Supporting Information

Tuning two-photon absorption cross-sections for triphenylamine derivatives

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1. Materials and Methods

1.1 Materials

Fluorene, triphenylamine, 1,3-dibromo-5,5-dimethylhydantoin, 4-iodo-*N*,*N*-diphenylbenzenamine, $Pd(PPh_3)_2Cl_2$, CuI and trimethylsilyl acetylene were used as purchased from Aldrich without further purification. Other organic solvents with ACS grade were purchased from Fisher.

1.2 Instrumental Methods

All reagents are used as received unless otherwise specified. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy. NMR spectra were collected on a Bruker DPX 300 or DPX 500 spectrometer with d-chloroform as the solvent. Absorption spectra were recorded with a SHIMAZU UV-Vis 1770 spectrometer. Emission spectra were recorded with a Perkin Elmer LS55 fluorometer. EI-mass and elemental analysis were carried out by the Chemical Molecular and Materials Analysis Centre (CMMAC) of the National University of Singapore. Cyclic voltammetric (CV) measurements were carried out with a computer-controlled Eco Chemie μAutolab III potentiostat utilizing a 1 mm diameter planar Pt working electrode. Potentials were referenced to the errocene/ferrocenium (Fc/Fc+) redox couple, which is used as an internal standard. The supporting electrolyte was 0.1 M Bu_4NPF_6 and analytical grade CH_2Cl_2 was used as the solvent and distilled over calcium hydride then transferred under nitrogen into the electrochemical cell.

Two-photon absorption cross sections were measured using a Z-scan method. The laser system employed was the Clark-MXR CPA- 2001 regenerative amplifier operating at a repetition rate of 250Hz, with a Light Conversion TOPAS optical parametric amplifier. The pulse duration was about 150 fs and the light intensities used were about 70 GW/cm^2. Solutions of measured samples with concentrations of 5 μM were prepared using chloroform as a solvent. The two-photon cross sections were calculated from dependences of the nonlinear absorption (which is proportional to the imaginary part of the nonlinear phase shift in a Z scan experiment) of solutions on the concentration.

2. Synthesis

2-Bromofluorene (**1**). A mixture consisting fluorene (5g, 30 mmol), 1,3-dibromo-5,5-dimethylhydantoin (4.3g, 15 mmol), H2SO4 (2M, 7.5ml) and dichloromethane (150ml) was stirred at room temperature for 2 hrs. The mixture was washed by water and dried over MgSO4. After the solvent was distilled out, the residue was purified over silica gel using hexane as the eluent to give white solid (6.37 g, 86%). 1H_NMR (CDCl3, 300 MHz) δ 7.72 (d, 1H), 7.61-7.52 (m, 2H), 7.49-7.42 (m, 2H), 7.36-7.25 (m, 2H), 3.82 (s, 2H); 13C_NMR (CDCl3, 75 MHz) δ 145.2, 143.1, 140.9, 130.1, 128.5, 127.3, 127.1, 125.2, 121.3, 120.7,110.9, 36.9. Anal. Calcd for C13H9Br: C, 63.70; H, 3.70; Found: C, 63.72; H, 3.78.

2-Bromo-9,9-dihexyl-fluorene **(2)**. To a mixture consisting 1 (6.37g), NaOH (2.29g), DMSO (40ml) and H2O (5ml), a solution of bromohexane (9.2ml) in DMSO (5ml) was added slowly. The mixture was cooled to room temperature and stirred overnight. The reaction mixture was poured into water and extracted with dichloromethane. The organic phase was washed with water and dried over MgSO4. After removal of solvent, the residue was purified over silica gel using hexane as the eluent to give yellowish oil (9.1 g , 85%). 1H_NMR (CDCl3, 300 MHz) δ 7.64-7.68 (m, 1H), 6.53-6.56 (d, 1H), 7.42-7.45 (m, 2H), 7.31-7.34 (m, 3H), 1.85-2.00 (m, 4H), 1.08-1.14 (m, 12H), 0.74-0.78 (m, 6H), 0.57-0.61 (m, 4H); 13C_NMR (75 MHz, CDCl3): δ 153.0, 150.3, 141.1, 140.1, 140.0, 129.8, 127.4, 126.9, 126.6, 126.1, 122.8, 121.0, 119.7, 55.3, 40.4, 31.4, 29.6, 23.6, 22.5, 13.9; EI-Mass: 412.2, 414.2. Anal. Calcd for C25H33Br: C, 72.63; H, 8.05; Found: C, 72.59; H, 8.09.

2-(Trimethylsilyl ethynyl)-9,9-dihexylfluorene **(3)**. A mixture consisting 2 (0.38 g), CuI (9 mg), Pd(PPh3)2Cl2 (33 mg) and triethylamine (20 ml) was degassed for 15 mins. Then trimethylsilyl acetylene (0.16 ml) was injected by a syringe. The mixture was stirred at 70°C overnight in argon atmosphere. The mixture was poured into water and extracted by dichloromethane. After the solvent was removed under reduced pressure, the residue was purified over silica gel using hexane as the eluent to give yellow solid (0.24 g, 61%). 1H_NMR (CDCl3, 300 MHz) δ 7.65-7.66 (m, 1H), 7.59-7.61 (m, 1H), 7.44-7.46 (m, 2H), 7.29-7.31 (m, 3H), 1.91-1.97 (t, 4H), 1.02-1.05 (m, 12H), 0.74-0.75 (t, 6H), 0.56-

0.58 (m, 4H). 0.28 (s, 9H). Anal. Calcd for C30H42Si: C, 83.65; H, 9.83; Found: C, 83.62; H, 9.86.

2-Ethynyl-9,9-dihexylfluorene **(4)**. A mixture consisting 3 (0.24 g), KOH (0.67 g), H2O (3 ml), THF (5 ml) and methanol (8 ml) was stirred at room temperature for 3 hrs. The reaction mixture was poured into water and extracted with dichloromethane, then dried over anhydrous Na2SO4. The solvent was removed under reduced pressure to give yellow solid (0.19 g, 96%). 1H_NMR (CDCl3, 300 MHz) δ7.65-7.69 (m, 1H), 7.62-7.63 (m, 1H), 7.46-7.49 (m, 2H), 7.31-7.32 (m, 3H), 3.13 (s, 1H), 1.91-1.97 (t, 4H), 1.11-1.13 (m, 12H), 0.73-0.78 (t, 6H), 0.56-0.58 (m, 4H).

N-4-Trimethylsilylethynylphenyl diphenylamine **(5)**. A 100ml round bottom flask equipped with a condenser was charged with 4-iodo-*N*,*N*-diphenylbenzenamine (0.45 g) and triethylamine (45 ml). After the reaction mixture was bubbled with argon for 15 minutes, CuI (13 mg), $Pd(PPh_3)_2Cl_2$ (81 mg) and trimethylsilyl acetylene (0.24 ml) were added consequently. The mixture was stirred at 50 ^{o}C under argon for 4 hours before the addition of water to quench the reaction. The mixture was extracted by CH_2Cl_2 and dried over anhydrous Na_2SO_4. The crude product was purified by chromatography on silica gel using hexane as the eluent to give a yellow solid (0.3 g, 63%). ^{1}H_NMR (300MHz, $CDCl_3$) δ 7.40 (d, 2H), 7.32 (tr, 4H), 7.14 (m, 6H), 7.03(d, 2H), 0.34 (s, 9H); ^{13}C_NMR (75MHz, $CDCl_3$) δ 148.0, 147.1, 132.9, 129.3, 124.9, 123.5, 122.1, 115.9, 105.4, 93.0, 0.07; Mass-ESI: 341.1(M+, 100); Anal. Calcd for C23H23NSi: C, 80.89; H, 6.79; N, 4.10; Found: C: 80.92; H, 6.81; N, 4.08.

N-4-ethynylphenyl diphenylamine **(6)**. A solution of **5** (0.36 g) in 1:1 MeOH/THF (20 ml) with KOH (0.67 g) in water (3 ml) was stirred for 2 hours. After extracted with

CH_2Cl_2, washed by brine and dried over anhydrous Na_2SO_4, solvent was removed and a yellow solid was obtained (0.27 g, 96%). The compound was used without further purification. ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.38 (d, 2H), 7.31 (tr, 4H), 7.14(m, 6H), 7.02(d, 2H), 3.06 (s, 1H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 148.3, 147.1, 133.0, 129.4, 125.0, 123.6, 122.0, 114.7, 83.9, 76.2; Mass-ESI: 269.1(M+, 100)

Tris(4-iodophenyl)amine **(7)**. **7** was synthesized using the reported method.[19] ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.53 (d, 6H), 6.80 (d, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 146.5, 138.4, 126.0, 86.5.

T3. A mixture consisting **T2** (0.045 g), **4** **(**0.1 g), $Pd(PPh_3)_4$ (13 mg), CuI (2.2 mg) and triethylamine (6 ml) was stirred overnight at 70°C under argon protection. The reaction mixture was poured into water and extracted by dichloromethane. After the solvent was removed under reduced pressure, the residue was purified over silica gel using hexane and 5:1 hexane/CH_2Cl_2 as eluents to give yellow solid (0.059 g, 59 %). ^{1}H_NMR ($CDCl_3$, 300 MHz) δ 7.66-7.70 (m, 6H), 7.48-7.52 (m, 12H), 7.32-7.33 (m, 9H), 7.10-7.13 (d, 6H), 1.94-2.00 (t, 12H), 1.05-1.08 (m, 36H), 0.74-0.79 (t, 18H), 0.60-0.63 (m, 12H); ^{13}C_NMR (75 MHz, $CDCl_3$): δ 151.0, 150.8, 146.7, 141.3, 140.5, 132.8, 130.5, 127.5, 126.9, 125.9, 124.1, 122.9, 121.5, 120.0, 119.6, 118.2, 90.5, 89.2, 55.1, 40.4, 31.5, 29.7, 23.7, 22.6, 14.0; FAB-Mass: 1315.0; Anal. Calcd for C99H111N: C, 90.43; H, 8.51; N, 1.07; Found: C, 90.41; H, 8.54; N, 1.13.

B3. A mixture consisting **B2** (0.056 g), **4** **(**0.1 g), $Pd(PPh_3)_4$ (13 mg), CuI (2.2 mg) and triethylamine (6 ml) was stirred overnight at 70°C under argon protection. The reaction mixture was poured into water and extracted by dichloromethane. After the solvent was removed under reduced pressure, the residue was purified over silica gel using hexane and 5:1 hexane/CH_2Cl_2 as eluents to give yellow solid (0.074 g, 68 %). ^{1}H_NMR ($CDCl_3$, 300 MHz) δ 7.68-7.71 (m, 6H), 7.63 (s, 6H), 7.56-7.58 (m, 6H), 7.33-7.35 (m, 9H), 1.97-2.02 (t, 12H), 1.71 (s, 18H), 1.06-1.11 (m, 36H), 0.75-0.79 (t, 18H), 0.59-0.63 (m, 12H); ^{13}C_NMR (75 MHz, $CDCl_3$): δ 151.0, 150.8, 141.3, 140.5, 131.3, 130.5, 130.2, 127.4, 127.1, 126.9, 125.9, 122.9, 121.6, 119.9, 119.6, 118.1, 90.2, 89.7, 55.1, 40.5, 35.6, 33.1, 31.5, 29.7, 23.7, 22.6, 14.0; FAB-Mass: 1434.9. Anal. Calcd for C108H123N: C, 90.39; H, 8.64; N, 0.98; Found, C, 90.36; H, 8.68; N, 0.94.

T4. A mixture containing **6** (75 mg), **7** (44 mg), $Pd(PPh_3)_4$ (8 mg), CuI (2 mg) and triethylamine (10 mL) was stirred at 60 °C overnight under nitrogen protection. The reaction mixture was quenched with water then extracted with CH_2Cl_2, washed by brine and dried over anhydrous Na_2SO_4. The crude product was purified over silica gel using hexane and 4:1 hexane/ CH_2Cl_2 as eluent to give **T4** as a yellow solid (51 mg, 70 %). ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.38-7.36 (m, 12 H), 7.25-7.22 (m, 12H), 7.17-7.14 (m, 6H), 6.92-6.89 (m, 12H), 6.64-6.62 (m, 12H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 148.5, 147.0, 133.8, 131.4, 125.2, 123.4, 123.1, 115.4, 90.5. Accurate Mass-FAB: Calcd, 1047.4348; Found, 1047.4339; Anal. Calcd for $C_{78}H_{54}N_4$: C, 89.45; H, 5.20; N, 5.35; Found: C, 89.62; H, 5.30; N, 5.39