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Intermolecular Interactions in Molecular Crystals and Their Effect on Thermally Activated Delayed Fluorescence of Helicene-Based Emitters

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S1. General experimental details

All reagents were purchased from commercial sources and used without further purification. Dry solvents were obtained from a solvent purification system (SPS 400 Innovative Technologies) with alumina as a drying agent. Glassware was dried in an oven at 120 °C overnight.

Microwave syntheses were performed using Biotage Initiator Classic microwave heating apparatus in 10-20 mL vials. Photochemical reactions were conducted under Black-Ray B-100AP High intensity UV Lamp with 365 nm wavelength.

Thin layer chromatography (TLC) was performed using Merck Silica gel 60 F_{254} TLC plates. Column chromatography was carried out on silica gel Zeoprep 60 Hyd (40-63 µm mesh).

Melting points were determined using Stuart Scientific SMP1 Melting Point apparatus.

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVIII 400 apparatus at 400 MHz and 100 MHz, or Brucker AV500 at 500MHz and 125MHz. Data are presented in following order: chemical shifts (δ) in ppm; multiplicity as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m); coupling constants (*J)* in Hz. Multiplets are reported over the range they appeared (in ppm). Signals were sharp unless stated as broad (br). Samples were referenced to residual solvent peaks.

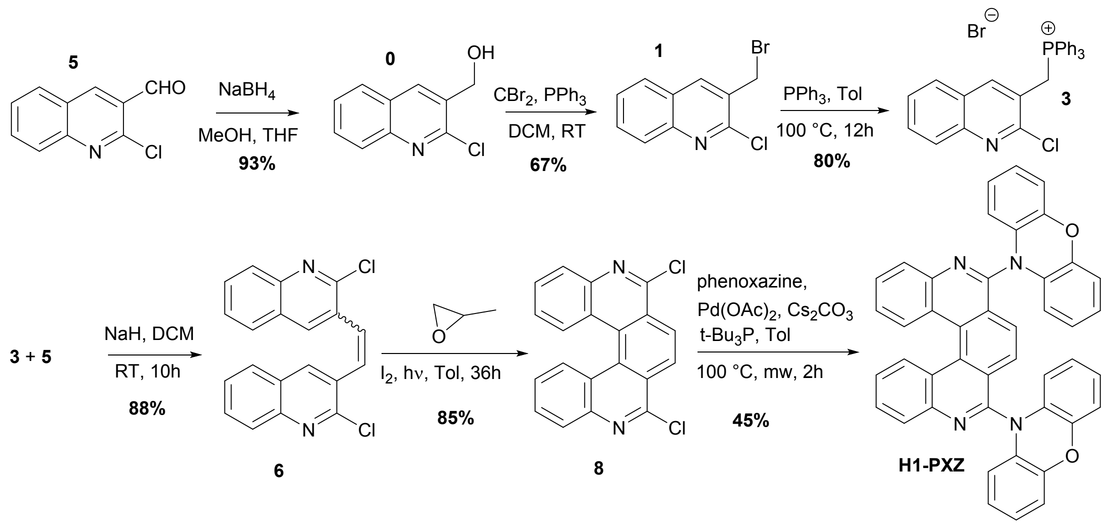
Z : E ratios for the products of Wittig olefination were determined after purification by column chromatography by comparing integrals for related signals in ^{1}H NMR spectra.

MS MALDI-TOF analyses were run on Shimazu Axima-CFR spectrometer (mass range 20-150000Da); GCMS were run on Thermo Finnigan Polaris Q spectrometer using electron ionization (EI) mode (mass range 50-650Da). The high resolution mass measurements were performed on the Waters Xevo G2S instrument (ASAP-TOF-MS) or on Finnigan MAT 95XP (EI).

S2. Synthesis and characterisation

Synthesis of H1-PXZ

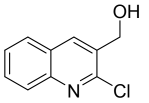
The synthesis of **0, 1, 3, 6** and **8** was performed based on a slightly modified literature procedure, and the NMR data were in agreement with reported.[1]



Scheme S2.1 Synthesis of H1-PXZ

Compound 0

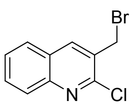
(2-chloroquinolin-3-yl)methanol



To a solution of 2-chloroquinoline-3-carboxaldehyde **5** (6 g, 31.3 mmol) in the mixture of MeOH (100 mL) and THF (100 mL) sodium borohydride (1.78 g, 47 mmol) was added at 0 °C, and the mixture was stirred for 30 min. The reaction mixture was quenched with water and diluted with Et_2O. The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure giving **0** (5.7 g, 93%) as a white solid: mp 168-170 °C; m/z (EI-GCMS) calculated for $C_{10}H_8ClNO$ 193.03, found m/z = 193 [M^+]; ^1H NMR (400MHz, DMSO-d_6): 8.47 (s, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 8.1, 1H), 4.70 (d, *J* = 3.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.39, 146.00, 135.86, 133.89, 130.13, 127.87,127.46, 127.22, 127.16, 59.88.

Compound 1

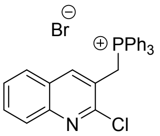
3-(bromomethyl)-2-chloroquinoline



The mixture of (2-chloroquinolin-3-yl)methanol **0** (5.7 g, 29.4 mmol) and tetrabromomethane (14.6 g, 44.2 mmol) in dry dichloromethane (100 mL) was cooled to 0 °C, and the solution of triphenylphosphine (11.6 g, 44.2 mmol) in dry dichloromethane (50 mL) was added dropwise. The reaction mixture was stirred at room temperature for 8 h, then quenched with water. The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with ethyl acetate : hexane (1:4) giving **1** as a pale-yellow solid (5.1 g, 67%): mp 120-122 °C; m/z (EI-GCMS) calculated for $C_{10}H_7BrClN$ 254.95, found m/z = 254.9 [M$^+$]; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.06 – 8.04 (m, 1H), 7.88 – 7.86 (1H, m), 7.84 – 7.76 (1H, m), 7.64 – 7.59 (1H, m), 4.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.57, 146.92, 138.83, 138.25, 130.61, 129.10, 127.87, 127.05, 126.70, 29.28.

Compound 3

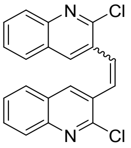
((2-chloroquinolin-3-yl)methyl)triphenylphosphonium bromide



The mixture of 3-(bromomethyl)-2-chloroquinoline **1** (2 g, 7.8 mmol) and triphenylphosphine (6.1 g, 23.4 mmol) was dissolved in toluene (100 mL) and refluxed for 12 h, then cooled to room temperature. The solid was filtered, washed with hexane and dried under vacuum to give product **3** as a white powder (3.25 g, 80%): mp 254-255 °C; m/z (MALDI-TOF) calculated for $C_{28}H_{22}ClNP$ [M - Br] 438.12, found 438.20 [M$^+$]; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.72 (d, *J* = 3.5 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.77 (m, 10H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.71 – 7.64 (m, 6H), 7.55 (t, *J* = 7.6 Hz, 1H), 6.02 (d, *J* = 14.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.55, 150.50, 146.60, 142.58, 142.52, 134.88, 134.85, 133.82, 133.81, 130.90, 129.99, 129.87, 127.80, 127.56, 127.14, 126.56, 126.53, 119.71, 119.63, 117.26, 116.40, 27.97, 27.49.

Compound 6

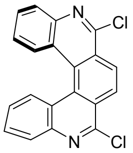
1,2-bis(2-chloroquinolin-3-yl)ethene



The mixture of phosphonium salt **3** (3 g, 5.7 mmol) and sodium hydride (608 mg, 14.5 mmol) was dissolved in dry dichloromethane (50 mL). The solution of 2-chloroquinoline-3-carbaldehyde **5** (923 mg, 4.8 mmol) in dry dichloromethane (20 mL) was added dropwise over 30 min. The reaction mixture was stirred at room temperature overnight, then quenched with water, extracted with dichloromethane, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with ethyl acetate : hexane (1:2) giving the product **6** as a pale yellow solid (1.5 g, 88%, Z/E ≈ 10:1): mp 218-220 °C; m/z (EI-GCMS) calculated for $C_{20}H_{12}Cl_2N_2$ 350.04, found 350.1 [M$^+$]; ^{1}H NMR (400MHz, $CDCl_3$): ***cis-isomer:*** δ 8.00 (dd, *J* = 7.49 Hz, 2H), 7.83 (s, 2H), 7.69 (ddd, *J* = 8.5, 6.7, 1.6 Hz, 2H), 7.53 – 7.38 (m, 4H), 7.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.77, 146.48, 137.82, 130.22, 128.54, 128.30, 127.71, 127.07, 126.74, 126.29.

Compound 8

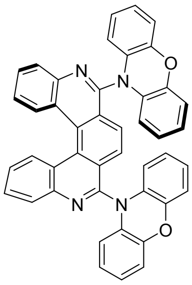
2,5-dichlorodibenzo[a,k][3,8]phenanthroline



The compound **6** (450 mg, 1.28 mmol) was dissolved in dry toluene (300 mL), and iodine (163 mg, 1.28 mmol) was added next. Nitrogen was bubbled through the solution for 30 min, and propylene oxide (45 mL) was added next. The reaction mixture was irradiated under UV lamp (Black-Ray® B-100AP High intensity UV Lamp, 365 nm) for 36 h, then washed with $Na_2S_2O_3$ aqueous solution, water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with ethyl acetate : hexane (1:6) giving the product **8** as a yellow solid (380 mg, 85%): mp 254-256 °C; m/z (MALDI-TOF) calculated for $C_{20}H_{10}Cl_2N_2$ 348.02, found 348.98 [M^+]; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.46 (d, *J* = 8.4 Hz, 2H), 8.19 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.76 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 2H), 7.41 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.34, 143.92, 131.31, 129.82, 128.33, 127.00, 126.56, 125.98, 125.53, 123.40.

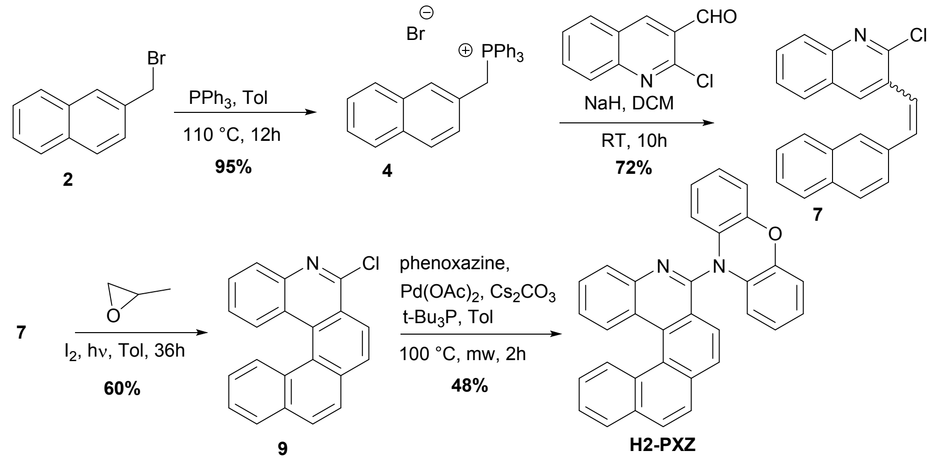
Compound H1-PXZ

2,5-di(10H-phenoxazin-10-yl)dibenzo[a,k][3,8]phenanthroline



The mixture of palladium (II) acetate (37 mg, 0.16 mmol), cesium carbonate (1.24 g, 3.8 mmol), phenoxazine (159 mg, 0.87 mmol) and **8** (170 mg, 0.54 mmol) was dissolved in dry toluene. The 1M solution of tri-*tert*-butylphosphine in toluene (0.35 mL) was added next and the solution was bubbled with Nitrogen for 30 min. The reaction mixture was heated at 100 °C in microwave for 2 h, then filtered through celite, washed with toluene and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with ethyl acetate : hexane (1:7) giving product as a dark-red solid (115 mg, 45%): mp >360 °C; m/z (MALDI-TOF) calculated for $C_{44}H_{26}N_4O_2$ 642.21, found 642.15 [M^+]; HRMS (ASAP-TOF-MS) calculated for $C_{44}H_{26}N_4O_2+H^+$ 643.2134, found 643.2134 [$M+H^+$]; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.80 (dd, *J* = 8.5, 0.9 Hz, 2H), 8.43 (s, 2H), 8.36 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.86 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 2H), 7.59 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 2H), 6.83 (dd, *J* = 7.9, 1.0 Hz, 4H), 6.73 (t, *J* = 7.3 Hz, 4H), 6.55 (br s, 4H), 6.16 (br s, 2H), 6.03 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.75, 144.93, 143.75, 133.35, 132.55, 129.46, 129.24, 127.02, 126.84, 126.11, 125.20, 124.14, 122.90, 122.09, 115.62, 113.48.

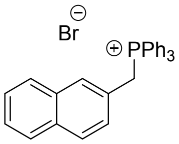
Synthesis of H2-PXZ



Scheme S2.2 Synthesis of H2-PXZ

Compound 4

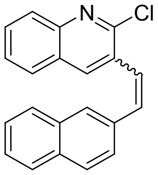
(naphthalen-2-ylmethyl)triphenylphosphonium



Synthesis according to general procedure leading to **3**. 2-(bromomethyl)naphthalene (1.5 g, 6.7 mmol), triphenylphosphine (4.34 g, 20.3 mmol), and toluene (100 mL). Phosphonium salt **4** was obtained as white solid (3.1 g, 95%): mp 246-248 °C; m/z (MALDI-TOF) calculated for $C_{29}H_{24}P$ [M - Br] 403.16, found 403.25 [M$^+$]; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 – 7.75 (m, 9H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.60 (m, 6H), 7.57 (m, 3H), 7.47 – 7.39 (m, 2H), 7.20 (dt, *J* = 8.4, 1.7 Hz, 1H), 5.65 (d, *J* = 14.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.43, 134.40, 134.05, 133.94, 132.49, 132.21, 130.79, 130.71, 129.74, 129.71, 129.67, 129.55, 128.19, 128.15, 127.91, 127.39, 127.06, 126.05, 125.87, 124.04, 123.95, 117.90, 117.05, 30.84, 30.38.

Compound 7

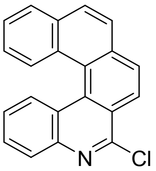
2-chloro-3-(2-(naphthalen-2-yl)vinyl)quinoline



Synthesis according to general procedure leading to **6.** Phosphonium salt **4** (3 g, 6.2 mmol), sodium hydride (0.65 g, 15.5 mmol), 2-chloroquinoline-3-carbaldehyde (0.99 g, 5.2 mmol), and dichloromethane (120 mL). The product **7** was obtained as pale yellow solid (1.31 g, 72%, Z/E ≈ 10:1): mp 112-114 °C; m/z (EI-GCMS) calculated for $C_{21}H_{14}ClN$ 315.08, found 314.9 [M$^+$]; HRMS (EI) calculated for $C_{21}H_{14}ClN$ 315.08, found 315.1 [M$^+$]; ***cis-isomer:*** ^{1}H NMR (400MHz, $CDCl_3$): δ 8.04 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.79 – 7.67 (m, 4H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.26 (dd, J = 8.7, 1.6 Hz, 1H), 7.06 (d, J = 12.2 Hz, 1H), 6.86 (dd, J = 12.1, 0.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.15, 146.32, 138.01,137.98, 132.98, 132.89, 132.84, 132.25, 129.88, 129.84, 129.50, 128.13, 127.72, 127.38, 127.17, 127.05, 126.52, 126.44, 125.80, 125.78, 125.09. ***trans-isomer:*** ^{1}H NMR (400MHz, CDCl$_3$): δ 8.48 (s, 1H), 8.04 (d, J = 9.2 Hz, 1H), 7.97 (s, 1H), 7.92 – 7.83 (m, 5H), 7.73 (d, J = 7.0 Hz, 1H), 7.69 (d, J = 13.9 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.51 (m, 2H), 7.41 (d, J = 16.2 Hz, 1H).

Compound 9

2-chloronaphtho[2,1-k]phenanthridine

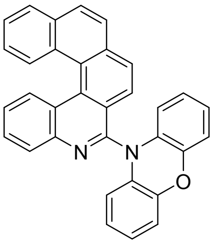


Synthesis according to general procedure leading to **8. 7** (500 mg, 1.58 mmol), iodine (216 mg, 1.7 mmol), propylene oxide (55 mL, 790 mmol), and toluene (600 mL). Product **9** was obtained as a pale-yellow solid (300 mg, 60%): mp 222-224 °C; m/z (EI-GCMS) calculated for $C_{21}H_{12}ClN$ 313.07, found 313.1 [M$^+$]; ^{1}H NMR (400MHz, CDCl$_3$): δ 8.54 (d, J = 8.5 Hz, 1H), 8.47 (d, J = 8.5 Hz, 2H), 8.16 (dd, J = 8.3, 1.0 Hz, 1H), 8.06 (dd, J = 10.9, 8.6 Hz, 2H), 8.01 (dd, J = 8.0, 1.2 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.69 (ddd, J = 8.3, 7.0, 1.4 Hz, 1H), 7.61 (ddt, J = 8.1, 4.6, 2.3 Hz, 1H), 7.35 (qdd, J = 10.5, 3.6, 0.9 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.76, 143.52, 134.35, 133.19, 132.86, 132.62, 132.41, 129.97, 129.75, 128.85, 128.58, 128.21, 127.97, 127.61, 127.43, 126.74, 126.07, 125.96, 125.42, 124.73, 124.03.

The NMR data were in agreement with literature values.[2]

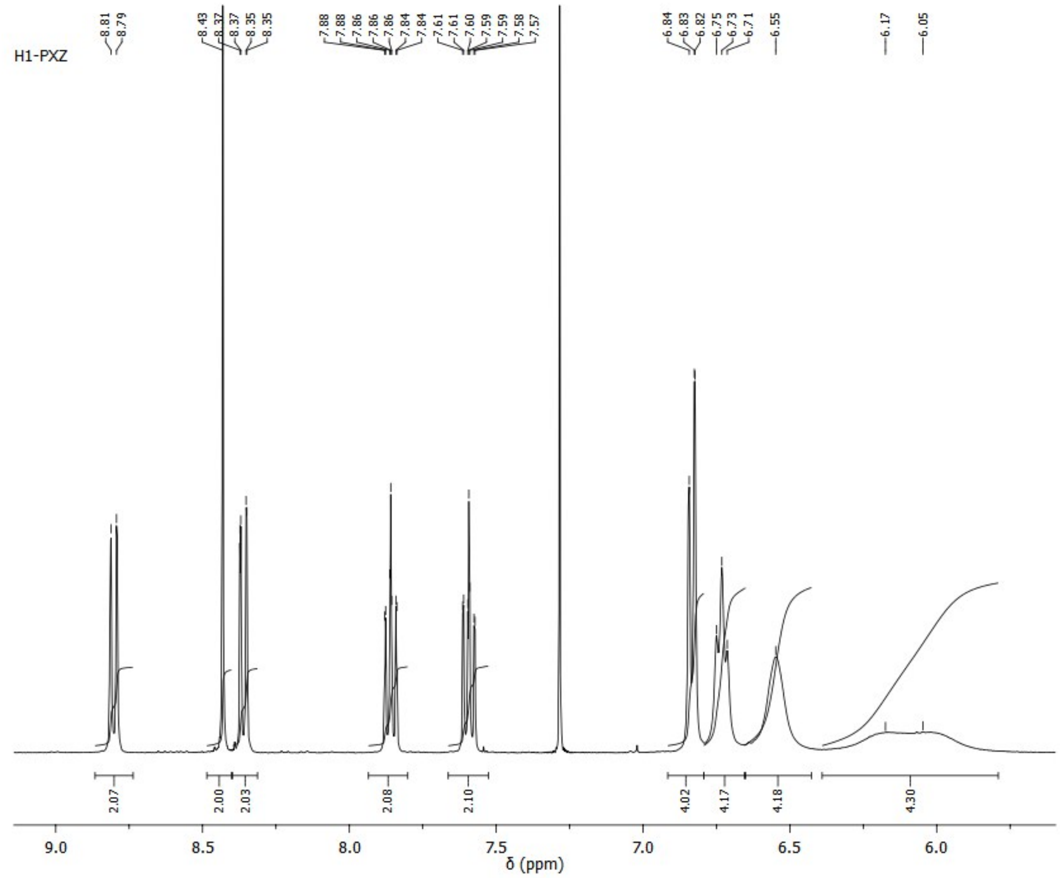
Compound H2-PXZ

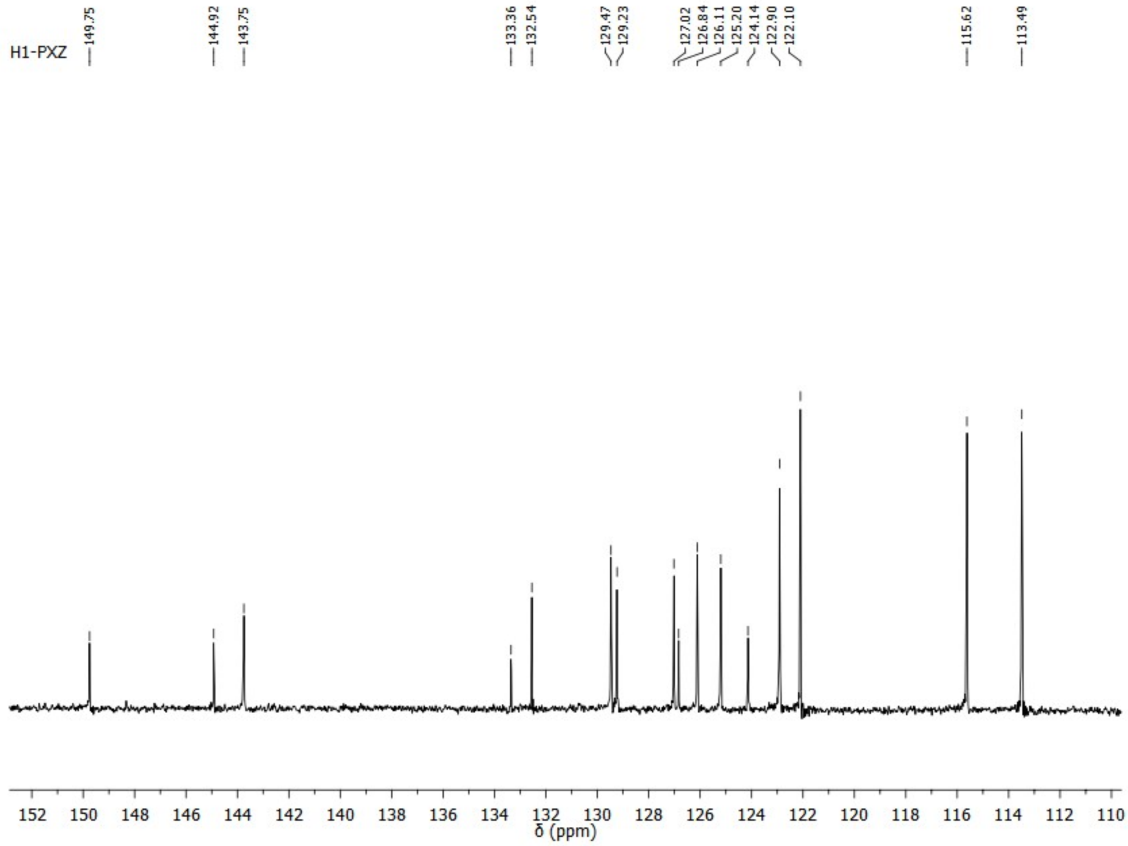
10-(naphtho[2,1-k]phenanthridin-2-yl)-10H-phenoxazine

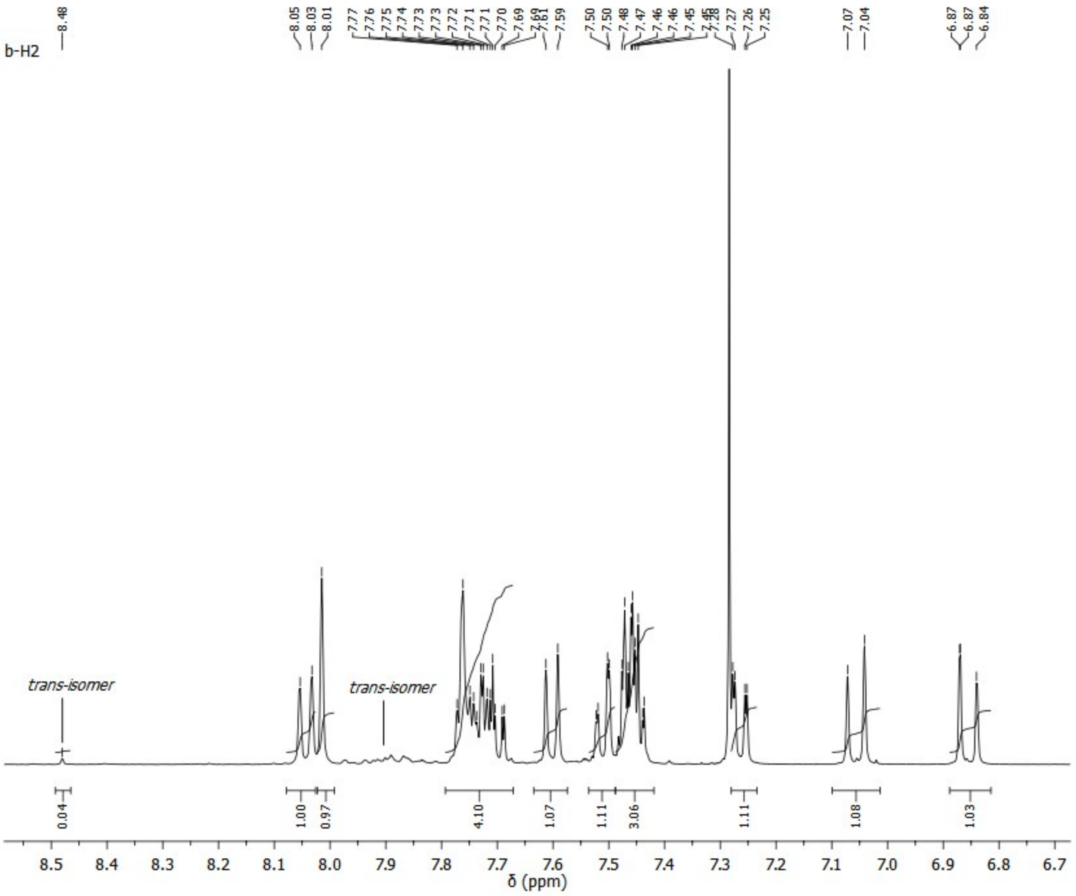


Synthesis according to general procedure leading to **H1-PXZ.** Palladium (II) acetate (36 mg, 0.16 mmol), cesium carbonate (1.21 g, 3.73 mmol), phenoxazine (195 mg, 1.06 mmol), **9** (167 mg, 0.53 mmol), 1M solution of tri-*tert*-butylphosphine in toluene (0.34 mL), and toluene (8 mL). The product was obtained as a yellow solid (120 mg, 48%): mp 336-338 °C; m/z (MALDI-TOF) calculated for $C_{33}H_{20}N_2O$ 460.16, found 460.12 [M$^+$]; HRMS (ASAP-TOF-MS) calculated for $C_{33}H_{20}N_2O+H^+$ 461.1653, found 461.1653 [M+H$^+$]; ^{1}H NMR (400MHz, CDCl$_3$): δ 8.70 (d, J = 8.4 Hz, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.30 (dd, J = 8.3, 1.1 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 8.04 (dd, J = 8.1, 1.0 Hz, 1H), 7.92 (dd, J = 14.3, 8.5 Hz, 2H), 7.76 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.64 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.44 (dddd, J = 8.4, 6.9, 4.1, 1.4 Hz, 2H), 6.85 (d, J = 7.1 Hz, 2H), 6.73 (br s, 2H), 6.60 (br s, 1H), 6.52 (br s, 1H), 6.14 (br s, 1H), 5.99 (br s, 1H).^{13}C NMR (100 MHz, CDCl$_3$): δ 149.95, 144.64, 143.64, 134.43, 133.78, 132.81, 132.36, 129.90, 129.60, 128.90, 128.67, 128.55, 128.24, 127.68, 127.34, 126.69, 125.93, 125.59, 125.30, 125.25, 124.77, 124.72, 124.43, 123.01, 122.92, 121.66, 115.37, 113.50.

S3. ^{1}H and ^{13}C NMR spectra for new compounds



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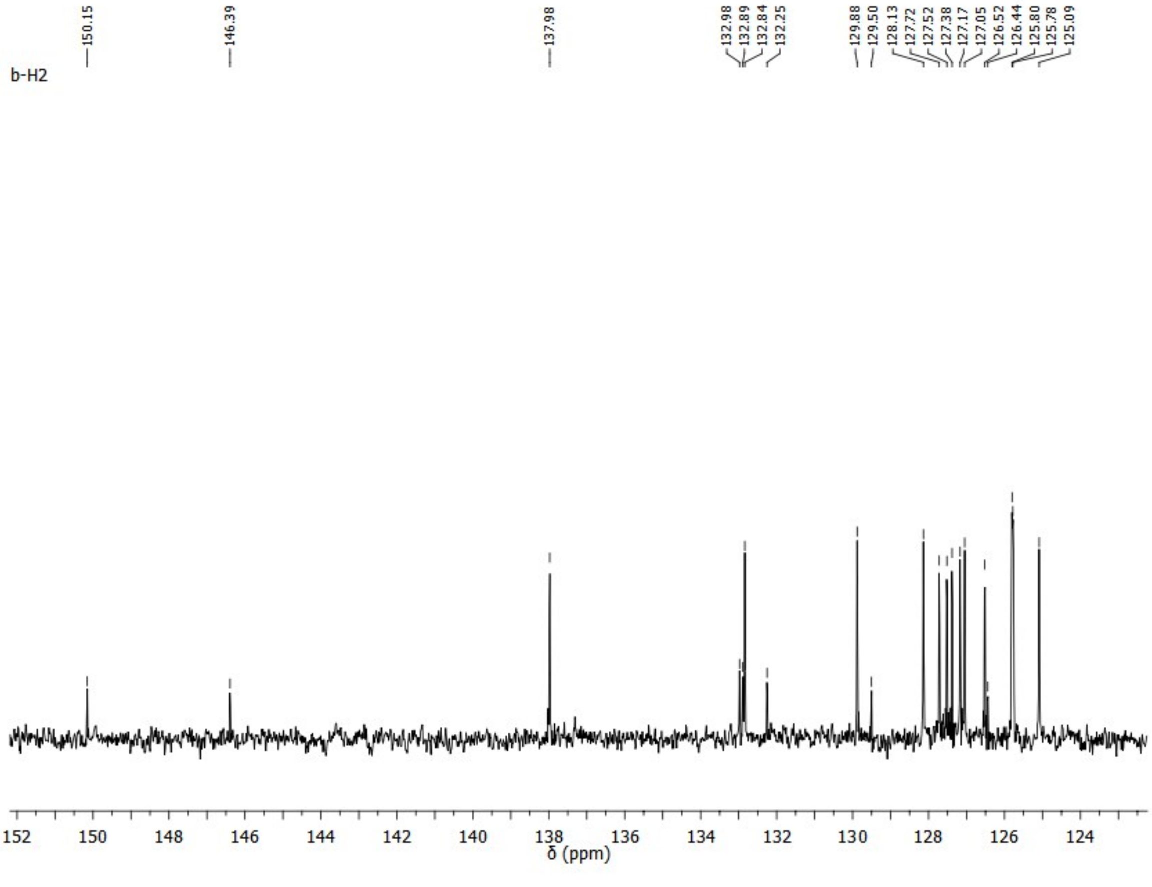
δ (ppm)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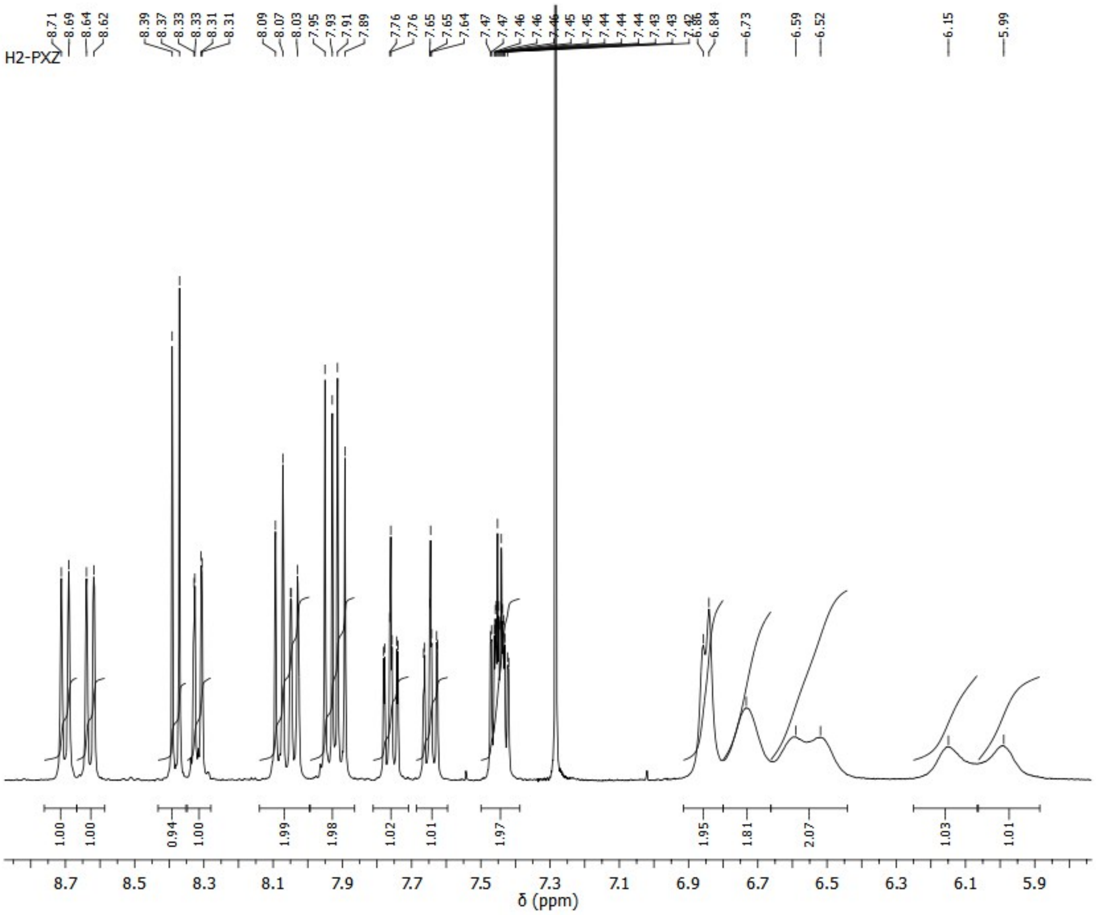
δ (ppm)


H2-PXZ
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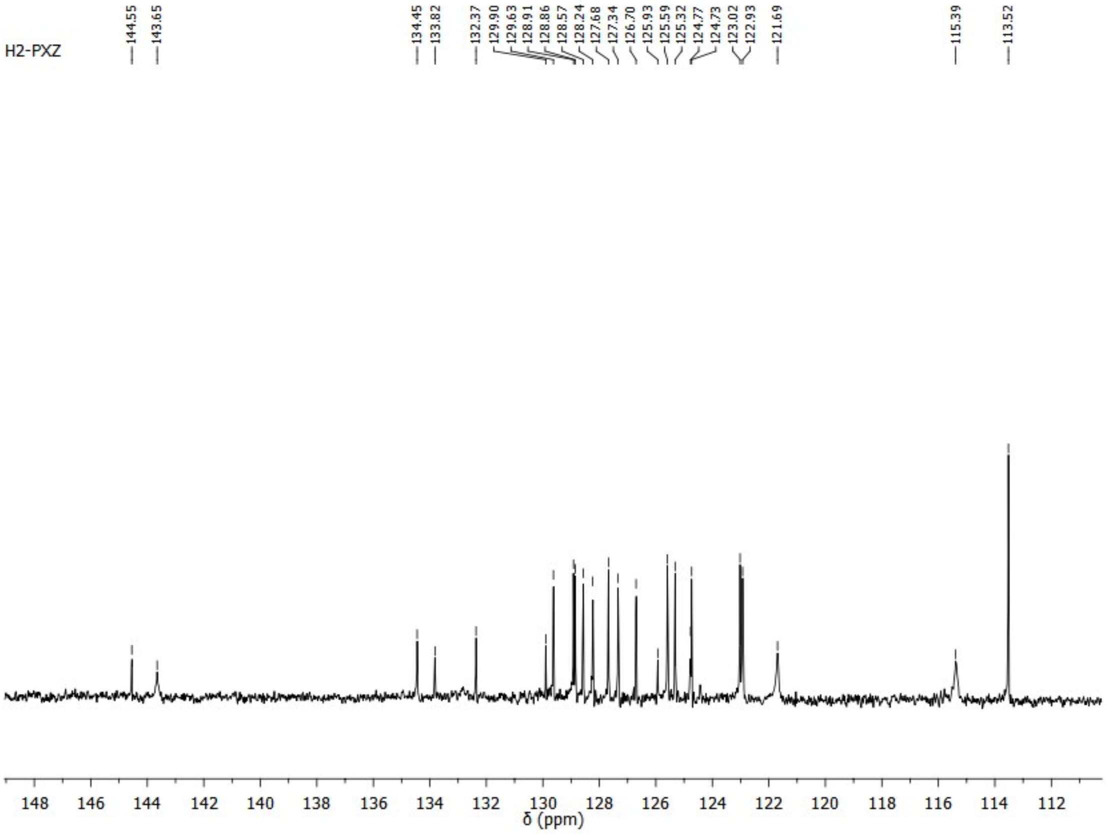
5.9
δ (ppm)


H2-PXZ
144.55
143.65
134.45
133.82
132.37
129.90
129.63
128.91
128.86
128.57
128.24
127.68
127.34
126.70
125.93
125.59
125.32
124.77
124.73
123.02
122.93
121.69
115.39
113.52
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
δ (ppm)

S4. Electrochemical characterisation

General conditions

Cyclic voltammetry measurements were performed using a CH Instruments 660A electrochemical workstation with *i*R compensation at a scan rate of 0.1 V s^{-1}. The electrochemical cell comprised of glassy carbon, platinum wire and silver wire as working, counter and reference electrodes respectively. The experiments were conducted at room temperature in degassed (Ar) 0.1 M solutions of tetrabutylammonium tetrafluoroborate in dichloromethane with *ca.* 0.6 mM concentrations of studied compounds.

All measurements were referenced against the half-wave potential ($E_{1/2}$) of the Fc/Fc^+ redox couple. The cathodic and anodic peaks are shown for reversible and irreversible (irr) processes (Table S4.1), and determined from the onset potentials. The HOMO and LUMO levels were determined according to the following equations:

LUMO = $-$ (E_{ox} + 4.8) (eV)

HOMO = $-$ (E_{red} + 4.8) (eV)

Table S4.1 HOMO-LUMO levels and E_g for H1- and H2-PXZ

	HOMO, eV	**LUMO, eV**	**E_g, eV**	**E_{ox}, eV**	**E red**
H1-PXZ	-5.24	-3.06	2.18	0.44	-1.74; -2.10(irr)
H2-PXZ	-5.15	-2.59	2.56	0.35	-2.21(irr)

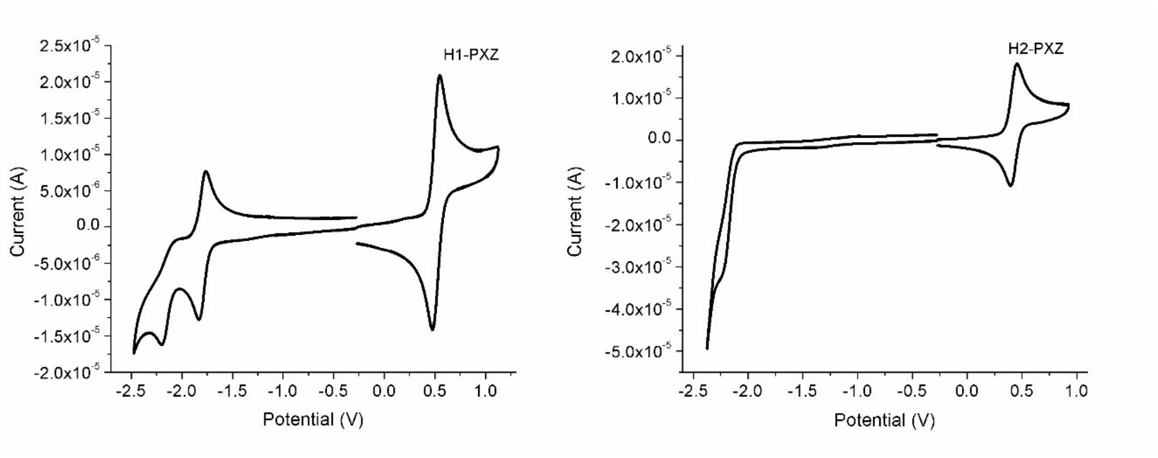


Figure S4.1 Cyclic voltammograms for **H1-PXZ** and **H2-PXZ**

S5. Thermal analysis

Thermogravimetric analyses (TGA) were performed on the Perkin-Elmer Thermogravimetric Analyser TGA7 under a constant flow of Argon (20 mL/min). The temperature was raised at a rate of 10 °C min^{-1} from 40 °C to 500 °C.

Differential scanning calorimetry was carried on a TA Instruments Q1000 with a RC-90 refrigerated cooling unit attached. The test procedure was a standard Heat-Cool-Reheat, and the temperature range was from 25 °C to 300 °C at 10 °C min^{-1}.

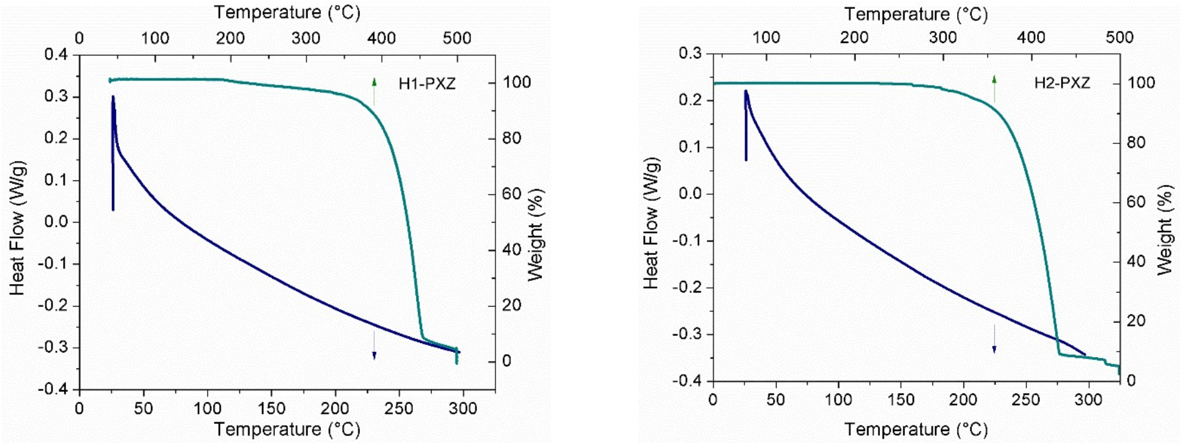


Figure S5.1 DSC (blue) and TGA (green) plots for **H1-PXZ** and **H2-PXZ**

S6. Crystallography data

Experimental (for all three data collections). A suitable crystal was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku 007HF diffractometer equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000HE detector. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal data for **H1-PXZ-o** : $C_{50}H_{40}N_4O_2$, M_r = 728.86, orange block, monoclinic, space group C2/c, a = 11.28030(10) Å, b = 14.5794(2) Å, c = 22.9364(2) Å, β = 97.5790(10)°, $\alpha = \gamma$ = 90°, V = 3739.17(7) Å^3, T = 100(2) K, Z = 4, Z' = 0.5, μ(CuK$_\alpha$) = 0.623 mm^{-1}, 31606 reflections measured, 3349 unique (R_{int} = 0.0300) which were used in all calculations. The final wR_2 was 0.1056 (all data) and R_1 was 0.0441 (I > 2(I)). CCDC 1853153.

Crystal data for **H1-PXZ-r** : $C_{44}H_{26}N_4O_2$, M_r = 642.69, dark red needle, monoclinic, space group C2/c, a = 25.514(2) Å, b = 9.0508(3) Å, c = 19.0317(16) Å, β = 136.902(16)°, $\alpha = \gamma$ = 90° , V = 3002.7(7) Å^3 , , T = 100(2) K, Z = 4, Z' = 0.5, μ(MoK$_\alpha$) = 0.089 mm^{-1}, 33178 reflections measured, 3451 unique (R_{int} = 0.0411) which were used in all calculations. The final wR_2 was 0.0978 (all data) and R_1 was 0.0384 (I > 2(I)). CCDC 1853154.

Crystal data for **H2-PXZ** : $C_{33}H_{20}N_2O$, M_r = 460.51, yellow block, triclinic, space group P-1, a = 14.2418(2) Å, b = 14.2451(2) Å, c = 22.5117(2) Å, α = 88.0520(10)°, β = 92.0040(10)°, γ = 101.8250(10)°, V = 4465.74(10) Å^3, T = 100(2) K, Z = 8, Z' = 4, μ(CuK$_\alpha$) = 0.650 mm^{-1}, 78986 reflections measured, 16070 unique (R_{int} = 0.0352) which were used in all calculations. The final wR_2 was 0.1956 (all data) and R_1 was 0.0714 (I > 2(I)). CCDC 1853155.

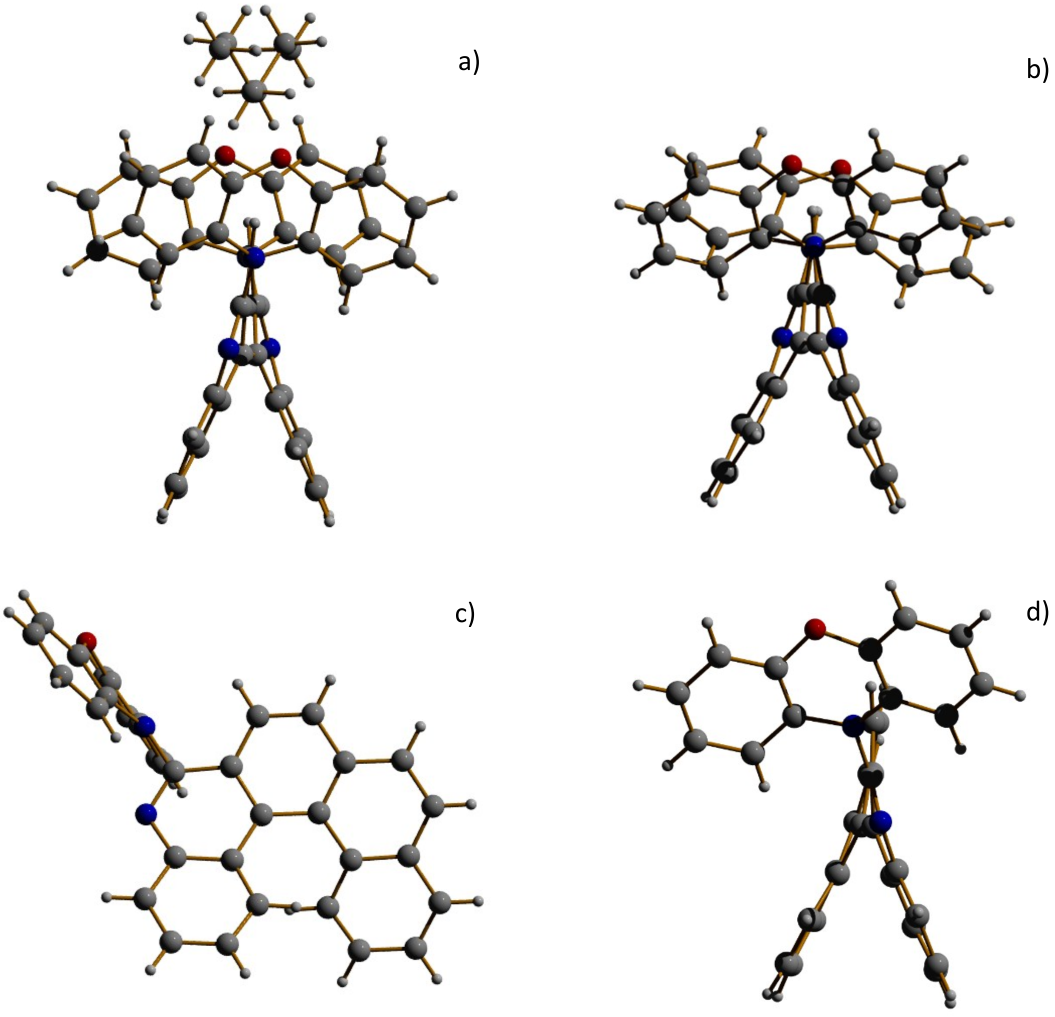
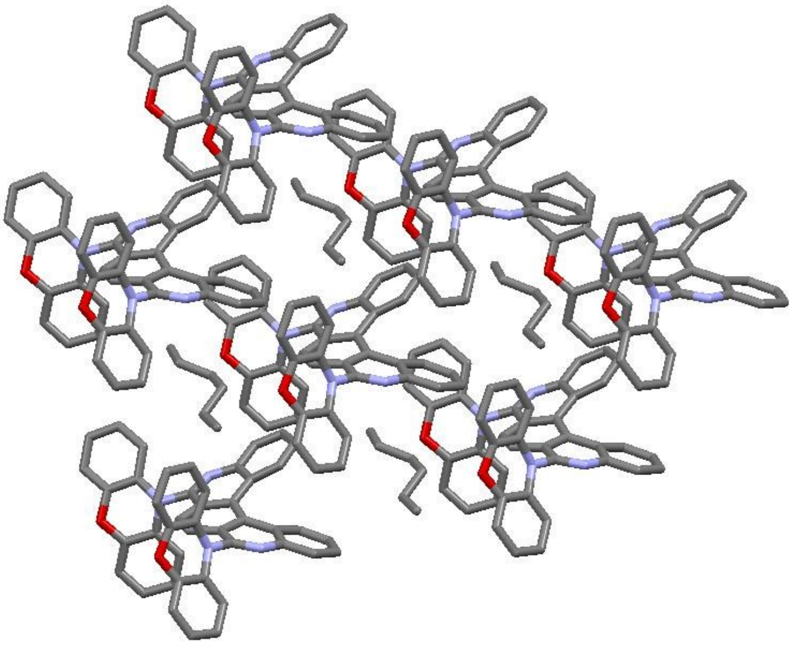


Figure S6.1 Molecular structures of **H1-PXZo** (a), **H1-PXZr** (b), **H2-PXZ** (c, d).

a)



b)

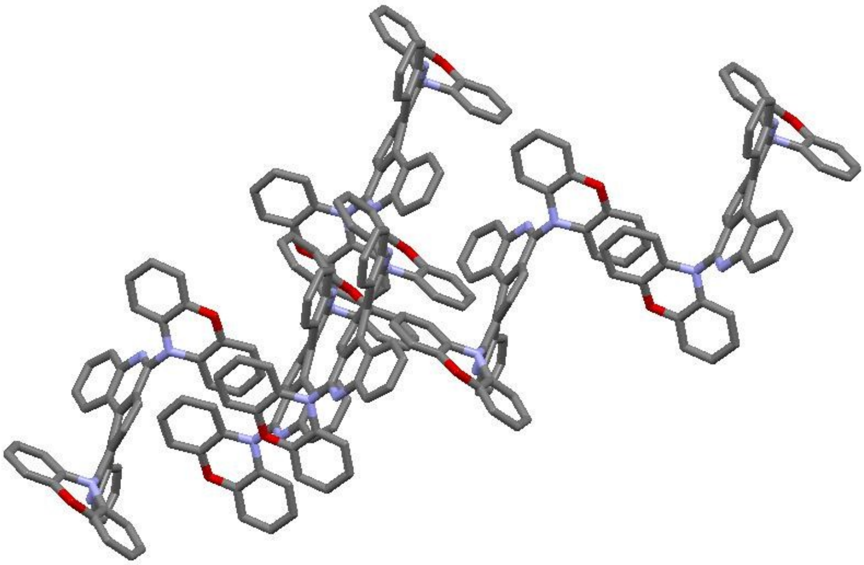


Figure S6.2 Crystal packing structure of **H1-PXZ-o** (a) and **H1-PXZ-r** (b). H atoms omitted for clarity.

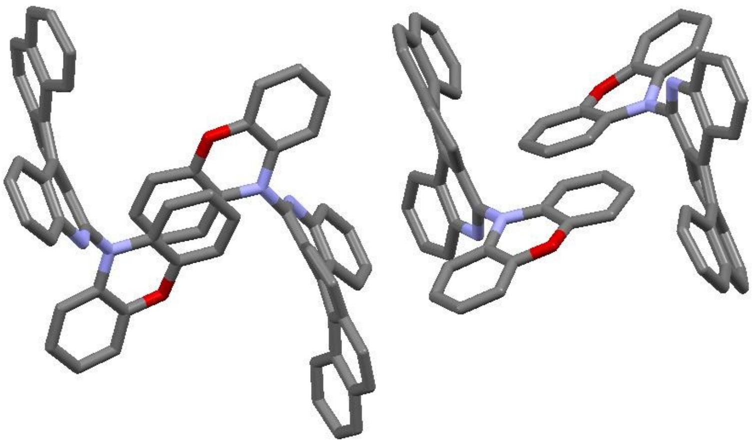


Figure S6.3 Dimers of **H2-PXZ** with H atoms omitted for clarity.

S7. Photophysics

Absorption spectra of 10^{-5} M solutions or films were recorded using a UV-3600 double beam spectrophotometer (Shimadzu). Photoluminescence (PL) spectra of 10^{-5} M solutions and films were recorded using FluoroMax-3 fluorescence spectrometer (Jobin Yvon). Photoluminescence and photoluminescence quantum yield of powders were recorded in an integrating sphere using a QEPro matrix spectrometer (Ocean Optics). Phosphorescence (PH), prompt fluorescence (PF), and delayed fluorescence (DF) spectra and fluorescence decay curves were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using either third harmonics of a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) or a N_2 laser emitting at 337 nm. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution. PF/DF time resolved measurements were performed by exponentially increasing gate and integration times. Temperature-dependent experiments were conducted using a continuous flow liquid nitrogen cryostat (Janis Research) under nitrogen atmosphere, while measurements at room temperature were recorded in vacuum in the same cryostat.

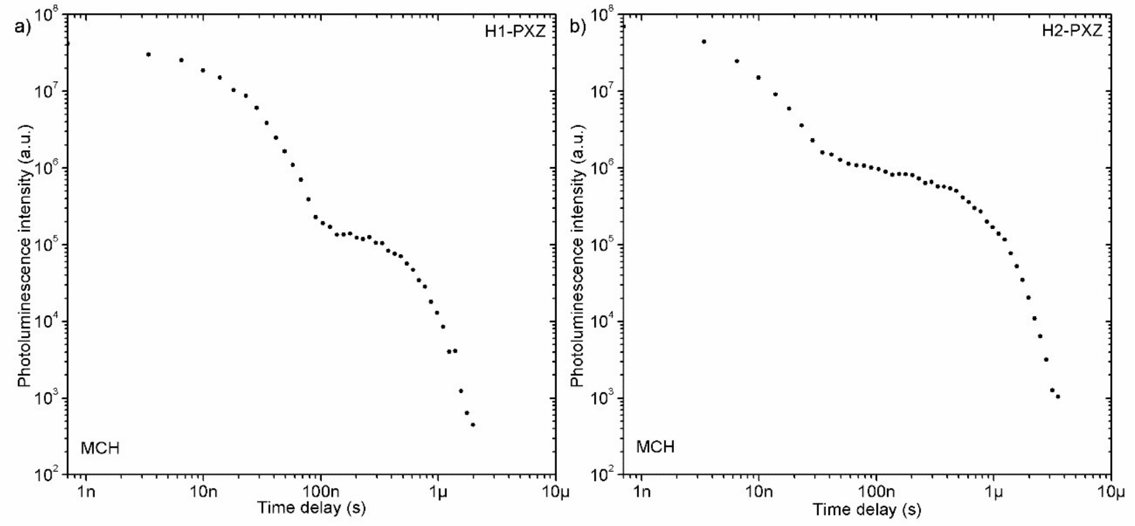


Figure S7.1 Photoluminescence decay of **H1-PXZ** and **H2-PXZ** in methylcyclohexane (MCH) solutions. Note: ^{1}LE emission decays within the first nanosecond and the presented decays reflect CT emission only.

Table S7.1 Photophysical properties in methylcyclohexane.

Compound	**λ_{max}, nm**[a]	**Φ_{PL}**[b]	**τ_{PF}, ns**[c]	**τ_{DF}, µs**[d]
H1-PXZ	611	0.07	15.0 ± 0.2	0.40 ± 0.02
H2-PXZ	536	0.04	6.1 ± 0.2	0.47 ± 0.02

[a] Charge transfer photoluminescence maximum λ_{exc} = 410 nm; [b] photoluminescence quantum yield in degassed solution, λ_{exc} = 410 nm ; [c] prompt fluorescence lifetime in a degassed solution; [d] delayed fluorescence lifetime in a degassed solution.

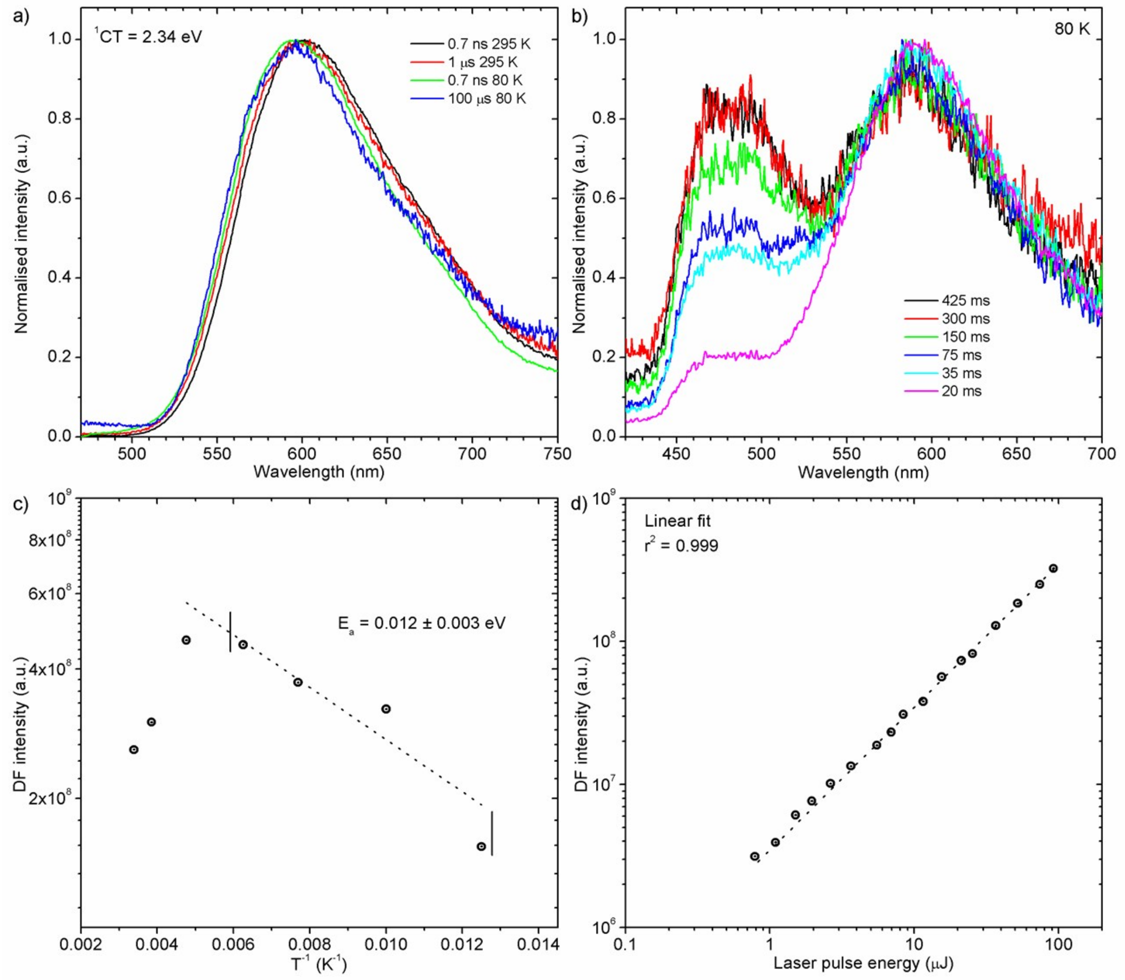


Figure S7.2 Time-resolved photoluminescence analysis of **H1-PXZ** in Zeonex film (1% w/w): a) time-resolved spectra at 295 and 80 K; b) time-resolved spectra recorded at late delay times at 80 K; c) temperature dependence of delayed fluorescence; d) power dependence of delayed fluorescence at 295 K.

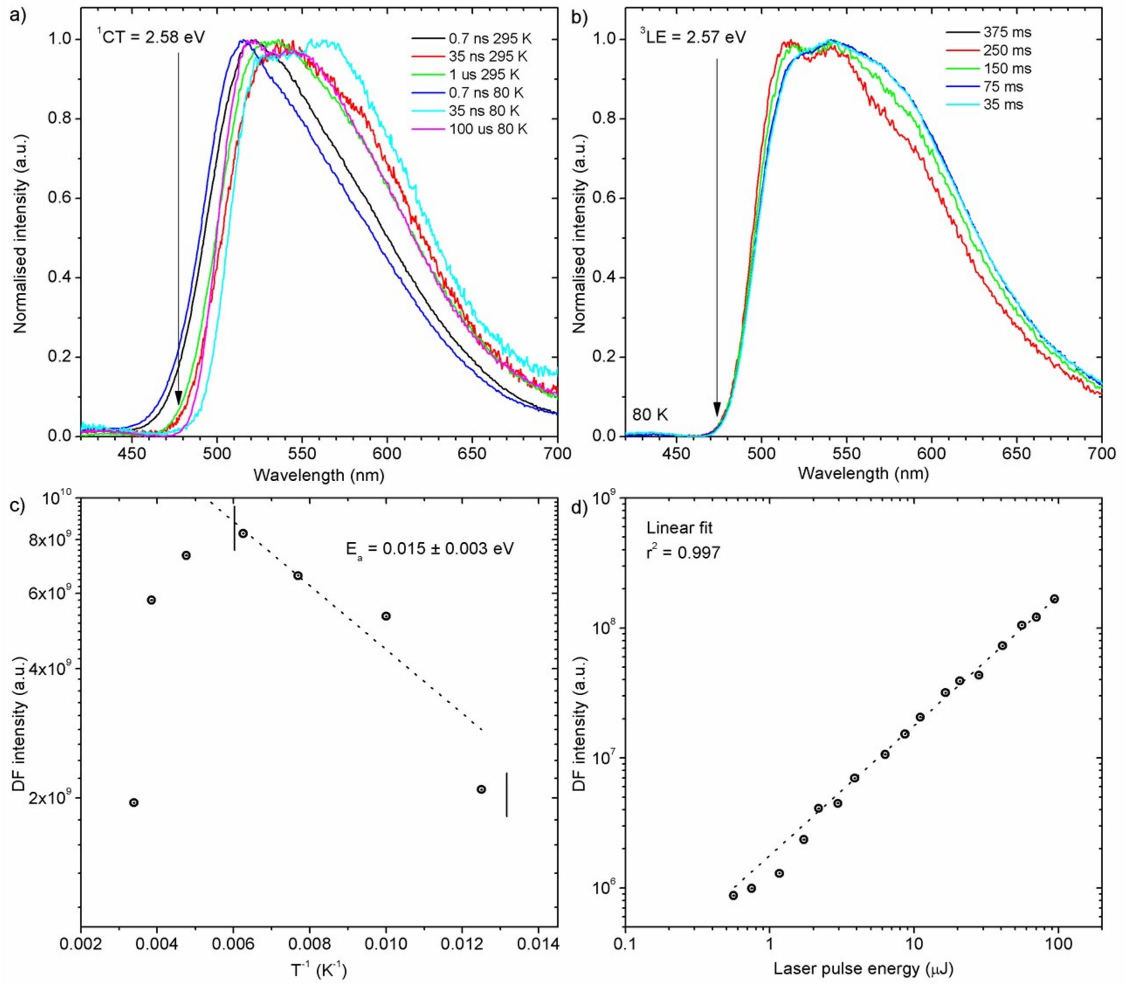


Figure S7.3 Time-resolved photoluminescence analysis of **H2-PXZ** in zeonex film (1% w/w): a) time-resolved spectra at 295 and 80 K; b) time-resolved spectra recorded at late delay times at 80 K; c) temperature dependence of delayed fluorescence; d) power dependence of delayed fluorescence at 295 K.

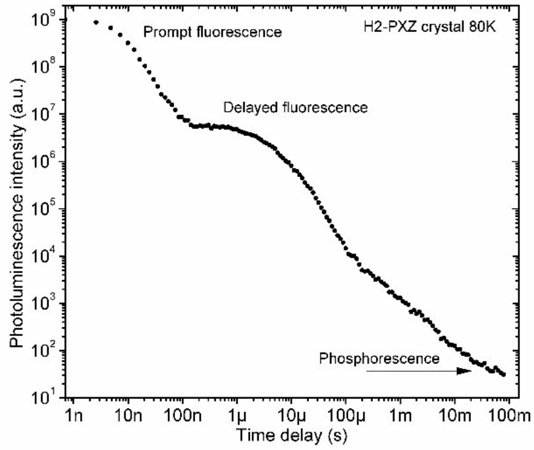


Figure S7.4 Photoluminescence decay of **H2-PXZ** crystals at 80 K in broad timescale.

S8. Organic light-emitting diodes

OLEDs were fabricated by spin-coating / evaporation hybrid method. Hole injection layer (Heraeus Clevios HIL 1.3N), electron blocking/hole transport layer (PVKH), and emitting layer (PVK:PBD with 5% of dopant) were spin-coated, whereas electron transport/hole blocking layer (TPBi) and cathode (LiF/Al) were evaporated. Devices of 4x2mm pixel size were fabricated. PVK – poly(9-vinylcarbazole) (MW = 90 000, Acros Organics), PVKH – poly(9-vinylcarbazole) (MW = 1 100 000, Sigma Aldrich), PBD - 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (99%, Sigma Aldrich), TPBi - 2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (sublimed, LUMTEC), LiF (99.995%, Sigma Aldrich), and aluminium wire (99.9995%, Alfa Aesar) were purchased from the companies indicated in parentheses. OLED devices were fabricated using pre-cleaned indium-tin-oxide (ITO) coated glass substrates after ozone plasma treatment with a sheet resistance of 20 Ω cm^{-2} and ITO thickness of 100 nm. Heraeus Clevios HIL 1.3N was spun-coated and annealed onto a hotplate at 200 ˚C for 3 min to give 45 nm film. Electron blocking/hole transport layer (PVKH), was spun from chloroform:chlorobenzene (95:5 v/v) (3 mg/mL) and annealed at 50 ˚C for 5 min to give 10 nm film.[3] Emitting layer was spun from toluene solution of PVK:PBD (60:40 w/w) and dopant with a total concentration of host at 10 mg/mL. The solution was spun onto the PVKH layer and then annealed at 50 ˚C for 5 min giving a 32 nm film. All solutions were filtrated directly before application using a PVDF or PTFE syringe filter with 0.45 µm pore size (except for PVKH solution). All other organic and cathode layers were thermally evaporated using Kurt J. Lesker Spectros II deposition system at 10^{-6} mbar. All organic materials and aluminum were deposited at a rate of 1 Å s^{-1}. The LiF layer was deposited at 0.1-0.2 Å s^{-1}. Characterisation of OLED devices was conducted in 10 inch integrating sphere (Labsphere) coupled with a USB spectrometer (Ocean Optics) and connected to a Source Measure Unit.

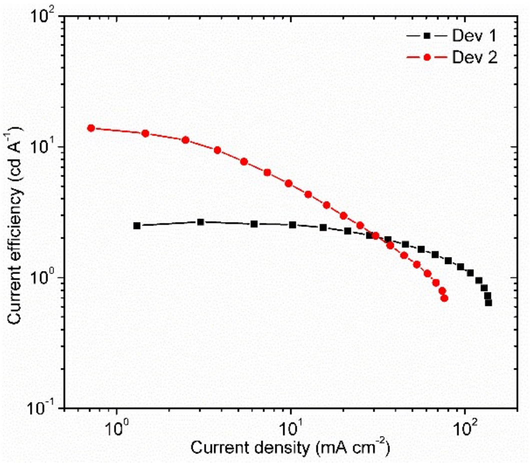


Figure S7.5 Current efficiency vs. current density characteristics of OLED devices.

1. D. Waghray, J. Zhang, J. Jacobs, W. Nulens, N. Basarić, L. V. Meervelt and W. Dehaen, *The Journal of Organic Chemistry*, 2012, **77**, 10176-10183.
2. D. C. Harrowven, I. L. Guy and L. Nanson, *Angewandte Chemie International Edition*, 2006, **45**, 2242-2245.

3. R. Pashazadeh, P. Pander, A. Lazauskas, F. B. Dias and J. V. Grazulevicius, *The Journal of Physical Chemistry Letters*, 2018, 1172-1177.