Supplementary Material (ESI) for Chemical Communications

Supporting Information

For

Diphenylamine end-capped 1,4-Diketo-3,6-diphenyl-pyrrolo-[3,4-*c*]-pyrrole (DPP) with large two-photon absorption cross-sections and strong two-photon excitation red-fluorescence†

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Synthesis and characteristics of the intermediates and the final compounds.

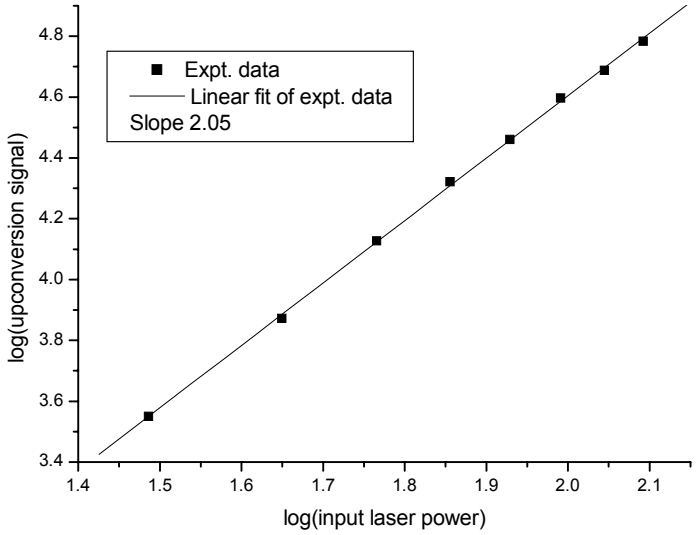
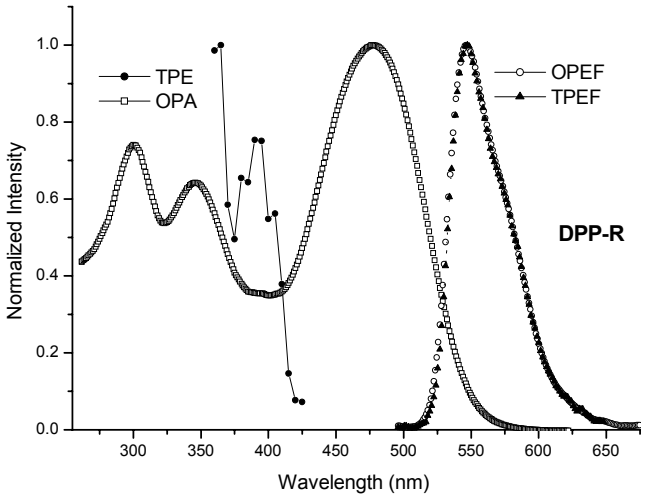
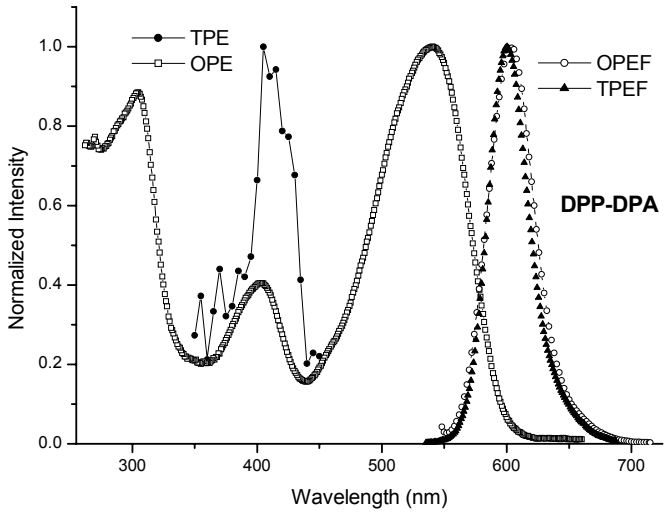


Figure S1. Depndence of output fluorescence intensity (up-conversion signal) of DPP-DPA excited at 800 nm in chloroform on the input laser power (20-170 mW).


TPE
OPA
OPEF
TPEF
DPP-R
Normalized Intensity
Wavelength (nm)


TPE
OPE
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TPEF
DPP-DPA
Normalized Intensity
Wavelength (nm)

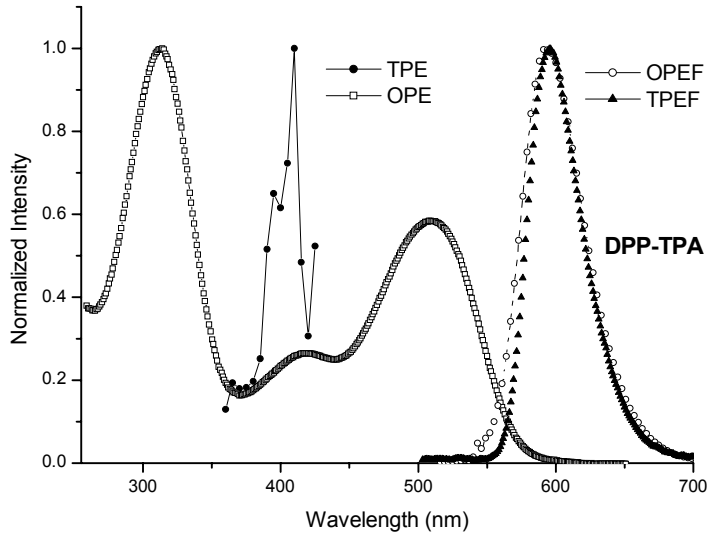
TPE
OPE
OPEF
TPEF
DPP-TPA
Normalized Intensity
Wavelength (nm)

Figure S2. Normalized one-photon absorption (OPE) and two-photon excitation (TPE) spectra (left) and one-photon (OPEF) and two-photon (TPEF) excitation fluorescence spectra (right) of **DPP-R**, **DPP-DPA** and **DPP-TPA**. The two-photon spectrum is plotted against λ/2 (twice the photon energy).

Materials. Toluene, benzene and tetrahydrofuran were distillated over metallic sodium before use. $Pd_2(dba)_3$, DPPF, and $Pd(PPh_3)_4$ were purchased from Aldrich Chemical Co.. Other solvents and reagents were analytical grade and used as received, unless otherwise claimed.

Measurements. All spectroscopic measurements were performed in toluene or dichloromethane solutions (spectroscopic grade). One-photon absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer, and the fluorescence spectra were obtained with an Amico Bowman series 2 luminescence spectrometer. The fluorescence quantum yield was determined in toluene by the literature method using fluorescein in water (pH = 11) as the reference. NMR spectra were recorded on a Bruker AV-500 spectrometer in chloroform solutions with tetramethylsilane (TMS) as an internal standard. The elemental analysis was performed on Perkin-Elmer 2400.

The two-photon absorption cross-section of the compounds has been measured with the two-photon-induced fluorescence method by using the femto-second laser pulses as described.[2-4] The excitation light source was a mode-locked Ti:sapphire fs laser (Spectra-Physics, Tsunami 3941, 700-910 nm, 80 MHz, <120fs) which was pumped

by a compact cw prolite diode laser (Spectra-physics, Millennia Pro 5S). The fluorescence signal was recorded by a spectrofluorometer (Ocean Optics, USB2000). Samples were dissolved in chloroform at concentrations of 1.0×10^{-4} M and the two-photon induced fluorescence intensity was measured at 700–910 nm by using rhodamine B (1.1×10^{-4} M in methanol) as the reference. The intensities of the two-photon induced fluorescence spectra of the reference and sample under the same measurement conditions were determined and compared (input power 100 mW, which is among the linear dependence of fluorescence intensity on the square of the excitation intensity). The TPA cross section of sample δ_s, measured by using the two-photon-induced fluorescence measurement technique, can be calculated by using the equation: $\delta_s = [(S_s\Phi_r c_r)/(S_r\Phi_s c_s)]\delta_r$, where the subscripts s and r stand for the sample and reference molecules respectively. S is the integral area of the two-photon fluorescence; Φ is the fluorescence quantum yield and c is the number density of the molecules in solution. δ_r is the TPA cross section of the reference molecule.

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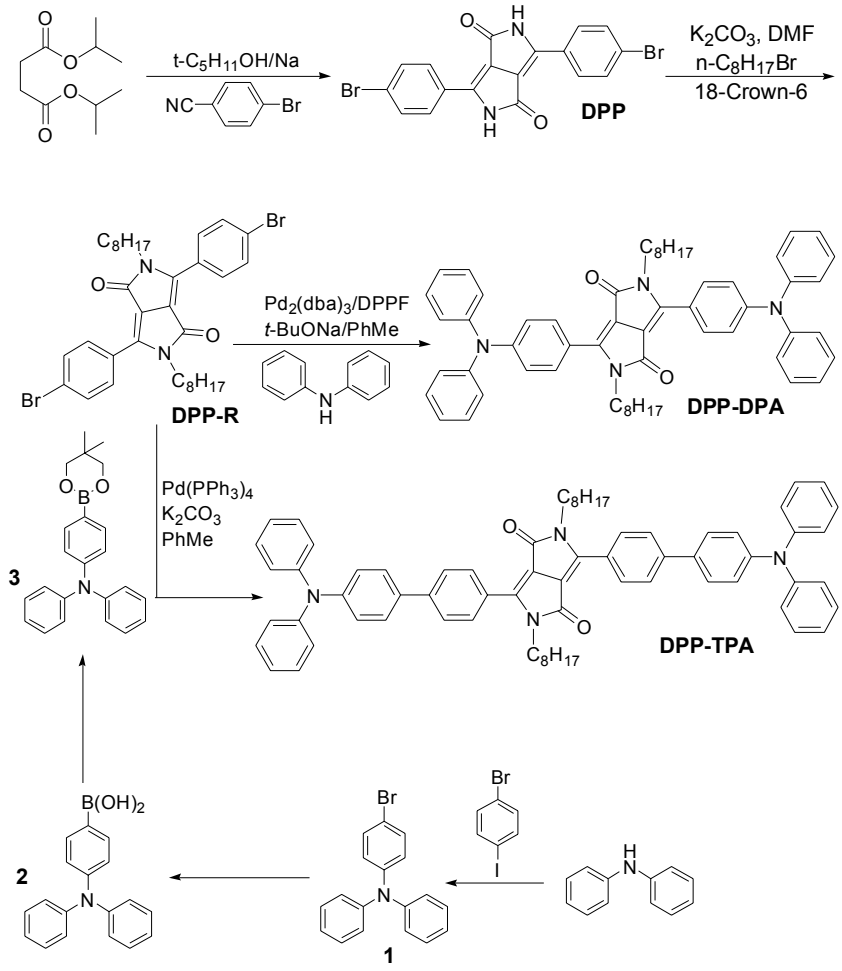
Synthesis of DPP derivatives



(4-Bromo-phenyl)-diphenylamine (1). 1-Bromo-4-iodobenzene (2.83 g, 10.0 mmol), $Pd_2(dba)_3$ (0.379 g, 0.411 mmol), DPPF (0.219 g, 0.3542 mmol) and toluene (50 mL) were added to a dried two-neck flask and purged with nitrogen. This solution was stirred for 1h under N_2 atmosphere and then diphenylamine (1.35 g, 8.01 mmol), and *t*-BuONa (3.85 g, 40.2 mmol) were added. The resulting mixture was stirred for 24h at 70 ^{o}C and then filtered. The filtrate was evaporated to remove the solvent. The crude product was purified by column chromatography on silica gel using hexane as eluent to afford white solid (1.87 g, 72.1%). ^{1}H NMR ($CDCl_3$): δ (ppm): 6.95 (d, 2H),

7.07 (m, 6H), 7.24 (t, 4H), 7.31 (d, 2H). Anal. Calcd for $C_{18}H_{14}BrN$: C, 66.68; H, 4.35; Br, 24365; N, 4.32. Found: C, 66.66; H, 4.37; Br, 24.64; N, 4.33.

4-(Diphenylamino)phenylboronic acid (2). A solution of **1** (1.56 g, 4.81 mmol) in anhydrous THF (35 mL) was slowly added *n*-butyllithium (1.8 mL, 2.85 M in hexane) under N_2 at -78 ^oC. The resulting solution was stirred for 1 h and then $B(OCH_3)_3$ (1.2 mL, 10.9 mmol) was added. After stirring 30 min at -78 ^oC, the mixture was stirred for additional 8 h at room temperature. The reaction was quenched with 1 M HCl (25 mL) and extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and solvent was removed. The crude product was re-crystallized two times from hexane to afford an off-white solid (0.91 g, 66%). This product was used in the next step without further purification and characterization.

[4-(5,5-Dimethyl-[1,3,2]dioxaborinan-2-yl)-phenyl]-diphenyl-amine (3). A mixture of 4-(diphenylamino)phenylboronic acid (0.88 g, 3.04 mmol) and 2,2-dimethyl-propane-1,3-diol (0.46 g, 4.42 mmol) in toluene (15 mL) was refluxed overnight. The solvent was removed and the crude product was purified by a column chromatography on silica gel using dichloromethane/hexane (1/5) as eluent to afford a white solid (0.97 g, 89%). ^1H NMR (500 MHz, $CDCl_3$), δ(ppm): 7.70 (d, 2H), 7.26 (m, 4H), 7.15 (t, 4H), 7.01 (t, 4H), 3.78 (s, 4H), 1.05 (m, 6H). Anal. Calcd for $C_{87}H_{124}B_2O_4$: C, 83.23; H, 9.95; B, 1.72; O, 5.10. Found: C, 83.07; H, 10.24.

3,6-Bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP). Sodium (2.3g, 100mmol) was first dissolved in 50 mL of *t*-amyl alcohol at about 90 ^oC. over 1 h with a catalytic amount of $FeCl_3$. The solution was cooled to about 50 ^oC, then 9.1 g

(50 mmol) of 4-bromobenzonitrile was added, and the mixture was heated to 90 ^{o}C. Then, 4.04 g (20 mmol) of diisopropyl succinate in 20 mL of *t*-amyl alcohol was added dropwise over 30 min. Subsequently, the resulting suspension was kept for 20 h more at 90 ^{o}C. The reaction mixture was then cooled to 50 ^{o}C, 20 mL of glacial acetic acid was slowly added and refluxed briefly, and the reaction mixture was filtered through a sinter glass filter (size G4). After the residue was washed several times with hot methanol and water, the resulting solid was dried overnight in oven at 110 ^{o}C. A bluish-red solid was obtained (4.85 g, 54%). IR (cm^{-1}): 3139 (N–H stretching), 1641 (C=O stretching), 1604 (N–H bending or Ar–C=C stretching), 1533, 1490, 1438, 1390, 819. Anal. Calcd for $C_{18}H_{10}Br_2N_2O_2$: C, 48.46; H, 2.26; Br, 35.82; N, 6.28; O, 7.17. Found: C, 48.54; H, 2.33; N, 6.41.

3,6-Bis(4-bromophenyl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4-dione (DPP-R). **DPP** (4.35 g, 3.91 mmol), K_2CO_3 (1.93 g, 14 mmol), and 18-crown-6 (10 mg) in 150 mL of dimethylformamide (DMF) were slowly added 1-bromooctane (2.89 g, 15mmol, in 30 mL DMF) at 120 ^{o}C. The reaction mixture was kept for an additional 6 h at 120 ^{o}C and then cooled to room temperature. The mixture was filtered and washed with 50 mL of chloroform. The filtrate was washed with water and the organic phase was dried over anhydrous $MgSO_4$. The crude product was purified via column chromatography on silica gel using petroleum ether to ethyl acetate/petroleum ether (1/30). The bright orange crystals were obtained (0.85 g, 33%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.60-7.70 (m, 8H), 3.70 (t, 4H), 1.52 (m, 4H), 1.21 (m, 20H), 0.86 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 162.17, 147.43, 132.02, 130.04,

126.76, 125.61, 109.67, 41.63, 31.55, 29.23, 29.01, 28.86, 26.54, 22.55, 14.04. Anal. Calcd for $C_{34}H_{42}Br_2N_2O_2$: C, 60.90; H, 6.31; Br, 23.83; N, 4.18; O, 4.77. Found: C, 60.83; H, 6.29; N, 4.11.

3,6-Bis(4-(diphenylamino)phenyl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4-dione (DPP-DPA). DPP-R (0.32 g, 0.48 mmol), $Pd_2(dba)_3$ (48 mg, 50.5 μmol), DPPF (28 mg, 45 μmol), and toluene (10 mL) were added to a 50 mL of dried two-necked flask under nitrogen. After stirring for 1 h under N_2 atmosphere, diphenylamine (0.23 g, 1.31 mmol) and *t*-BuONa (0.48 g, 5.0 mmol) were added. This mixture was stirred for 24 h at 85 ^oC and then cooled to room temperature. The solid was filtered off and the solvent was removed. The crude product was purified by a column chromatography on silica gel using dichloromethane/hexane (1/2) as eluent to give a deep-red solid (0.31 g, 77%). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.31 (d, 4H), 7.29 (m, 8H), 7.15 (t, 8H), 7.12 (d, 4H), 7.05 (d, 4H), 3.74 (t, 4H), 1.58 (m, 4H), 1.21 (m, 20H), 0.80-0.86 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 160.18, 150.18, 147.27, 146.32, 130.06, 129.58, 126.04, 126.03, 124.53, 120.43, 120.26, 42.30, 31.78, 29.718, 29.60, 29.11, 26.83, 22.64, 14.12. Anal. Calcd. for $C_{58}H_{62}Br_2N_4O_2$: C, 82.23; H, 7.38; N, 6.61; O, 3.78. Found: C, 82.31; H, 7.36; N, 6.71.

3,6-Bis-(4'-diphenylamino-biphenyl-4-yl)-2,5-dioctyl-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP-TPA). DPP-R (0.32g, 0.48 mmol), $Pd(PPh_3)_4$ (36 mg, 31 μmol), $(C_4H_9)_4NBr$ (0.012 g), [4-(5,5-Dimethyl-[1,3,2]dioxaborinan-2-yl)-phenyl]-diphenyl-amine (0.43 g, 1.2 mmol), 2M Na_2CO_3 (6 mL), and toluene (10 mL) were added to a 50 mL of one-neck flask under nitrogen. The mixture was refluxed 24 h under N_2

atmosphere and then extracted with toluene. The organic phase was dried over $MgSO_4$ and the solvent was removed. The crude product was purified by a column chromatography on silica gel using dichloromethane/hexane (1/2) as eluent to afford a red solid (0.39 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$), δ(ppm): 7.75 (d, 4H), 7.68 (d, 4H), 7.53 (d, 4H), 7.33 (m, 12H), 7.15 (m, 8H), 7.06 (m, 4H), 3.82 (t, 4H), 1.64 (m, 4H), 1.25 (m, 20H), 0.84 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 160.37, 145.94, 144.92, 140.70, 130.78, 126.84, 126.73, 125.27, 125.15, 124.25, 123.92, 122.25, 120.81, 120.78, 107.27, 39.60, 29.22, 26.98, 26.61, 26.51, 24.24, 20.09, 11.57. Anal. Calcd. for $C_{70}H_{70}N_4O_2$: C, 84.13; H, 7.06; N, 5.61; O, 3.20. Found: C, 84.17; H, 7.15; N, 5.69.