Electronic supplementary information

for

New heterobimetallic Au(I)-Pt(II) polyynes achieving good trade-off between transparency and optical power limiting performance[†]

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Experimental

Synthesis

2,7-Dibromo-9,9-didodecyl-fluorene

The mixture of 2,7-dibromofluorene (5.0 g, 15.4 mmol), 1-bromododecane (11.5 g, 46.3 mmol), NaOH (1.7 g, 42.5 mmol) and DMSO (30 mL) were heated at 90 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into ice water (100 mL) and extracted with petroleum ether (4×30 mL). The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The crude product was further purified by column chromatography on silica gel using petroleum ether as the eluent to obtain the title product as yellow oil (8.21 g, 80.6%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.52 (d, *J* = 8.4 Hz, 2H), 7.46–7.44 (m, 4H), 1.93–1.88 (m, 4H), 1.26-1,04 (m, 36H), 0.87 (t, *J* = 6.8 Hz, 6H), 0.56 (m, 4H); FAB-MS (m/z): 660 [M]⁺.

1-Bromo-4-(dodecyloxy)benzene

4-Bromophenol (5.0 g, 28.9 mmol), 1-bromododecane (16.3 g, 65.2 mmol) and K₂CO₃ (6.0 g, 43.4 mmol) were mixed in ethanol (50 mL) at 80 °C and stirred for 24 h. After cooling to room temperature, water (50 mL) was added and mixture was extracted with CH₂Cl₂ (4×30 mL). The collected organic phase was dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. The liquid residue was purified by column chromatography on silica gel with petroleum ether to obtain colorless oil (5.8 g, 78%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.36 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.91 (t, *J* = 6.8 Hz, 2H), 1.80–1.73 (m, 2H), 1.37–1.26 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); FAB-MS (m/z): 340, 342 [M]⁺.

4-(Dodecyloxy)-*N*,*N*-diphenylbenzenamine

Under N2 atmosphere, 1-bromo-4-(dodecyloxy)benzene (6.0 g, 43.4 mmol) diphenylamine (4.5

g, 26.7 mmol), *t*-BuOK (3.6 g, 32.1 mmol), Pd(OAc)₂ (0.2 g, 0.9 mmol), and *t*-Bu₃P (1.8 mmol) were mixed in *p*-xylene, and then mixture was stirred at 120 °C for 16 h. After cooling to room temperature, the reaction mixture was filtrated, concentrated under vacuum. Then concentrated liquid was purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (3/1, v/v) to get white solid (5.1 g, 65%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.22–7.18 (m, 4H), 7.06–7.18 (m, 6H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.93 (t, 2H, *J* = 6.6 Hz), 1.81–1.74 (m, 2H), 1.35–1.27 (m, 18H), 0.88 (t, 3H, *J* = 7.2 Hz); FAB-MS (m/z): 429 [M]⁺.

4-(Dodecyloxy)-4',4''-(dibromo)triphenylamine

4-(Dodecyloxy)-*N*,*N*-diphenyl-benzenamine (2.0 g, 4.5 mmol) was dissolved in CH₂Cl₂ (15 mL) and glacial acetic acid (0.5 mL) was added. NBS (1.7 g, 9.6 mmol) was added by portions at 0 °C. After addition, the reaction mixture was stirred at room temperature for 12 h. After removing a small amount of white solid through filtration, the reaction mixture was concentrated and purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (5/1, v/v) to get pale yellow oil (2.4 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.29 (d, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 4H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 1.81–1.73 (m, 2H), 1.34–1.26 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); FAB-MS (m/z): 585 [M]⁺.

N-Dodecyl-carbazole

Carbazole (6.0 g, 36.0 mmol), KOH (6.0 g, 107.2 mmol) and DMSO (50 mL) were mixed in round-bottom flask. The mixture was heated to reflux for 10 min. 1-Bromododecane (13.8 g, 55.6 mmol) was added slowly. After addition, the reaction mixture was refluxed for 2 h. Then the mixture was cooled to room temperature, and poured into ice water (100 mL). The brown precipitate was collected, washed with water (5×30 mL) and dissolved with CH_2Cl_2 (90 mL).

After drying over anhydrous Na₂SO₄, the solvent was removed. The crude product was purified by column chromatography silica gel with petroleum ether/CH₂Cl₂ (5/1, v/v) to get yellow oil (11.9 g, 93%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.49–7.40(m, 4H), 7.22 (t, J = 7.2 Hz, 2H), 4.30 (t, J = 7.2 Hz, 2H), 1.90–1.83 (m, 2H), 1.41-1.24 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); FAB-MS (m/z): 335 [M]⁺.

N-Dodecyl-3,6-diiodo-carbazole

N-Dodecyl-carbazole (5.0 g, 14.9 mmol) and KI (3.2 g, 19.4 mmol) were added in acetic acid (60 mL). The mixture was heated to reflux for 30 min. After cooling for a while, KIO₃ (4.8 g, 22.4 mmol) was slowly added under stirring. After gradual disappearance of purple color, the reaction mixture was reheated to reflux for 30 min. After cooling to room temperature, the mixture was poured into ice water (100 mL). The mixture was extracted by CH₂Cl₂ (4×40 mL) and the organic phase was washed with 0.5 M Na₂CO₃ (30 mL). After drying over anhydrous Na₂SO₄, the solvent was removed. The crude product were purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (5/1, v/v) to give the brown solid (4.3 g, 81%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.33 (s, 2H), 7.71(d, *J* = 8.6 Hz, 2H), 7.17 (t, *J* = 8.8 Hz, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 1.90–1.83 (m, 2H), 1.41–1.24 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); FAB-MS (m/z): 587 [M]⁺.

General synthetic procedure for FLU-SiMe₃, TPA-SiMe₃ and CAZ-SiMe₃.

The aromatic halide (1.0 equiv), trimethylsilylacetylene (4.0 equiv), Pd(PPh₃)₂Cl₂ (0.05 equiv) and CuI (0.05 equiv) was mixed in the Et₃N (20 mL) and stirred at room temperature for 30 min. Then, the reaction was allowed to proceed at 70 °C for 12 h. After cooling to room temperature, the precipitation was removed by filtration. The filtrate was concentrated under vacuum. The crude product was further purified by column chromatography on silica gel with petroleum ether

as eluent to obtain the pure product.

FLU-SiMe₃: (Yield: 89%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.59 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 6.4 Hz, 2H), 7.26 (s, 2H) 1.94–1.90 (m, 4H), 1.22-1.01 (m, 36H), 0.86 (t, J = 7.0 Hz, 6H), 0.51 (br, 4H), 0.28 (s, 18H); FAB-MS (m/z): 694 [M]⁺.

TPA-SiMe₃: (Yield: 88%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.30 (t, 4H, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 4H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 2H), 1.81–1.74 (m, 2H), 1.31–1.26 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.23 (s, 18H); FAB-MS (m/z): 621 [M]⁺.

CAZ-SiMe₃: (Yield: 86%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.20 (s, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.4 Hz, 2H), 4.23 (t, J = 7.2 Hz, 2H), 1.84–1.80 (m, 2H), 1.41–1.22 (m, 18H), 0.89 (t, J = 6.8 Hz, 3H), 0.30 (s, 18H); FAB-MS (m/z): 527 [M]⁺.

General synthetic procedure for L-FLU, L-TPA and L-CAZ.

Under a N₂ atmosphere, **FLU-SiMe₃/TPA-SiMe₃/CAZ-SiMe₃** (1.0 equiv) and [*n*-Bu₄N]F (2.2 equiv) were mixed in CH₂Cl₂ (30 mL). The reaction mixture was stirred for 30 min at room temperature and then was washed with water (3×20 mL). The organic phase was dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by column chromatography on silica gel with petroleum ether as eluent to get the pure product as colorless oil.

L-FLU: (Yield: 92%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.63 (d, *J* = 8.0 Hz, 2H), 7.49–7.46 (m, 4H, Ar), 3.15 (s, 2H), 1.93 (m, 4H), 1.28–1.03 (m, 36H), 0.86 (t, *J* = 5.2 Hz, 6H), 0.56 (m, 4H); ¹³CNMR (100 MHz, CDCl₃): δ (ppm) 151.03, 140.97, 131.23, 126.53, 120.81, 119.96, 84.51, 55.19, 40.21, 31.90, 29.94, 29.59, 29.54, 29.32, 29.24, 23.65, 22.68; FAB-MS (m/z): 550 [M]⁺.

L-TPA: (Yield: 89%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.33 (d, J = 8.4 Hz, 4H), 7.04 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 8.0 Hz, 2H), 3.94 (t, J = 6.4 Hz, 2H), 3.03 (s, 2H), 1.78 (m, 2H, CH₂), 1.47–1.26 (m, 18H), 0.88 (t, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.78, 145.91, 137.10, 131.21, 126.16, 120.21, 113.67, 113.22, 81.89, 66.34, 30.04, 27.80, 27.77, 27.74, 27.53, 27.48, 27.42, 24.19, 20.82, 12.27; FAB-MS (m/z): 477 [M]⁺. **L-CAZ**: (Yield: 91%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.20 (s, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 3.07 (s, 2H), 1.83 (m, 2H), 1.29–1.21(m, 18H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 138.74, 128.22, 122.87, 120.32, 110.74, 107.06, 82.83, 73.56, 41.43, 30.01, 27.68, 27.63, 27.56, 27.43, 27.00, 25.32, 20.79, 12.24; FAB-MS (m/z): 383 [M]⁺.

L-P1

Under a N₂ atmosphere, to the mixture of 1,4-diiodobenzene (1.32 g, 4.00 mmol) and THF (40 mL), *n*-BuLi (3.52 mL, 2.5 M in hexane) was added slowly with a syringe at -78 °C. After addition, the reaction mixture was allowed to stir for 30 min at this temperature. Then, chlorodiphenyl phosphine (1.58 ml, 8.80 mmol) was added. The reaction temperature was raised to room temperature slowly and the reaction mixture was stirred for 1 h. After water quenching, the reaction mixture was extracted with CH_2Cl_2 and the organic phase was dried over anhydrous Na₂SO₄. After concentration, the crude product was purified by preparative TLC on silica eluting with petroleum ether/ CH_2Cl_2 (9/1, v/v) to obtain the product as white solid (0.82 g, 46%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.35–7.29 (m, 20H), 7.25–7.22 (m, 4H); ³¹P NMR (161.9 MHz, CDCl₃): -5.70; FAB-MS (m/z): 446 [M]⁺.

General synthetic procedure for L-P1-Au/L-P2-Au

NaAuCl₄ (0.50g, 1.39 mmol) was dissolved in mixed solvent EtOH/H₂O (10 mL, v:v =1:1) and

methyl sulfide was added drop wisely until white precipitation appeared. The white product was obtained by filtration and dried (0.39 g). Under a N₂ flow, the white solid (2.1 equiv) and L-**P1/L-P2** (1.0 equiv) were added to CH_2Cl_2 (20 mL) at room temperature. After stirring for 1.5 h, the solvent was removed and the white solid was washed with ether (5×10 mL). The compounds were obtained as white solid with high yields.

L-P1-Au

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.59–7.49 (m, 24H); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 33.04; FAB-MS (m/z): 910 [M]⁺.

L-P2-Au

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.66–7.61 (m, 8H), 7.54–7.45 (m, 12H), 2.82–2.73 (m, 4H), 1.98–1.56 (m, 2H); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 26.72; FAB-MS (m/z): 876 [M]⁺.

General synthetic procedure for Pt(II) monomeric acetylides

Under N_2 atmosphere, *trans*-[PtCl₂(PBu₃)₂] (1.0 equiv) was added to the solution of the corresponding diethynyl aromatic ligand (2.1 equiv) in EtN₃/CH₂Cl₂ (v:v=1:1). Then, a small amount of CuI was added. The reaction mixture was stirred for 10 h at room temperature. After removing the solvent, the residue was purified by preparative TLC. The title products were obtained with high yields.

FLU-Pt-FLU

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.56 (d, J = 7.6 Hz, 2H, Ar), 7.52 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.42 (s, 2H), 7.24 (d, J = 8.4 Hz, 2H, Ar), 3.12 (s, 2H,), 2.22-2.18 (m, 12H), 1.95-1.83 (m, 8H), 1.67-1.64 (m, 12H), 1.52-1.43 (m, 12H), 1.29-1.02 (m, 72H), 0.94 (t, J= 8.0 Hz, 18H), 0.86 (t, J = 6.8 Hz ,12H), 0.57 (br, 8H); ¹³CNMR (100 MHz, CDCl₃): δ (ppm) 150.85, 142.24, 137.39, 131.25, 129.89, 128.37, 126.51, 125.36, 119.72, 119.53, 119.33, 110.38, 109.08, 85.10, 54.99, 40.67, 34.47, 32.06, 30.31, 29.83, 29.76, 29.75, 29.72, 29.53, 29.00, 26.55, 24.68, 24.62, 24.55, 24.32, 24.15, 23.98, 23.91, 22.83, 14.26, 14.01; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 2.93 (¹*J*_{P-Pt}= 2348 Hz).

TPA-Pt-TPA

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.32 (d, J = 6.8 Hz, 4H), 7.19 (d, J = 7.2 Hz, 4H), 7.08 (d, J = 6.8 Hz, 4H), 6.94 (t, J = 8.8 Hz, 8H), 6.87 (d, J = 7.6 Hz, 4H), 3.97 (t, J = 5.2 Hz, 4H), 3.03 (s, 2H), 2.17 (m, 12H), 1.81-1.80 (m, 4H), 1.63 (m, 12H), 1.51-1.46 (m, 12H), 1.37-1.31 (m, 36H), 0.98-0.94 (m, 24H); ¹³CNMR (100 MHz, CDCl₃): δ (ppm) 156.26, 148.77, 144.15, 139.73, 133.02, 131.78, 127.69, 124.08, 120.51, 115.46, 113.47, 108.57, 84.30, 75.91, 68.33, 32.05, 29.80, 29.77, 29.72, 29.54, 29.48, 29.46, 26.46, 26.21, 24.62, 24.55, 24.49, 24.12, 23.95, 23.78, 22.82, 14.27, 13.99; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 2.77 (¹ $J_{P-Pt}= 2362$ Hz).

CAZ-Pt-CAZ

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.16 (s, 2H), 7.99 (s, 2H), 7.55 (dd, J = 8.4, 1.6 Hz, 2H), 7.43 (dd, J = 8.4, 1.2 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 4.24 (t, J =7.2 Hz, 4H), 3.07 (s, 2H), 2.25-2.22 (m, 12H), 1.85-1.80 (m, 4H), 1.69-1.67 (m, 12H), 1.53-1.46 (m, 12H), 1.32-1.23 (m, 36H), 0.97 (t, J = 7.2 Hz, 18H), 0.88 (t, J = 6.8 Hz, 6H); ¹³CNMR (100 MHz, CDCl₃): δ (ppm) 140.70, 138.81, 129.71, 129.54, 124.71, 122.78, 122.70, 122.32, 120.68, 111.78, 108.74, 108.57, 85.39, 75.08, 43.38, 32.05, 29.74, 29.71, 29.65, 29.53, 29.48, 29.12, 27.42, 26.58, 24.74, 24.67, 24.60, 24.31, 24.14, 23.97, 22.84, 14.28, 14.07; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 2.93 (¹ $J_{P-Pt}= 2371$ Hz).

General synthetic procedure for Pt(II) homometallic polyynes

Under N₂ atmosphere, trans-[PtCl₂(PBu₃)₂] (1.0 equiv) and corresponding diethynyl aromatic

ligand (1.0 equiv) were mixed in EtN₃/CH₂Cl₂ (v:v=1:1). After completely dissolved, a small amount of CuI was added. The reaction mixture was stirred for 10 h at room temperature. After concentration, the residue was purified by preparative TLC. The products were obtained with high yields.

FLU-Pt

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.46-7.44 (d, 2H, Ar), 7.21 (m, 4H, Ar), 2.19 (br, 12H, PBu₃), 1.85 (br, 4H, –CH₂–), 1.66 (br, 12H, PBu₃), 1.50-1.45 (m, 12H, PBu₃), 1.25-1.02 (m, 36H), 0.96(t, 18H, PBu₃), 0.86 (t, 6H, –CH₃), 0.62 (br, 4H, –CH₂–); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 2.81.

TPA-Pt

¹H NMR (400 MHz, CDCl₃):*δ* (ppm) 7.10-7.08 (d, 4H, Ar), 7.04-7.00 (m, 2H, Ar), 6.87-6.78 (m, 6H, Ar), 3.92 (t, 2H, –OCH₂–), 2.11 (br, 12H, PBu₃), 1.76 (m, 2H, –CH₂–), 1.57 (m, 12H, PBu₃), 1.48-1.39 (m, 12H, PBu₃), 1.32-1.26 (m, 18H, –CH₂–), 0.93-0.84 (m, 21H, PBu₃ and – CH₃); ³¹P NMR (161.9 MHz, CDCl₃): *δ* (ppm) 2.65.

CAZ-Pt

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.97-7.94 (d, 2H, Ar), 7.40-7.38 (d, 2H, Ar), 7.21-7.19 (d, 2H, Ar), 4.20 (t, 2H, -NCH₂-), 2.24 (br, 12H, PBu₃), 1.86 (br, 2H, -CH₂-), 1.69 (br, 12H, PBu₃), 1.54-1.47 (m, 12H, PBu₃), 1.33-1.25 (m, 18H, -CH₂-), 0.99-0.95 (t, 18H, PBu₃), 0.90-0.86 (t, 3H, -CH₃); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 2.98.



Scheme S1 Synthetic scheme for the monomeric Pt(II) acetylides, the homometallic Pt(II) polyynes and the Au(I) precursors.



Fig. S1 UV-vis absorption spectra for homometallic Pt(II) polyynes in CH₂Cl₂ at 298 K.



Fig. S2 UV-vis absorption spectra for monomeric Pt(II) acetylides in CH₂Cl₂ at 298 K.

			1 1			
Compound	λ_{max}	$\lambda_{cut\text{-}off}$	Blue-shift value of	Blue-shift value of	Red-shift value of	Red-shift value of
	(nm)	(nm)	λ_{max} referring to	$\lambda_{\text{cut-off}}$ referring to	λ_{max} referring to	$\lambda_{\text{cut-off}}$ referring to
			homometallic Pt(II)	homometallic Pt(II)	monomeric Pt(II)	monomeric Pt(II)
			polyynes (nm)	polyynes (nm)	acetylides (nm)	acetylides(nm)
P1-FLU	387	416	12	2	15	16
P1-TPA	377	414	9	2	7	16
P1-CAZ	317	389	36	13	17	14
P2-FLU	384	413	15	5	12	13
P2-TPA	373	412	13	4	3	14
P2-CAZ	316	386	37	16	16	11
FLU-Pt	399	418			27	18
TPA-Pt	386	416			16	18
CAZ-Pt	353	402			53	27
FLU-Pt-FLU	372	400				
TPA-Pt-TPA	370	398				
CAZ-Pt-CAZ	300	375				

Table S1 Data for the heterobimetallic Au(I)-Pt(II) polyynes, monomeric Pt(II) acetylides and homometallic Pt(II) polyynes in absorption spectra.



Fig. S3 PL spectra of the heterobimetallic Au(I)-Pt(II) polyynes in CH₂Cl₂ at 77 K. (a) **P1-FLU** and **P2-FLU**, (b) **P1-TPA** and **P2-TPA**, (c) **P1-CAZ** and **P2-CAZ**



Fig. S4 OPL mechanism of reverse saturable absorption (RSA) mechanism of the T_1 states for nano-second laser.



Fig. S5 Open-aperture Z-scan results for the homometallic Pt(II) polyynes (T_0 ca. 90%).



Fig. S6 PL spectra of P1-FLU doped in PS film and P2-FLU doped in PS film.