Electronic Supplementary Information (ESI):

**Substituent effects on the aggregation-induced emission and two-photon absorption properties of triphenylamine-dibenzo[a,c]phenazine adducts**

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Scheme S1 Synthetic routes to Q1–Q5.

Experimental section

Materials

Synthesis of 4, 4'-[(dibenzo[a,c]phenazine-10,13-diyl)bis(N,N-diphenylaniline)] (Q1). A mixture of 10,13-dibromodibenzo[a,c]phenazine (219 mg, 0.5 mmol), (4-(diphenylamino)phenyl)boronic acid (434 mg, 1.0 mmol), and Pd(PPh$_3$)$_4$ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/DCM (2/1, v/v) as eluent to obtain compound Q1 (620 mg, 54% yield) as a yellow solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.17 (dd, $J = 8.0, 1.4$ Hz, 4H), 8.00 (s, 2H),
Synthesis of 4, 4'-((dibenzo[<i>a</i>,<i>c</i>]phenazine-10,13-diyl)bis(N,N-bis(4-octylphenyl)aniline) (Q3). A mixture of 10,13-dibromodibenzo[<i>a</i>,<i>c</i>]phenazine (220 mg, 0.5 mmol), (4-(bis(4-octylphenyl)amino)phenyl)boronic acid (520 mg, 1.0 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/DCM (1/1, v/v) as eluent to generate Q3 (350 mg, 57% yield) as an orange solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-<i>d</i>) δ 9.23–9.16 (m, 2H), 8.56 (d, <i>J</i> = 8.0 Hz, 2H), 8.00 (s, 2H), 7.90 (d, <i>J</i> = 8.6 Hz, 4H), 7.78 (t, <i>J</i> = 7.5 Hz, 2H), 7.72–7.66 (m, 2H), 7.34–7.26 (m, 12H), 7.17 (d, <i>J</i> = 8.6 Hz, 8H), 1.75 (s, 8H), 1.40 (s, 24H), 0.79 (s, 36H). <sup>13</sup>C NMR (100 MHz, Chloroform-<i>d</i>) δ 147.72, 144.99, 144.66, 141.03, 140.23, 138.83, 132.15, 131.87, 131.80, 130.73, 130.05, 129.22, 127.95, 127.03, 126.61, 123.95, 122.87, 122.23, 57.25, 38.26, 32.50, 31.82, 31.54. HRMS (ESI) (m/z): [M+H] Calcd for C<sub>88</sub>H<sub>103</sub>N<sub>4</sub>: 1215.8183, found: 1215.8186.

Synthesis of 4, 4'-((dibenzo[<i>a</i>,<i>c</i>]phenazine-10,13-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (Q4). A mixture of 10,13-dibromodibenzo[<i>a</i>,<i>c</i>]phenazine (358 mg, 0.8 mmol),
(4-(bis(4-methoxyphenyl)amino)phenyl)boronic acid (570 mg, 1.6 mmol), and Pd(PPh₃)₄ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/DCM (1/2, v/v) as eluent to obtain Q4 (520 mg, 72% yield) as a red solid. ¹H NMR (400 MHz, Chloroform-d) δ 9.18 (dd, J = 7.9, 1.5 Hz, 2H), 8.55 (d, J = 8.1 Hz, 2H), 7.97 (s, 2H), 7.88 (d, J = 8.5 Hz, 4H), 7.81–7.74 (m, 2H), 7.69 (t, J = 7.5 Hz, 2H), 7.29–7.26 (m, 4H), 7.16 (q, J = 8.7 Hz, 16H), 2.36 (s, 12H). ¹³C NMR (100 MHz, Chloroform-d) δ 155.94, 148.25, 141.03, 140.27, 138.72, 131.79, 130.04, 129.17, 127.96, 126.82, 122.86, 119.83, 114.75, 55.55. HRMS (ESI) (m/z): [M+H] Calcd for C₆₀H₄₇N₄O₄: 887.3597, found: 887.3594.

**Synthesis of 4, 4'-((dibenzo[a,c]phenazine-10,13-diyl)bis(N,N-bis(4-(octyloxy)phenyl)aniline) (Q5).** A mixture of 10,13-dibromodibenzo[a,c]phenazine (173 mg, 0.4 mmol), (4-(bis(4-(octyloxy)phenyl)amino)phenyl)boronic acid (430 mg, 0.8 mmol), and Pd(PPh₃)₄ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over Na₂SO₄. After removal
of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/DCM (1/2, v/v) as eluent to obtain Q5 (365 mg, 72% yield) as a red solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.18 (d, $J = 7.9$ Hz, 2H), 8.55 (d, $J = 8.1$ Hz, 2H), 7.95 (s, 2H), 7.85 (d, $J = 8.5$ Hz, 4H), 7.80–7.72 (m, 2H), 7.72–7.65 (m, 2H), 7.24–7.15 (m, 12H), 6.89 (d, $J = 8.8$ Hz, 8H), 3.96 (t, $J = 6.5$ Hz, 8H), 1.86–1.73 (m, 8H), 1.46 (dt, $J = 11.4$, 5.3 Hz, 8H), 1.35–1.27 (m, 32H), 0.89 (t, $J = 6.4$ Hz, 12H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 155.54, 148.29, 140.9, 140.83, 140.25, 138.69, 132.11, 131.76, 130.76, 130.56, 129.97, 129.13, 127.94, 126.82, 126.62, 124.48, 124.00, 122.82, 119.70, 115.30, 68.31, 31.86, 30.22, 29.43, 29.29, 26.14, 22.70, 14.14. HRMS (ESI) (m/z): [M+H] Calcd for C$_{88}$H$_{103}$N$_4$O$_4$: 1279.7979, found: 1279.7971.

Characterization:

Fig. S1 $^1$H NMR of Q1.
Fig. S2 High-res ESI-TOF mass spectrum of Q1.

Fig. S3 $^1$H NMR of Q2.
**Fig. S4** $^{13}$C NMR of compound Q2.

**Fig. S5** High-res ESI-TOF mass spectrum of Q2.
Fig. S6 $^1$H NMR of Q3.

Fig. S7 $^{13}$C NMR of compound Q3.
Fig. S8 High-res ESI-TOF mass spectrum of Q3.

Fig. S9 $^1$H NMR of Q4.
Fig. S10 $^{13}$C NMR of compound Q4.

Fig. S11 High-res ESI-TOF mass spectrum of Q4.
Fig. S12 $^1$H NMR of Q5.

Fig. S13 $^{13}$C NMR of compound Q5.
Fig. S14 High-res ESI-TOF mass spectrum of Q5.