Electronic Supplementary Information for:

Triplet Excited State Properties in Variable Gap π-Conjugated Donor-Acceptor-Donor Chromophores

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I. Synthesis (Schemes, Procedures, Characterization)

**Scheme S1.** Synthesis of precursor 2.

\[
\begin{align*}
\text{Br-S} & \quad + \quad \text{TIPS} \quad \equiv \quad \text{H} \\
& \quad \xrightarrow{\text{PdCl}_2(\text{PPh}_3)_2, \text{CuI, Et}_3\text{N}} \quad \xrightarrow{50^\circ\text{C}, \text{overnight}} \quad \xrightarrow{85\%} \quad \text{1} \\
& \quad \text{TIPS} \quad \equiv \quad \text{TIPS} \\
& \quad \xrightarrow{\text{BuLi, SnBu}_3\text{Cl}} \quad \text{THF} \quad \xrightarrow{-78^\circ\text{C to RT, overnight}} \quad \xrightarrow{94\%} \quad \text{2}
\end{align*}
\]

**Scheme S2.** Synthesis of thiophene containing molecules.

\[
\begin{align*}
\text{Br-Ar-Br} & \quad + \quad \text{TIPS} \quad \equiv \quad \text{S-SnBu}_3 \\
& \quad \xrightarrow{\text{Pd(PPh}_3)_4 \text{Toluene}} \quad \xrightarrow{120^\circ\text{C, overnight}} \quad \xrightarrow{2}
\end{align*}
\]

\[
\begin{align*}
\text{TIPS} \quad \equiv \quad \text{S} \quad \equiv \quad \text{S} \quad \equiv \quad \text{TIPS} & \quad \xrightarrow{\text{TBAF}} \quad \text{THF} \quad \text{RT, 1h} \\
3a \quad \text{Ar} &= \text{BTz 89\%} \\
3b \quad \text{Ar} &= \text{TPd 77\%} \\
3c \quad \text{Ar} &= \text{Qx 76\%} \\
3d \quad \text{Ar} &= \text{BT 74\%} \\
3e \quad \text{Ar} &= \text{TP 78\%}
\end{align*}
\]

\[
\begin{align*}
\text{H} \quad \equiv \quad \text{S} \quad \equiv \quad \text{S} \quad \equiv \quad \text{H} & \quad + \quad \text{Ph-PBu}_3 \quad \equiv \quad \text{Ph-Cl} \quad \equiv \quad \text{Ph-PBu}_3 \\
& \quad \xrightarrow{\text{Cul}} \quad \text{RT, 30 min} \\
4a \quad \text{Ar} &= \text{BTz 85\%} \\
4b \quad \text{Ar} &= \text{TPd 89\%} \\
4c \quad \text{Ar} &= \text{Qx 60\%} \\
4d \quad \text{Ar} &= \text{BT 93\%} \\
4e \quad \text{Ar} &= \text{TP 70\%}
\end{align*}
\]

\[
\begin{align*}
\text{Ph-PBu}_3 \quad \equiv \quad \text{S} \quad \equiv \quad \text{S} \quad \equiv \quad \text{Ph-PBu}_3 & \quad \xrightarrow{\text{Cul}} \quad \text{RT, 30 min} \\
5a, \text{TBTz} \quad \text{Ar} &= \text{BTz 85\%} \\
5b, \text{TPD} \quad \text{Ar} &= \text{TPd 30\%} \\
5c, \text{TQT} \quad \text{Ar} &= \text{Qx 78\%} \\
5d, \text{TBT} \quad \text{Ar} &= \text{BT 49\%} \\
5e, \text{TPT} \quad \text{Ar} &= \text{TP 41\%}
\end{align*}
\]

\[
\begin{align*}
\text{Ar} &= \quad \text{BTz} \\
& \quad \text{TPd} \\
& \quad \text{Qx} \\
& \quad \text{BT} \\
& \quad \text{TP}
\end{align*}
\]
Scheme S3. Synthesis of EDOT containing molecules.

![Scheme S3. Synthesis of EDOT containing molecules.](image)

Materials and Instrumentation

Starting materials used in the synthesis of acceptors and precursor 2, Pd(PPh₃)₄, CuI and TBAF were obtained from commercial sources. Compounds 1, 5, 6, 2-methyl-2H-benzo[d][1,2,3]triazole (BTz), 5-methyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPd), quinoxaline (Qx), thieno[3,4-b]pyrazine (TP), TBT and EBE were synthesized according to the literature procedures. All reactions were performed under argon atmosphere in anhydrous solvents, which were dried prior use by the standard procedures. Merck silica gel 60 (particle size 0.04−0.063 mm) was used for flash chromatography.

**Triisopropyl-(4-tributylstannanyl-thienylethynyl)-silane (2)** To a solution of 0.500 g of 1 (1.92 mmol, 1 equiv) in 20 mL of THF, 0.85 mL of n-Butyllithium (2.11 mmol, 1.1 equiv) was added dropwise at -78°C via syringe. The reaction mixture was stirred for 45 min before 0.60 mL of tri-n-butyltin chloride was added dropwise (2.11 mmol, 1.1 equiv). The reaction mixture was allowed

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to warm up to room temperature, then quenched with water (50 mL), extracted with Et₂O (25 mL), and dried over MgSO₄. The resulting product was a yellowish liquid and used for the next step without further purification (1.00 g, 94%). ¹H NMR (500 MHz, CDCl₃): 7.33 (d, J = 3.5 Hz, 1H), 6.99 (d, J = 3.5 Hz, 1H) 1.55 (m), 1.34 (m), 1.12 (s), 1.09 (m), 0.89 (t, 3H); ¹³C-NMR (125.7 MHz, CDCl₃): 140.80, 135.00, 133.32, 129.02, 99.78, 96.29, 29.05, 27.38, 18.83, 13.78, 11.51, 11.05.

4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)2-methyl-benzo[d][1,2,3]triazole (3a) A Solution of 0.200 g of dibromo-BTz (0.7 mmol, 1 equiv) and 0.92 g of compound 2 (1.75 mmol,
2.5 equiv) in 45 mL toluene was degassed for 45 min by bubbling with argon. 80 mg of Pd(PPh₃)₄ (0.07 mmol, 0.1 equiv) was added under argon and the resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water, extracted with CH₂Cl₂, and dried over MgSO₄. The residue was purified by silica column chromatography with CH₂Cl₂ / hexane (3:7). The desired product was obtained a yellow solid (0.410 g, 89%). ¹H-NMR (500 MHz, CDCl₃): 7.90 (d, J = 4 Hz, 2H), 7.59 (s, 2H), 7.28 (d, J = 4 Hz, 2H), 4.63 (s, 3H), 1.15 (s, 42H); ¹³C-NMR (75.4 MHz, CDCl₃): 142.39, 140.85, 133.59, 126.76, 123.99, 123.39, 123.08, 99.76, 97.45, 43.86, 18.84, 11.50; HRMS (ESI) Calculated for C₃₇H₅₁N₃S₂Si₂ (M+H)⁺: m/z 658.3165. Found: m/z 658.3136.

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4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)5-octyl-thieno[3,4-c]pyrrole-4,6(5H)-dione (3b) Compound 3b was synthesized by the same procedure as 3a. The residue was purified by silica column chromatography with CH$_2$Cl$_2$ / hexane (1:2). The desired product was obtained as an orange-yellow solid (0.433 g, 77%). $^{1}$H-NMR (500 MHz, CDCl$_3$): 7.82 (d, $J = 4$ Hz, 2H), 7.19 (d, $J = 4$ Hz, 2H), 3.65 (t, 2H), 1.67 (m, 2H), 1.28 (m, 12H) 1.13 (s, 42H), 0.87 (t, 3H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 162.59, 135.86, 133.53, 133.11, 129.68, 129.20, 127.08, 99.81, 98.68, 38.87, 31.93 (2C), 29.30, 28.64, 27.12, 22.77, 18.79, 14.23, 11.43; HRMS (ESI) Calculated for C$_{44}$H$_{63}$NO$_2$S$_3$Si$_2$ (M+H)$^+$: m/z 790.3632. Found: m/z 790.3612.

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4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)quinoxaline (3c)  Compound 3c was synthesized by the same procedure as 3a. The residue was purified by silica column chromatography with CH$_2$Cl$_2$ / hexane (1:3). The desired product was obtained as an orange solid (0.220 g, 78%). $^1$H-NMR (500 MHz, CDCl$_3$): 9.00 (s, 2H), 8.14 (s, 2H), 7.68 (d, $J = 4$ Hz, 2H), 7.29 (d, $J = 4$ Hz, 2H), 1.15 (s, 42H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 143.74, 139.71, 139.17, 132.26, 131.80, 127.46, 127.20, 126.48, 100.01, 97.46, 18.85, 11.51; HRMS (MALDI) Calculated for C$_{38}$H$_{52}$N$_2$S$_2$Si$_2$ (M+H)$^+$: m/z 656.3104. Found: m/z 656.3115.

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4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)thieno[3,4-b]pyrazine (3e) Compound 3e was synthesized by the same procedure as 3a. The residue was purified by silica column chromatography with CH$_2$Cl$_2$ / hexane (3:7). The desired product was obtained as a blue solid (0.3494 g, 78%). $^1$H-NMR (500 MHz, CDCl$_3$): 8.54 (s, 2H), 7.45 (d, $J$ = 4 Hz, 2H), 7.21 (d, $J$ = 4 Hz, 2H), 1.14 (s, 42H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 145.05, 140.01, 135.21, 133.04, 125.99, 125.49, 124.86, 99.75, 98.79, 19.08, 11.75; HRMS (ESI) Calculated for C$_{36}$H$_{48}$N$_2$S$_3$Si$_2$ (M+H)$^+$: m/z 661.2591. Found: m/z 661.2606.
4,7-bis(5-Ethynylthiophen-2-yl) 2-methyl-benzo[d][1,2,3]triazole (4a) 0.180 g of compound 3a (0.27 mmol, 1 equiv) was dissolved in 20 mL of THF and degassed for 45 min by bubbling with argon. 0.8 mL of 1 M TBAF in THF (0.822 mmol, 3 equiv) was then added via syringe. The resulting solution was stirred at room temperature for 90 minutes. The reaction mixture was quenched with water, extracted with DCM, and dried over MgSO₄. Removal of the solvent gave the desired product as a yellow solid (0.080 g, 80%). ¹H-NMR (500 MHz, CDCl₃): 7.93 (d, J = 3.5 Hz, 2H), 7.60 (s, 2H), 7.34 (d, J = 3.5 Hz, 2H), 4.62 (s, 3H), 3.46 (s, 2H); ¹³C-NMR (125.7

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4,7-bis(5-Ethynylthiophen-2-yl) 5-octyl-thieno[3,4-c]pyrrole-4,6(5H)-dione (4b) Compound 4b was synthesized by the same procedure as 4a. The desired product was obtained as a yellow solid (0.213 g, 89%). $^1$H-NMR (500 MHz, CD$_2$Cl$_2$): 7.87 (d, $J = 3.5$ Hz, 2H), 7.29 (d, $J = 3.5$ Hz, 2H), 3.66 (t, 2H), 3.59 (s, 2H), 1.67 (m, 10H), 0.88 (t, 3H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 162.40, 135.60, 134.21, 133.67, 129.66, 129.54, 84.41, 76.38, 38.85, 31.93, 31.73, 29.30,
28.59, 27.09, 22.77, 14.22; HRMS (ESI) Calculated for C_{26}H_{23}NO_{3}S_{3} (M+H)^+: m/z 478.0964. Found: m/z 478.0983.

4,7-bis(5-Ethynylthiophen-2-yl)quinoxaline (4c) Compound 4c was synthesized by the same procedure as 4a. The desired product was obtained as a red solid (0.108 g, 60%). $^1$H-NMR (500 MHz, CDCl$_3$): 8.99 (s, 2H), 8.16 (s, 2H), 7.70 (d, $J = 4$ Hz, 2H), 7.35 (d, $J = 4$ Hz, 2H), 3.48 (s, 2H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 143.80, 139.72, 139.65, 132.83, 131.75, 127.54, 126.49,
125.50, 82.92, 77.58; HRMS (ESI) Calculated for C_{20}H_{12}N_{2}S_{2} (M+H)^+: m/z 344.0320. Found: m/z 344.0353.

4,7-bis(5-Ethynylthiophen-2-yl) thieno[3,4-b]pyrazine (4e) 0.290 g of compound 3e (0.38 mmol, 1 equiv) was dissolved in 15 mL of THF and degassed for 45 min by bubbling with argon. 0.492 g of TBAT (0.91 mmol, 2.4 equiv) was added under argon. The resulting solution was stirred at 50°C overnight. The reaction mixture was quenched with water, extracted with DCM, and dried

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over MgSO₄. The desired product was obtained as a dark red solid (0.107 g, 70%). ¹H-NMR (500 MHz, CDCl₃): 8.55 (s, 2H), 7.48 (d, J = 4 Hz, 2H), 7.28 (d, J = 4 Hz, 2H), 3.49 (s, 2H); ¹³C-NMR (125.7 MHz, CDCl₃): 144.32, 139.16, 134.82, 132.56, 125.33, 124.91, 124.15, 99.63, 98.27; HRMS (ESI) Calculated for C₁₈H₈N₂S₃ (M+H⁺): m/z 348.9922. Found: m/z 348.9934.

**TBTz (5a)**: 0.052 g of compound 4a (0.15 mmol, 1 equiv) and 0.235 g of trans-ethynylphenylchlorobis(tri-n-butylphosphine)platinum(II) (5) (0.32 mmol, 2.1 equiv) were dissolved in a piperidine/toluene mixture [1:1 (v/v), 20 mL] and degassed for 45 min by bubbling.
with argon. Then 1 mg CuI (0.008 mmol, 0.05 equiv) was added. The resulting mixture was stirred at room temperature for 1 hour. Silica gel was then added to the reaction mixture, and the solvent was evaporated. The product was purified by silica column chromatography using CH$_2$Cl$_2$ / hexane (1:1) as the eluent. The product was obtained as a viscous orange oil (176 mg, 85%). $^1$H-NMR (500 MHz, CD$_2$Cl$_2$): 7.90 (d, $J = 3.5$ Hz, 2H), 7.49 (s, 2H), 7.24 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.88 (d, $J = 3.5$ Hz, 2H), 4.58 (s, 3H), 2.14 (m, 24H), 1.63 (m, 24H), 1.50 (sext, 24H), 0.96 (t, 36H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 142.50, 136.67, 130.90, 130.24, 129.11, 128.64, 127.98, 127.04, 124.99, 123.21, 122.37, 117.63, 109.38, 107.65, 101.82, 43.58, 26.52, 24.55, 24.11, 13.99; $^{31}$P-NMR (121.44 MHz, CDCl$_3$): 3.23 ($J_{Pt-P} = 2352$ Hz); HRMS (MALDI) Calculated for C$_{83}$H$_{127}$N$_3$Pt$_4$S$_2$ (M$^+$): $m/z$ 1744.7727. Found: $m/z$ 1744.7744.
**TPD (5b)** Compound 5b was synthesized by the same procedure as 5a. The product was purified by silica column chromatography using CH₂Cl₂ / hexane (2:3) as the eluent. The desired product was obtained as an orange oil (74 mg, 30%). $^1$H-NMR (500 MHz, CD₂Cl₂): 7.93 (d, $J = 3.5$ Hz, 2H), 7.24 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.82 (d, $J = 3.5$ Hz, 2H), 3.62 (t, 2H), 2.13 (m, 24H), 1.61 (m, 24H), 1.49 (m, 24H), 1.27 (m, 12H), 0.95 (t, 36H), 0.88 (t, 3H); $^{13}$C-NMR (125.7 MHz, CDCl₃): 162.93, 136.38, 133.57, 130.89, 130.38, 129.06, 128.98, 128.86, 128.00, 127.46, 125.10, 121.85, 109.65, 107.16, 101.67, 38.59, 31.94, 29.37, 29.31, 28.67, 27.11, 26.52, 24.54,
24.12, 22.77, 14.22, 13.98; $^{31}$P-NMR (121.44 MHz, CDCl$_3$): 3.37 ($J_{\text{Pt-P}} = 2352$ Hz); HRMS (MALDI) Calculated for C$_{90}$H$_{139}$NO$_2$P$_4$Pt$_2$S$_3$ ($M^+$): $m/z$ 1876.8223. Found: $m/z$ 1876.8253.

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**TQT (5c)** Compound 5c was synthesized by the same procedure as 5a. The product was purified by silica column chromatography using CH$_2$Cl$_2$ / hexane (1:1) as the eluent. The desired product was obtained as a dark red solid (240 mg, 78%). $^1$H-NMR (500 MHz, CD$_2$Cl$_2$): 8.90 (s, 2H), 8.08 (s, 2H), 7.68 (d, $J = 4$ Hz, 2H), 7.24 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.90 (d, $J = 4$ Hz, 2H), 2.16 (m, 24H), 1.64 (m, 24H), 1.50 (m, 24H), 0.96 (t, 36H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 143.01, 139.80, 135.09, 133.32, 131.44, 130.84, 129.09, 127.92, 127.31, 126.91, 126.72, 124.93, 117.47, 109.32, 107.72, 101.96, 26.48, 24.50, 24.07, 13.96; $^{31}$P-NMR (121.44 MHz, CDCl$_3$): 3.17 ($J_{Pt-P} = 2354$ Hz); HRMS (MALDI) Calculated for C$_{84}$H$_{126}$N$_2$P$_4$Pt$_2$S$_2$ (M$^+$): m/z 1741.7618. Found: m/z 1741.7615.
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TPT (5e) Compound 5e was synthesized by the same procedure as 5a. The product was purified by silica column chromatography using CH$_2$Cl$_2$ / hexane (1:1) as the eluent. The desired product was obtained as a green oil (54 mg, 41%). $^1$H-NMR (500 MHz, CD$_2$Cl$_2$): 8.43 (s, 2H), 7.46 (d, $J = 4$ Hz, 2H), 7.25 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.82 (d, $J = 4$ Hz, 2H), 2.14 (m, 24H), 1.62 (m, 24H), 1.48 (m, 24H), 0.96 (t, 36H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 144.21, 139.50, 131.77, 131.38, 131.16, 129.36, 128.24, 128.14, 125.56, 125.26, 125.15, 119.68, 109.70, 107.84, 102.13, 26.78, 24.80, 24.36, 14.25; $^{31}$P-NMR (121.44 MHz, CDCl$_3$): 3.26 ($J_{Pt-P} = 2351$ Hz); HRMS (MALDI) Calculated for C$_{82}$H$_{124}$N$_2$P$_4$Pt$_2$S$_3$ (M$^+$): m/z 1747.7180. Found: m/z 1747.7178.

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5,8-bis(3,4-dihydro-2H-thieno[3,4-b]pyran-5-yl)quinoxaline (7a) A solution of 0.250 g of dibromo-Qx (0.87 mmol, 1 equiv) and 0.90 g of compound 6 (2.08 mmol, 2.6 equiv) in 20 mL of toluene was degassed for 1 hour by bubbling with argon. Then 100 mg of Pd(PPh$_3$)$_4$ (0.09 mmol, 0.1 equiv) and 8 mg CuI (0.004 mmol, 0.05 equiv) were added under argon. The resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water (50 mL), extracted with Et$_2$O (25 mL), and dried over MgSO$_4$. The product was purified by silica column chromatography using CH$_2$Cl$_2$/hexane (4:1) as the eluent. The product was obtained as dark orange solid (0.35 g, 98%). $^1$H-NMR (500 MHz, CDCl$_3$): 8.92 (s, 2H), 8.57
(s, 2H), 6.55 (s, 2H), 4.37-4.31 (m, 8H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 142.53, 141.52, 140.46, 139.93, 129.62, 128.87, 113.02, 103.08, 65.10, 64.49; HRMS (ESI) Calculated for C$_{20}$H$_{14}$N$_2$O$_4$S$_2$ (M+H)$^+$: $m/z$ 411.0468. Found: $m/z$ 411.0472.

5,8-bis(7-iodo-3,4-dihydro-2H-thieno[3,4-b]pyran-5-yl)quinoxaline (8a) To a solution of 0.358 g of 7a (0.87 mmol, 1 equiv) in CHCl$_3$/acetic acid [2:1 (v/v), 120 mL], 0.50 g of NIS (2.17 mmol, 2.5 equiv) was added. The reaction mixture was stirred at room temperature for 2 days. The precipitate formed was collected by suction filtration, washed with water, ethanol, and chloroform. The desired product was obtained as dark red solid (0.34 g, 60%). 8a could not be characterized.
by $^{13}$C-NMR due to solubility problems. $^1$H-NMR (500 MHz, CDCl$_3$): 8.95 (s, 2H), 8.64 (s, 2H), 4.41 (s, 8H); HRMS (ESI) Calculated for C$_{20}$H$_{12}$I$_2$N$_2$O$_4$S$_2$ (M+H)$^+$: $m/z$ 662.8401. Found: $m/z$ 662.84010.

5,8-bis(7-(trimethylsilyl)-3,4-dihydro-2H-thieno[3,4-b]pyran-5-yl)quinoxaline (9a) A solution of 0.335 g of 8a (0.5 mmol, 1 equiv) in THF/piperidine [5:1 (v/v), 25 mL] was degassed for 45 min by bubbling with argon. Then 58 mg of Pd(PPh$_3$)$_4$ (0.05 mmol, 0.1 equiv) and 5 mg of CuI (0.002 mmol, 0.05 equiv) were added under argon. Then 0.2 mg of trimethylsilylacetylene (2 mmol, 4 equiv) was added via syringe. The resulting mixture was refluxed overnight. Upon cooling to room temperature silica gel was added to the reaction mixture, and the solvent was evaporated under reduced pressure. The product was purified by silica column chromatography using CH$_2$Cl$_2$ / hexane (1:1) as the eluent. The product was obtained as red solid (0.21 g, 69%). $^1$H NMR (500 MHz, CDCl$_3$): 8.92 (s, 2H), 8.69 (s, 2H), 4.39 (s, 8H), 0.27 (s, 18H); $^{13}$C-NMR (125.7 MHz, CDCl$_3$): 144.19, 142.18, 139.73, 139.33, 128.85, 128.58, 114.19, 103.66, 101.99, 95.61, 64.81, 64.78, 0.23; HRMS (ESI) Calculated for C$_{30}$H$_{30}$N$_2$O$_4$S$_2$Si$_2$ (M+H)$^+$: $m/z$ 603.1258. Found: $m/z$ 603.1263.

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EQE (10a) 0.075 g of compound 9a (0.124 mmol, 1 equiv), 0.22 g of trans-
ethynylphenylchlorobis(tri-n-butylphosphine)platinum(II) (3) (0.30 mmol, 2.4 equiv) and 1 mg of
CuI (0.006 mmol, 0.05 equiv) were dissolved in a THF/triethylamine mixture [1:1 (v/v), 40 mL]
and degassed for 1 hour by bubbling with argon. Then 81 mg of TBAF (0.311 mmol, 2.5 equiv)
was added via syringe. The resulting mixture was stirred at room temperature overnight. Silica gel
was then added to the reaction mixture, and the solvent was evaporated. The product was purified
by silica column chromatography using ethylacetate / hexane (1:4) as the eluent. The product was
obtained as a purple solid (0.098 g, 42%). 1H-NMR (500 MHz, CD2Cl2): 8.83 (s, 2H), 8.63 (s, 2H),

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7.24 (d, 4H), 7.20 (m, 4H), 7.10 (t, 2H), 4.36 (m, 4H), 4.28 (m, 4H), 2.17 (m, 24H), 1.63 (m, 24H), 1.51 (m, 24H), 0.96 (t, 36H); \(^{13}\)C-NMR (125.7 MHz, CDCl\(_3\)): 141.74, 141.04, 140.17, 139.83, 130.87, 129.27, 128.91, 128.13, 127.93, 124.83, 120.25, 109.35, 109.12, 108.94, 108.31, 98.96, 64.91, 64.19, 26.50, 24.47, 23.94, 14.00; \(^{31}\)P-NMR (121.44 MHz, CDCl\(_3\)): 2.57 \((J_{\text{Pt-P}} = 2347 \text{ Hz})\);

HRMS (MALDI) Calculated for C\(_{84}\)H\(_{126}\)N\(_2\)P\(_4\)Pt\(_2\)S\(_2\) (M\(^+\)): m/z 1857.7745. Found: m/z 1857.7728.

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II. Electrochemical Data

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III. Photophysical Data

Figure S1. Normalized absorption and emission spectra of the unmetallated DAD chromophores (4a-e) and their Pt complexes.
**Figure S2.** UV-VIS spectra (in THF, left), and photoluminescence spectra (in THF, right).

**Figure S3.** Low-temperature luminescence spectra (77 K) of TBTz and TPD in 2-MeTHF, degassed by five repeated cycles of freeze-pump-thaw on a high-vacuum line. The stared feature is the phosphorescence band.

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Figure S4. Fluorescence decay plots of molecules collected by TCSPC in anhydrous THF.

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Figure S5. Photophysical properties of the unmetallated ligands (thiophene series are in orange, EDOT series are in blue) on the left panel and the structures of the ligands on the right panel. a) Fluorescence quantum yield measured in THF using quinoline sulfate in 0.1 M H$_2$SO$_4$ solution ($\Phi_f=0.577$)$^9$ as an actinometer. b) Fluorescence lifetime measured in THF by TCSPC. C) Singlet oxygen quantum yield measured in deuterated chloroform using terthiophene ($\Phi_f=0.84$) as an actinometer.
**Figure S6.** Normalized nanosecond transient absorption difference spectra of Pt-substituted chromophores, following nanosecond-pulsed 355 nm excitation (4mJ/pulse) in argon-purged THF.

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Figure S7. Femtosecond transient absorption difference spectra of the Pt-substituted chromophores at indicated delay times following 355 nm laser excitation pulse (35 fs pulse width, 1.5 μJ/pulse) in air saturated THF.

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**Figure S8.** Fitting of the fs transient absorption decay kinetics at the indicated wavelengths. The lifetimes are fitted by mono or bi exponential parameters on Surface Xplorer v4. The $\tau_S$ is reported from the decay of near-IR band. A short-lived rise component is observed for some of the entries.

**Figure S9.** The natural log of intersystem crossing rate vs. singlet-triplet splitting energy.
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IV. Computational Data

Figure S10. DFT optimized singlet state structure of TBTz'.

Figure S11. LUMO of TBTz'.

Figure S12. HOMO of TBTz'.

Figure S13. DFT optimized triplet state structure of TBTz'.

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Figure S14. DFT optimized singlet state structure of TPD’.

Figure S15. LUMO of TPD’.

Figure S16. HOMO of TPD’.

Figure S17. DFT optimized triplet state structure of TPD’.

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**Figure S18.** DFT optimized singlet state structure of TQT’.

**Figure S19.** LUMO of TQT’.

**Figure S20.** HOMO of TQT’.

**Figure S21.** DFT optimized triplet state structure of TQT’.

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Figure S22. DFT optimized singlet state structure of EQE’.

Figure S23. LUMO of EQE’.

Figure S24. HOMO of EQE’.
Figure S25. DFT optimized triplet state structure of EQE’.

Figure S26. DFT optimized singlet state structure of TBT’.

Figure S27. LUMO of TBT’.

Figure S28. HOMO of TBT’.

Electronic Supplementary Information. Cekli S., Winkel R. W., Alarousu E., Mohammed O. F., Schanze K. S.
Figure S29. DFT optimized triplet state structure of TBT’.

Figure S30. DFT optimized singlet state structure of EBE’.

Figure S31. LUMO of EBE’.

Figure S32. HOMO of EBE’.

Electronic Supplementary Information. Cekli S., Winkel R. W., Alarousu E., Mohammed O. F., Schanze K. S.
Figure S33. DFT optimized triplet state structure of EBE’.

Figure S34. DFT optimized singlet state structure of TPT’.

Figure S35. LUMO of TPT’.

Figure S36. HOMO of TPT’.

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Figure S37. DFT optimized triplet state structure of TPT'.

Table S1. Computed energies of the lowest energy singlet and triplet state geometries.

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<th>$E_{S0}$ (hartrees)</th>
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<th>$\Delta E_{S0-T1}$ (hartrees)</th>
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Table S2. Computed frontier orbital energies of the molecules.

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<th>$E_{LUMO}$ (eV)</th>
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<tr>
<td>TBT'</td>
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<td>TPT'</td>
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<td>-4.28</td>
<td>2.13</td>
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</tbody>
</table>

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V. References for Electronic Supplementary Information


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