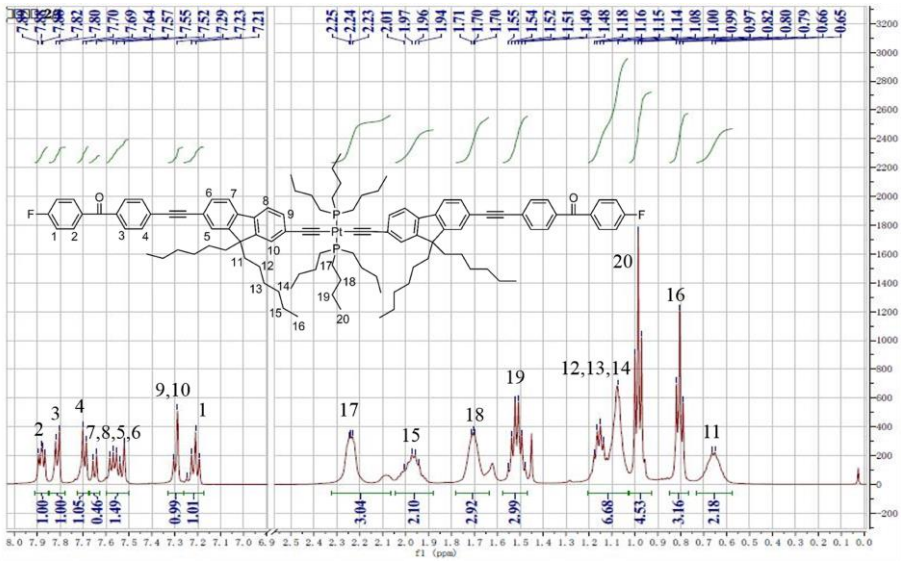

Fig. S5 ^{1}H NMR spectrum of FK-Pt-2.

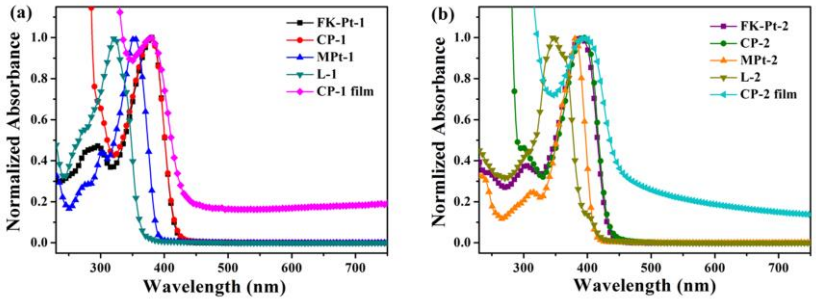

Fig. S6 Normalized UV-vis absorption spectra of (a) L-1, FK-Pt-1, MPt-1, CP-1, and CP-1 film, (b) L-2, FK-Pt-2, MPt-2, CP-2, and CP-2 film.

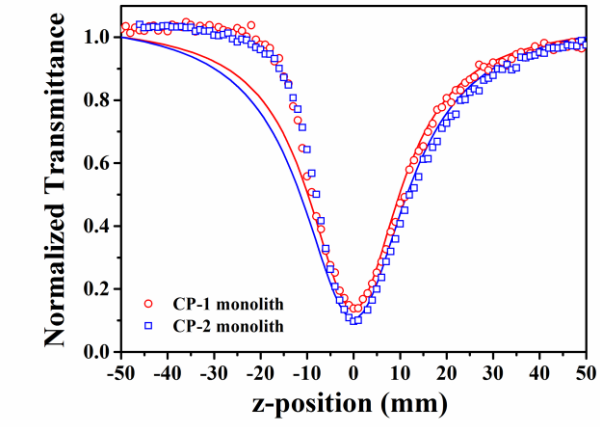

Fig. S7 Open aperture nanoseconds z-scan curves of CP-1 and CP-2 monoliths.

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