Chemistry–A European Journal

Supporting Information

Di- and Tetracyano-Substituted Pyrene-Fused Pyrazaacenes: Aggregation in the Solid State

Lucas Ueberricke,[a] Ioana Ciubotaru,[a] Farhad Ghalami,[b] Felix Mildner,[a] Frank Rominger,[a] Marcus Elstner,[b] and Michael Mastalerz*[a]

-Supporting Information-

Content

1 Experimental Section

1.1 General Remarks

All reagents and solvents were purchased from Fisher Scientific, Alfa Aesar, Sigma-Aldrich, TCI or VWR and were used without further purification unless otherwise noted. For thin-layer chromatography, silica gel 60 F254 plates from Merck were used and examined under UV irradiation (λ = 254 and 365 nm). Flash column chromatography was performed on silica gel from Sigma-Aldrich (particle size 0.04-0.063 mm) with dichloromethane as the eluent. Filtrations were carried out using polyamide microfilters from Sartorius except from highly acidic media. Melting points (not corrected) were measured by using a Büchi Melting Point B-545 instrument. IR spectra were recorded on a Ge ATR crystal by using a Bruker Lumos spectrometer. NMR spectra were recorded by using Bruker Avance DRX (300 MHz), Bruker Avance III (300 MHz), Bruker Avance III (400 MHz), and Bruker Avance III (500 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million [ppm] relative to trace undeuterated solvent in the corresponding deuterated solvent. HRMS experiments were carried out by using a Fourier-Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source. Absorption spectra were recorded on a Jasco UV-VIS V-730. Emission spectra were recorded on a Jasco FP-8300. Quantum yields were determined using an emission spectrometer equipped with an integration sphere (LabSphere®; diameter 6´´, coated with Spectraflect®). The system was calibrated with a primary light source.[S1] The procedure from Würth *et. al*.[S2] was used with following settings for the emission spectrometer: bandwidth 5 nm, emission bandwidth 5 nm, integration time 1 s. Electrochemical data were obtained in a solution of TBAPF (tetra-*n*-butyl ammonium hexafluorophoshate) (0.05 M) in CH_2Cl_2 that contained 1 mM of the investigated compound, as indicated. Ferrocene (1 mM) was used as an internal standard. Cyclic voltammograms were obtained at a scan rate of 0.05 Vs^{-1} with a Pt working electrode (0.78 mm^2), a Pt counter electrode, and an Ag reference electrode. Crystal structure analysis was accomplished by using a Bruker Apex-II diffractometer with a molybdenum source ($\lambda(Mo_{K\alpha})$= 0.71073 Å). Data were corrected for sample illumination, air and detector absorption, Lorentz, and polarization effects;[S3] absorption by the crystal was treated numerically (Gaussian grid).[S3-4] The structures were solved by using intrinsic phasing[S5] or direct methods with dual-space recycling[S6] and refined by using full-matrix least-squares methods on F2 against all unique reflections.[S7] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model. When necessary, disordered groups and/or solvent molecules were subjected to suitable geometry and adp restraints and/or constraints. CCDC 2002728-2002735 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/).

1.2 Synthetic Procedures

The general procedures GP1 and GP2 were adapted from a literature known procedure.[3b]

General Procedure for the synthesis of pyrene-fused pyrazaacenes using 2,3-diaminomaleonitrile (**GP1**): Pyrenedione **1**[16] or -tetraones **2a/2b**[16-17] and 2,3-diaminomaleonitrile **3** were suspended in a 1:1 mixture of AcOH and EtOH and stirred at 80 °C for 19 h. After cooling the reaction mixture to room temperature, the dark brown suspension was filtered over a polyamide microfilter and washed with MeOH (50 mL). The dark brown solid was refluxed in 30% nitric acid (50 mL) for 5 min. and filtered while still hot.[11] After washing with dest. water (50 mL) and MeOH (30 mL) the beige colored solid was extracted via a Soxhlet apparatus with THF (70 mL) for 15 h. The following steps were done as indicated below for the individual compounds.

General Procedure for the synthesis of pyrene-fused pyrazaacenes using 4,5-diaminophthalonitrile (**GP2**): Pyrenedione **1**[16] or tetraone **2a/2b**[16-17] and 4,5-diaminophthalonitrile **4** were suspended in a 1:1 mixture of AcOH and EtOH and stirred at 80 °C for 19 h. After cooling to room temperature, the suspension was filtered over a microfilter (polyamide) and washed with MeOH (50 mL). The following steps were done as indicated below for the individual compounds.

Phenanthro[4,5-*fgh*]quinoxaline-10,11-dicarbonitrile (**PQDC**): According to **GP1** **PQDC** was synthesized from pyrenedione **1** (380 mg, 1.64 mmol) and 2,3-diaminomaleonitrile **3** (230 mg, 2.13 mmol) in a mixture of AcOH (8.7 mL) and EtOH (8.7 mL). The extract was precipitated with MeOH (150 mL), filtered over a polyamide microfilter, washed with MeOH (50 mL) and dried in vacuo to obtain **PQDC** as a metallic golden powder (323 mg, 64%). mp 364°C (decomp.). ^{1}H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 9.40 (d, *J* = 7.8 Hz, 2H, *H*-1), 8.46 (d, *J* = 7.7 Hz, 2H, *H*-3), 8.19 (t, *J* = 7.7, 2H, *H*-2), 8.13 (s, 2H, *H*-4). ^{13}C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 144.1 (*C*-13), 131.7 (*C*-8a), 131.6 (*C*-3), 130.6 (*C*-10), 127.80 (*C*-2/4), 127.79 (*C*-2/4), 126.9 (*C*-3a), 126.7 (*C*-8b), 125.4 (*C*-1), 114.0 (*C*-10´). IR (ATR): $\tilde{\nu}$ [cm^{-1}] =3059 (vw), 3018 (vw), 2239 (vw), 1985 (vw), 1927 (vw), 1857 (vw), 1803 (vw), 1772 (vw), 1715 (vw), 1624 (m), 1603 (w), 1574 (vw), 1562 (vw), 1545 (vw), 1533 (vw), 1514 (w), 1495 (m), 1473 (w), 1446 (w), 1425 (w), 1387 (w), 1362 S, 1325 (m), 1296 (m), 1256 (vw), 1240 (vw), 1225 (w), 1215 (w), 1177 (m), 1142 (w), 1105 (w), 1076 (vw), 1066 (w), 1047 (vw), 1005 (vw), 999 (vw), 980 (vw), 935 (vw), 922 (vw), 837 (vs), 793 (vw), 775 (m), 717 (vs), 683 (vw), 669 (vw), 629 (vw). UV/Vis (CH_2Cl_2): λ_{abs} [nm] = 447, 354, 313, 284, 258. Fluorescence (CH_2Cl_2): λ_{em} [nm] (λ_{ex} [nm]) = 510(sh), 533 (445). PLQY: Φ [%] (λ_{ex} [nm], solvent) = 31 (354, CH_2Cl_2). HRMS (EI+): *m/z* = 304.0751 $[M]^+$ (calc. for $[M]^+$: *m/z* = 304.0749). Elemental analysis calc. for $C_{20}H_8N_4$ [%]: C 78.94, H 2.65, N 18.41. Found: C 78.55, H 2.88, N 18.66.

Phenanthro[4,5-*abc*]phenazine-11,12-dicarbonitrile (**PPDC**): According to **GP2** **PPDC** was synthesized from pyrenedione **1** (464 mg, 2.00 mmol) and 4,5-diaminophthalonitrile **4** (321 mg, 2.00 mmol) in a mixture of AcOH (10 mL) and EtOH (10 mL). The crude product was refluxed in a mixture of THF (300 mL) and MeOH (100 mL), filtered over a polyamide microfilter while still hot. After cooling to room temperature and dried in vacuo to give as **PPDC** bright orange powder (582 mg, 82%). An aliquot was further purified by sublimation at a Kugelrohrofen (250 °C, $3\text{-}6\times10^{-3}$ mbar) to obtain fine orange needles. mp 393.3-398.5 °C (after sublimation). ^{1}H-NMR (600 MHz, THF-d8): δ [ppm] = 9.56 (d, *J* = 7.7 Hz, 2H, *H*-1), 8.81 (s, 2H, *H*-10), 8.41 (d, *J* = 7.7 Hz, 2H, *H*-3), 8.15 (t, *J* = 7.7 Hz, 2H, *H*-2), 8.10 (s, 2H, *H*-4). ^{13}C-NMR (151 MHz, THF-d8): δ [ppm] = 147.1 (*C*-15), 142.4 (*C*-9a/11), 137.5 (*C*-10), 131.8 (*C*-3), 131.6 (*C*-8b), 128.3 (*C*-8a), 127.7 (*C*-4), 127.6 (*C*-2), 126.9 (*C*-3a), 125.6 (*C*-1), 115.4 (*C*-9a/11/11´), 113.5 (*C*-9a/11/11´). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3090 (vw), 3063 (vw), 3036 (vw), 2235 (w), 1956 (vw), 1851 (vw), 1824 (vw), 1770 (vw), 1689 (vw), 1620 (w), 1605

(w), 1545 (vw), 1520 (vw), 1497 (vw), 1468 (w), 1446 (w), 1433 (w), 1400 (m), 1358 (m), 1346 (w), 1313 (m), 1298 (m), 1261 (vw), 1236 (w), 1223 (vw), 1173 (w), 1147 (w), 1095 (w), 1076 (w), 1063 (w), 1045 (vw), 982 (vw), 920 (m), 887 (m), 845 (vs), 827 (w), 789 (w), 775 (w), 717 (vs), 629 (m). UV/Vis (CH_2Cl_2): λ_{abs} [nm] = 485, 460, 348, 333, 319, 289. Fluorescence (CH_2Cl_2): λ_{em} [nm] (λ_{ex} [nm]) = 534 (475). PLQY: Φ [%] (λ_{ex} [nm], solvent) = 37 (330, CH_2Cl_2). HRMS (EI+): *m/z* = 354.0859 $[M]^+$ (calc for $[M]^+$: *m/z* = 354.0905). Elemental analysis calc. for $C_{24}H_{10}N_4$ [%]: C 81.35, H 2.84, N 15.81. Found: C 81.35, H 2.98, N 16.05.

Pyrazino[2',3':9,10]phenanthro[4,5-*fgh*]quinoxaline-5,6,12,13-tetracarbonitrile (**PPQTC**): According to **GP1 PPQTC** was synthesized from pyrene tetraone **2a** (240 mg, 0.90 mmol) and 2,3-diaminomaleonitrile **3** (255 mg, 2.35 mmol) in a mixture of AcOH (4.8 mL) and EtOH (4.8 mL). After cooling the reaction mixture to room temperature, the extract was filtered over a polyamide microfilter, washed with MeOH (50 mL) and dried in vacuo to obtain **PPQTC** as dark yellow flakes (241 mg, 65%). mp 265°C (decomp.). ^{1}H-NMR (600 MHz, THF-d8): δ [ppm] = 9.72 (d, *J* = 7.9 Hz, 4H, *H*-1), 8.47 (t, *J* = 7.8 Hz, 2H, *H*-2). ^{13}C-NMR (151 MHz, THF-d8): δ [ppm] = 143.6 (*C*-15), 133.0 (*C*-3b/5), 130.9 (*C*-1), 130.5 (*C*-2), 129.8 (*C*-3b/5), 128.7 (*C*-3a), 115.0 (*C*-5´). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3065 (vw), 3047 (vw), 2978 (vw), 2872 (vw), 2241 (vw), 2012 (vw), 1686 (vw), 1527 (vw), 1499 (w), 1454 (w), 1391 (m), 1364 (vs), 1323 (w), 1300 (w), 1271 (vw), 1248 (vw), 1213 (m), 1167 (w), 1149 (vw), 1140 (w), 1128 (w), 1117 (w), 1097 (w), 1055 (w), 1030 (vw), 1009 (vw), 997 (vw), 916 (vw), 893 (w), 860 (w), 825 (m), 727 (m), 706 (vw), 692 (vw), 677 (vw), 658 (vw). UV/Vis (CH_2Cl_2): λ_{abs} [nm] = 411, 389, 330, 288, 267. Fluorescence (CH_2Cl_2): λ_{em} [nm] (λ_{ex} [nm]) = 437 (401). PLQY: Φ [%] (λ_{ex} [nm], solvent) = 37 (330, CH_2Cl_2). HRMS (DART+): *m/z* = 424.1052 $[M+NH_4]^+$ (calc. for $[M+NH_4]^+$: *m/z* = 424.1054). Elemental analysis calc. for $C_{24}H_6N_8$ [%]: C 70.94, H 1.49, N 27.58. Found: C 70.39, H 1.82, N 27.46.

2,9-Di-*tert*-butylpyrazino[2',3':9,10]phenanthro[4,5-*fgh*]quinoxaline-5,6,12,13-tetracarbonitrile (**^{t}Bu-PPQTC**): According to **GP1 ^{t}Bu-PPQTC** was synthesized from pyrene tetraone **2a** (374 mg, 1.00 mmol) and 2,3-diaminomaleonitrile **3** (281 mg, 2.60 mmol) in a mixture of AcOH (5 mL) and EtOH (5 mL). After cooling to room temperature, the Soxhlet extract was filtered over a polyamide microfilter and washed with MeOH (50 mL). The precipitate from the filtrate was filtered off, washed with MeOH (50 mL) again and dried in vacuo to obtain **^{t}Bu-PPQTC** as pale-yellow flakes (336 mg, 65%). mp > 410 °C (decomp.). ^{1}H-NMR (600 MHz, CD_2Cl_2): δ [ppm] = 9.71 (s, 4 H, *H*-1), 1.67 (s, 18 H, *H*-^{t}Bu). ^{13}C-NMR (151 MHz, CD_2Cl_2): δ [ppm] = 153.9 (*C*-2), 143.9 (*C*-15), 131.5 (*C*-3b/5), 128.5 (*C*-1), 127.3 (*C*-3a), 114.5 (*C*-5´), 36.7 (*C*-2´), 31.9 (*C*-2´´). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2970 (m), 2932 (w), 2910 (w), 2874 (w), 2241 (vw), 1844 (vw), 1605 (w), 1526 (w), 1495 (m), 1479 (m), 1466 (m), 1429 (vs), 1412 (s), 1373 (s), 1365 (s), 1342 (vs), 1281 (s), 1238 (s), 1225 (m), 1202 (w), 1153 (s), 1068 (vw), 1030 (vw), 1005 (w), 987 (w), 933 (w), 908 (s), 872 (w), 850 (w), 760 (vw), 735 (s), 706 (w), 677 (vw), 650 (w), 606 (m). UV/Vis (CH_2Cl_2): λabs [nm] = 418, 345, 296. Fluorescence (CH_2Cl_2): λ_{em} [nm] (λ_{ex} [nm]) = 461, 529 (408). PLQY: Φ [%] (λ_{ex} [nm], solvent) = 15 (346, CH_2Cl_2). HRMS (DART+): *m/z* = 536.2295 $[M+NH_4]^+$ (calc. for $[M+NH_4]^+$: *m/z* = 536.2306). Elemental analysis calc. for $C_{24}H_6N_8$ [%]: C 74.12, H 4.28, N 21.61. Found: C 73.60, H 4.52, N 21.16.

Quinoxalino[2',3':9,10]phenanthro[4,5-*abc*]phenazine-6,7,15,16-tetracarbonitrile (QPPTC): According to **GP2 QPPTC** pyrene tetraone **2a** (197 mg, 0.75 mmol) and 4,5-diaminophthalonitrile **4** (335 mg, 2.12 mmol) in a mixture of AcOH (10 mL) and EtOH (10 mL). The crude product was extracted via a Soxhlet apparatus with THF for 19 h

and dried in vacuo to give the product as yellow powder (203 mg, 53%). mp >410 °C (decomp.). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3072 (vw), 3043 (vw), 2237 (w), 1736 (vw), 1678 (vw), 1610 (vw), 1597 (vw), 1566 (vw), 1535 (w), 1458 (m), 1412 (m), 1400 (m), 1362 (w), 1342 (s), 1306 (w), 1225 (w), 1175 (vw), 1161 (vw), 1103 (s), 1036 (vw), 1007 (vw), 995 (vw), 968 (w), 951 (vw), 922 (m), 895 (vs), 868 (vw), 833 (w), 814 (s), 771 (vw), 752 (vw), 737 (w), 719 (vs), 690 (vw), 617 (w). UV/Vis (*o*DCB): λ_{abs} [nm] = 440, 412, 390, 335, 309. Fluorescence (*o*DCB): λ_{em} [nm] (λ_{ex} [nm]) = 449, 475, 526^{sh} (430). PLQY: Φ [%] (λ_{ex} [nm], solvent) = 8.9 (412, *o*DCB). HRMS (DART): *m/z* = 524.1364 $[M+NH_4]^+$ (calc. for $[M+NH_4]^+$: *m/z* = 524.1367). Elemental analysis calc. $C_{32}H_{10}N_8 \cdot (H_2O)_{0.5}$ [%]: for C 74.56, H 2.15, N 21.74. Found: C 74.44, H 2.23, N 21.75.

2 ^{1}H and ^{13}C NMR Spectra

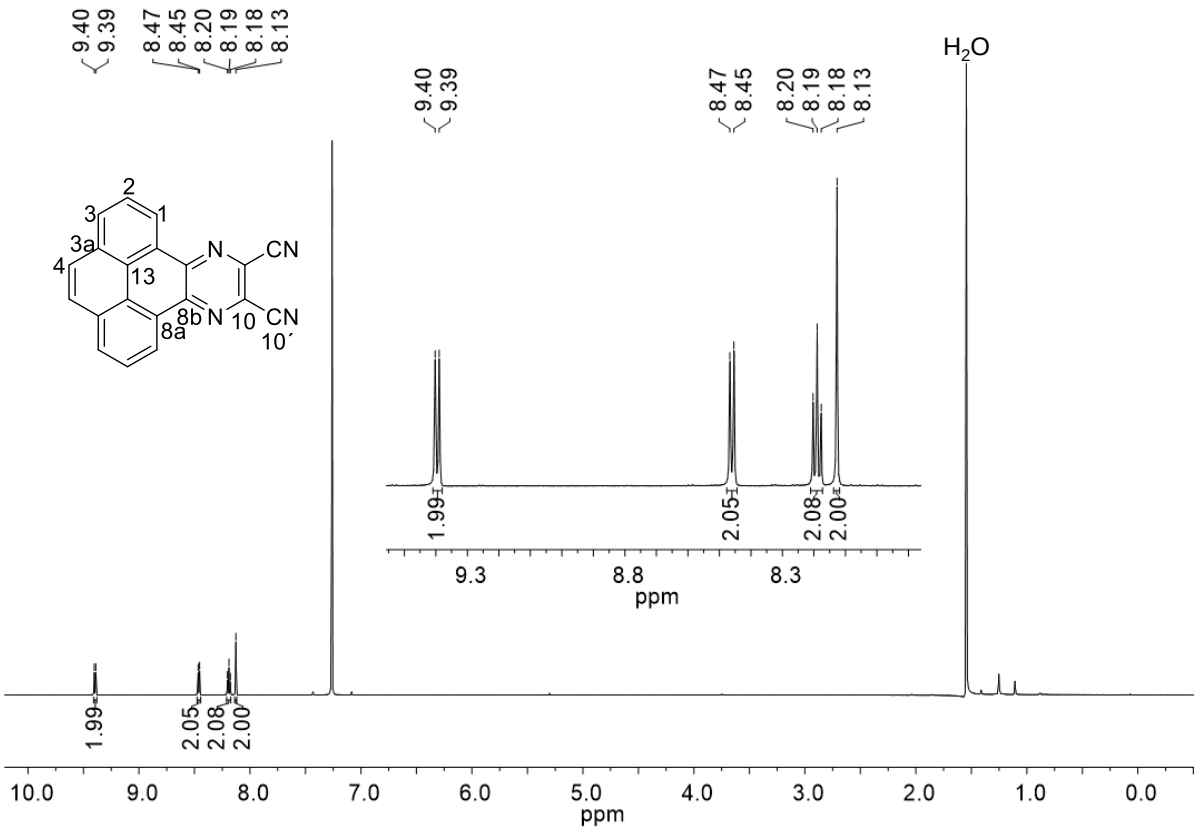

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **PQDC**.

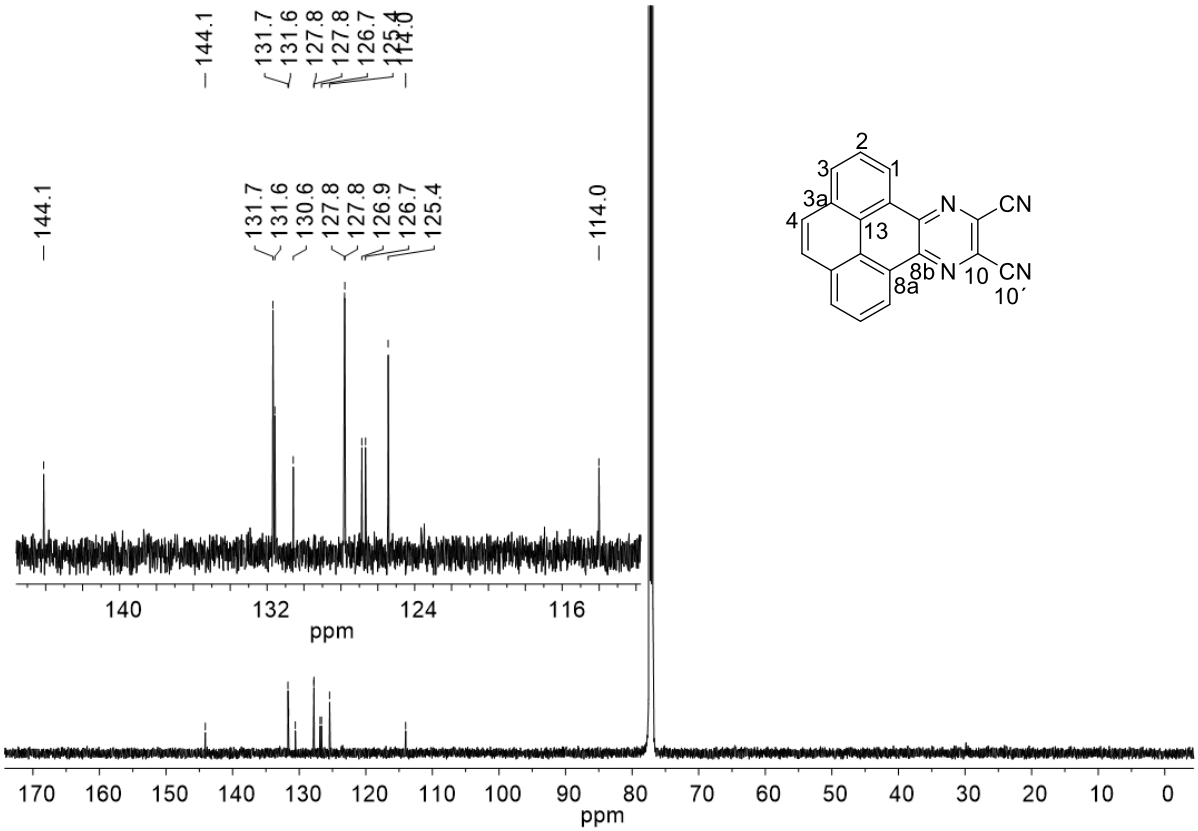

Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of **PQDC**.

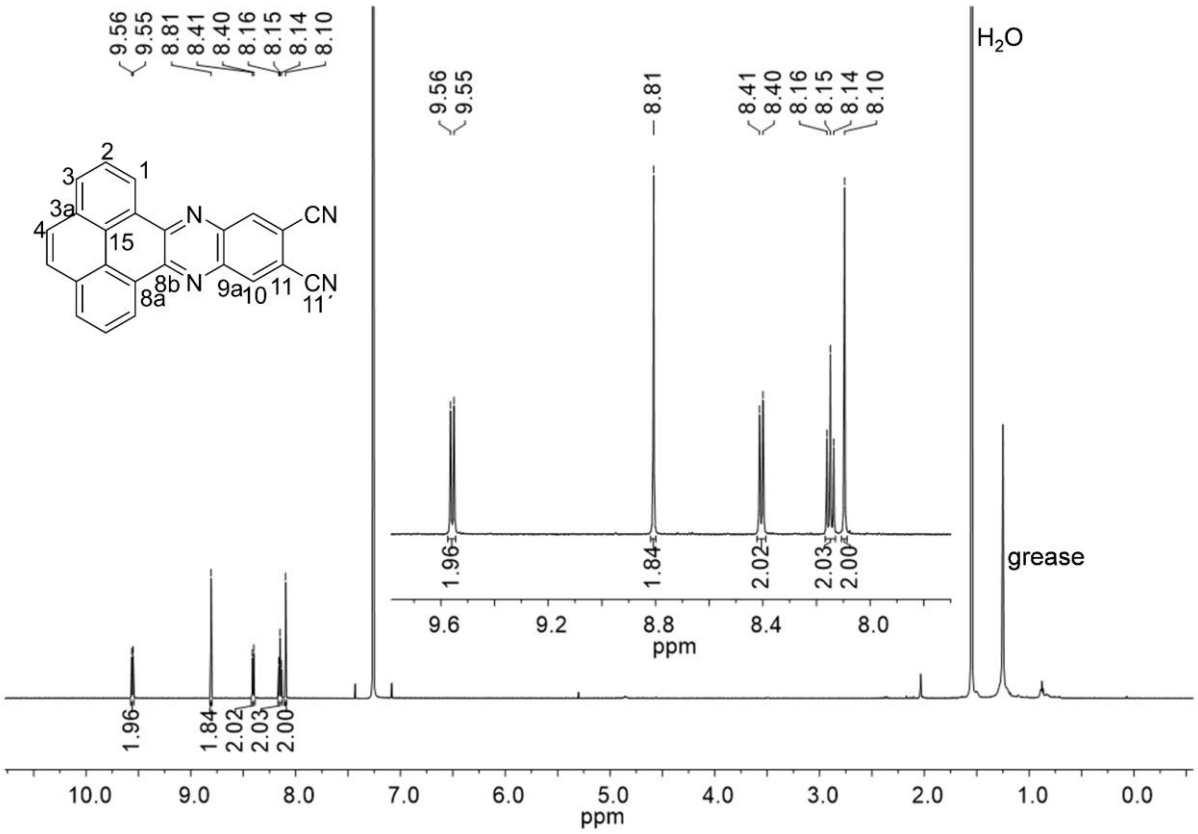

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **PPDC**.

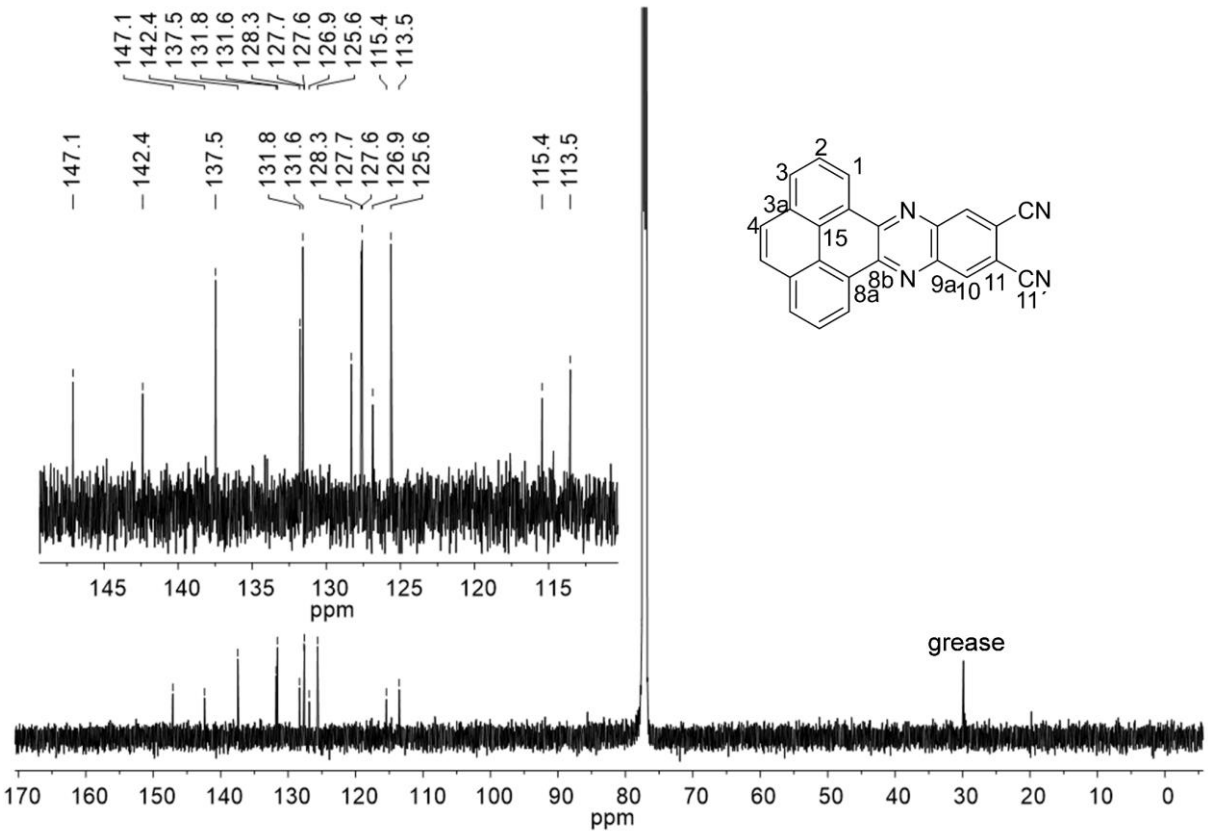

Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of **PQDC**.

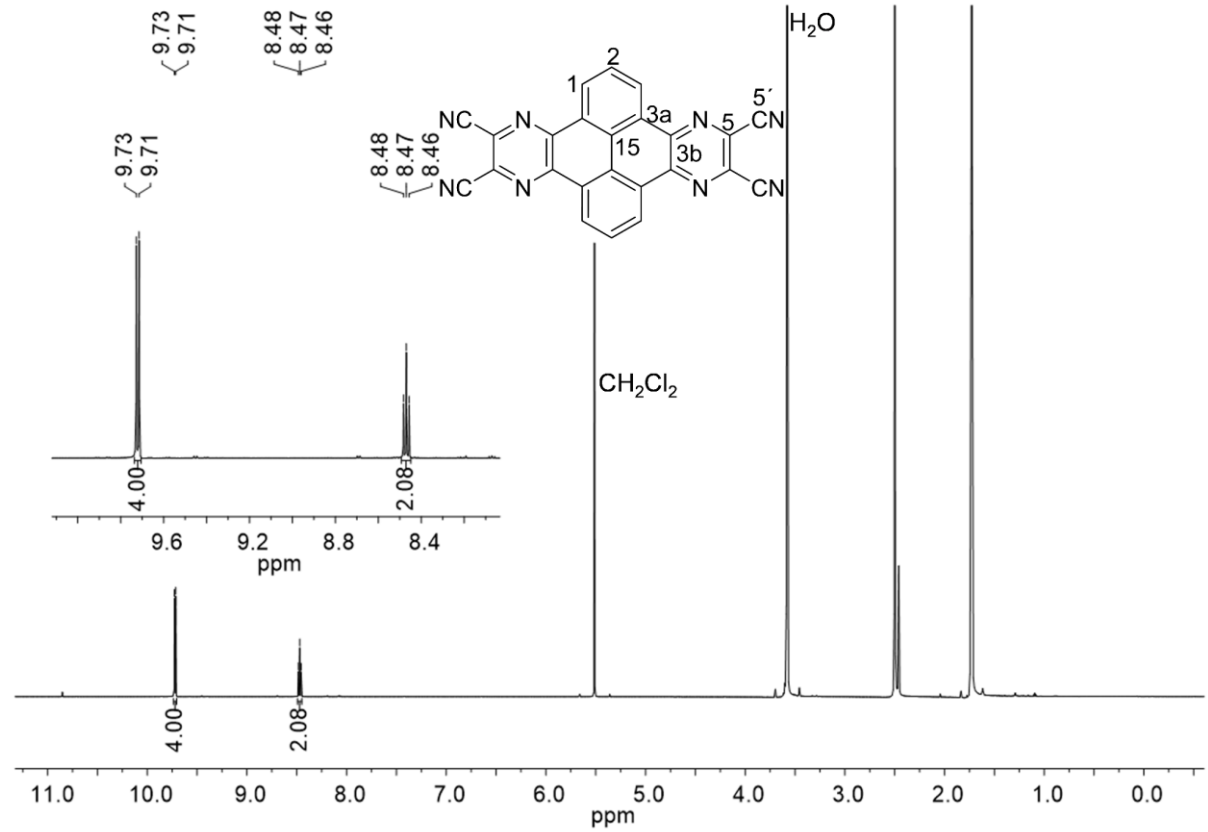

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **PPQTC**.

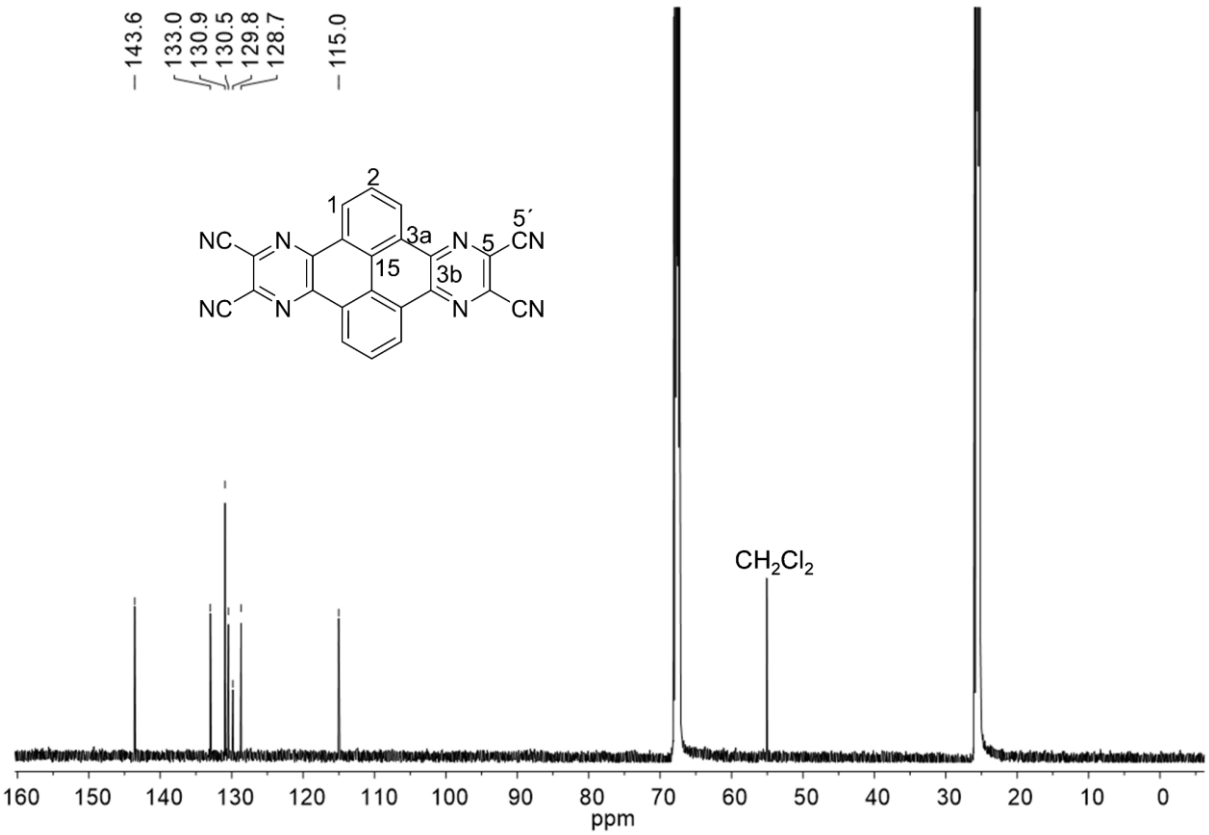

Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of **PPQTC**.

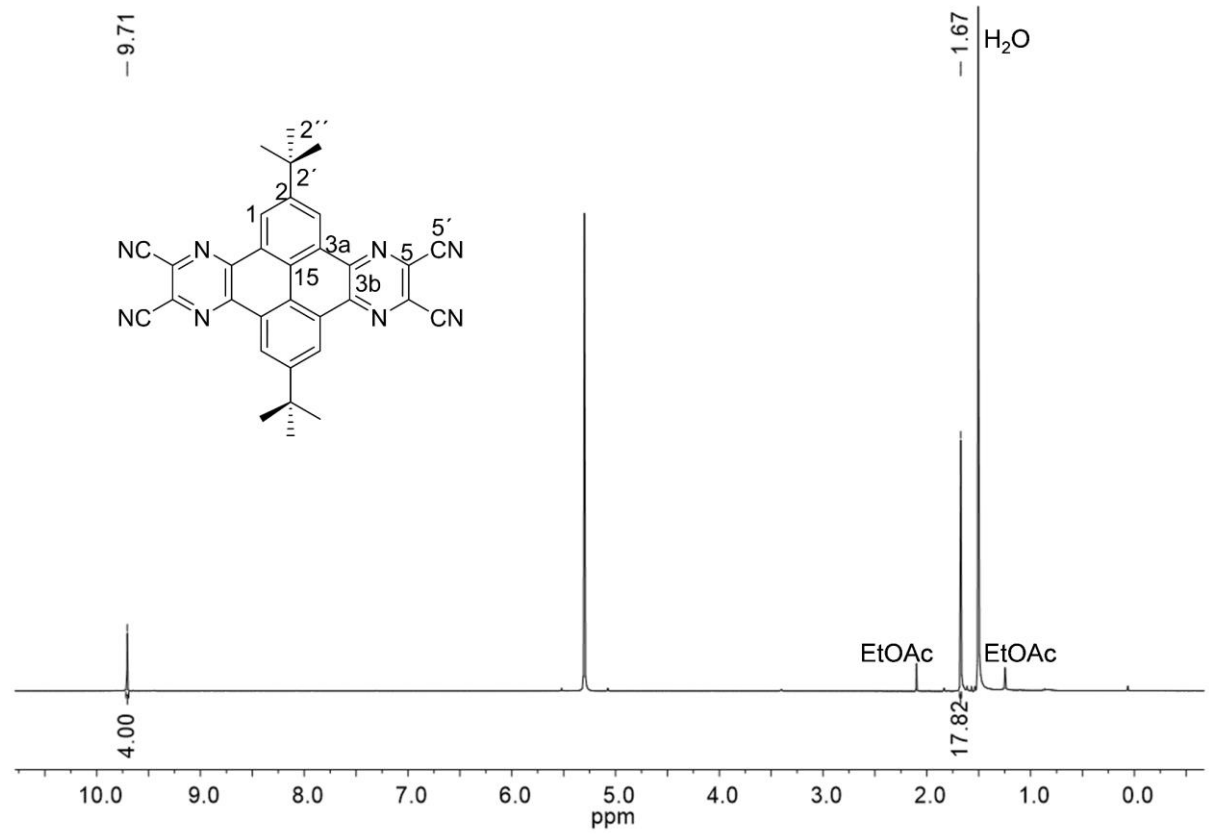

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **^{t}Bu-PPQTC**.

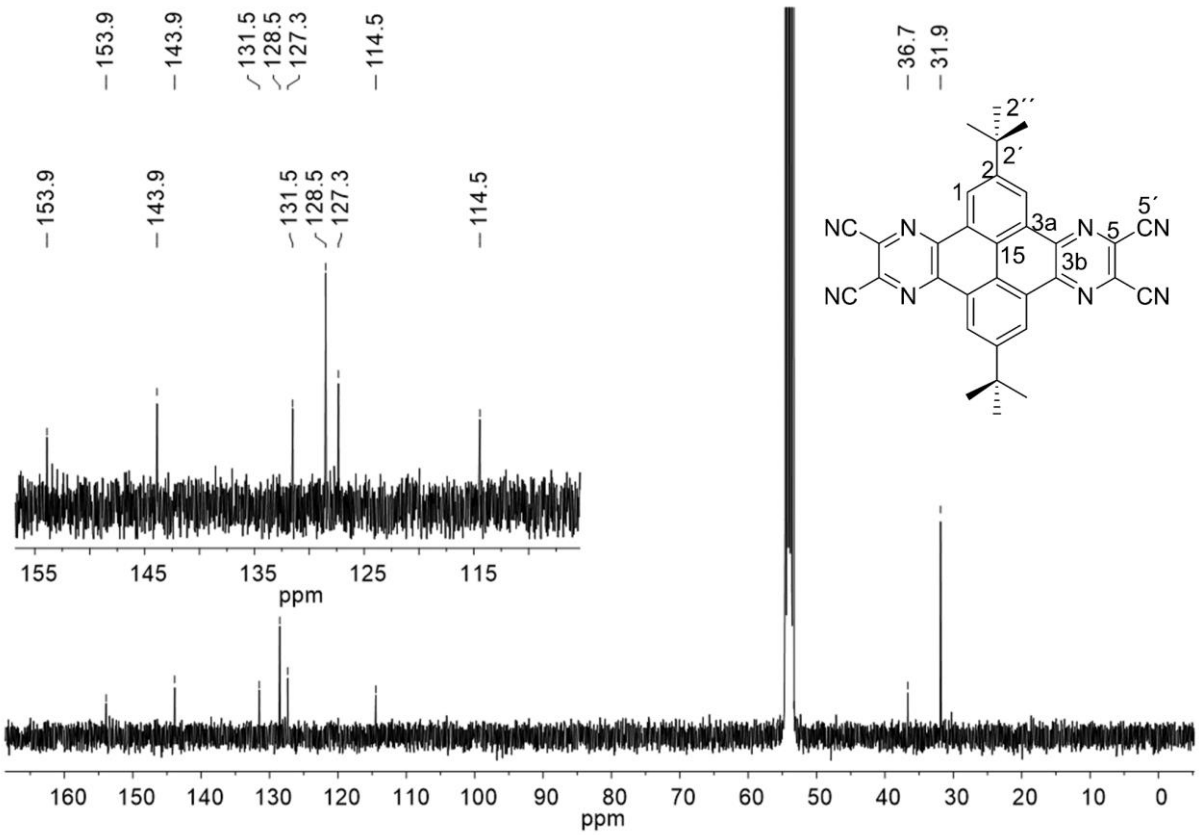

Figure S8. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **ᵗBu-PPQTC**.

3 FT-IR Spectra

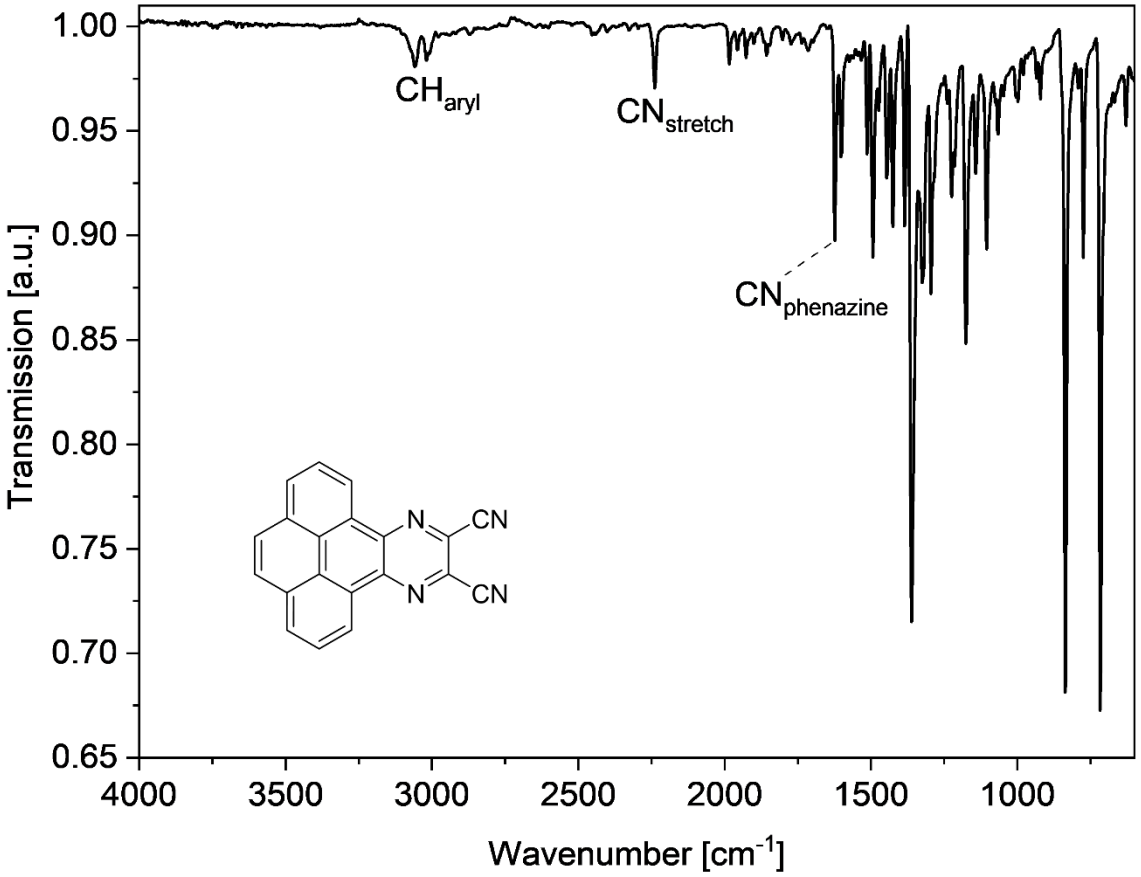

Figure S9. IR spectrum (ATR) of **PQDC**.

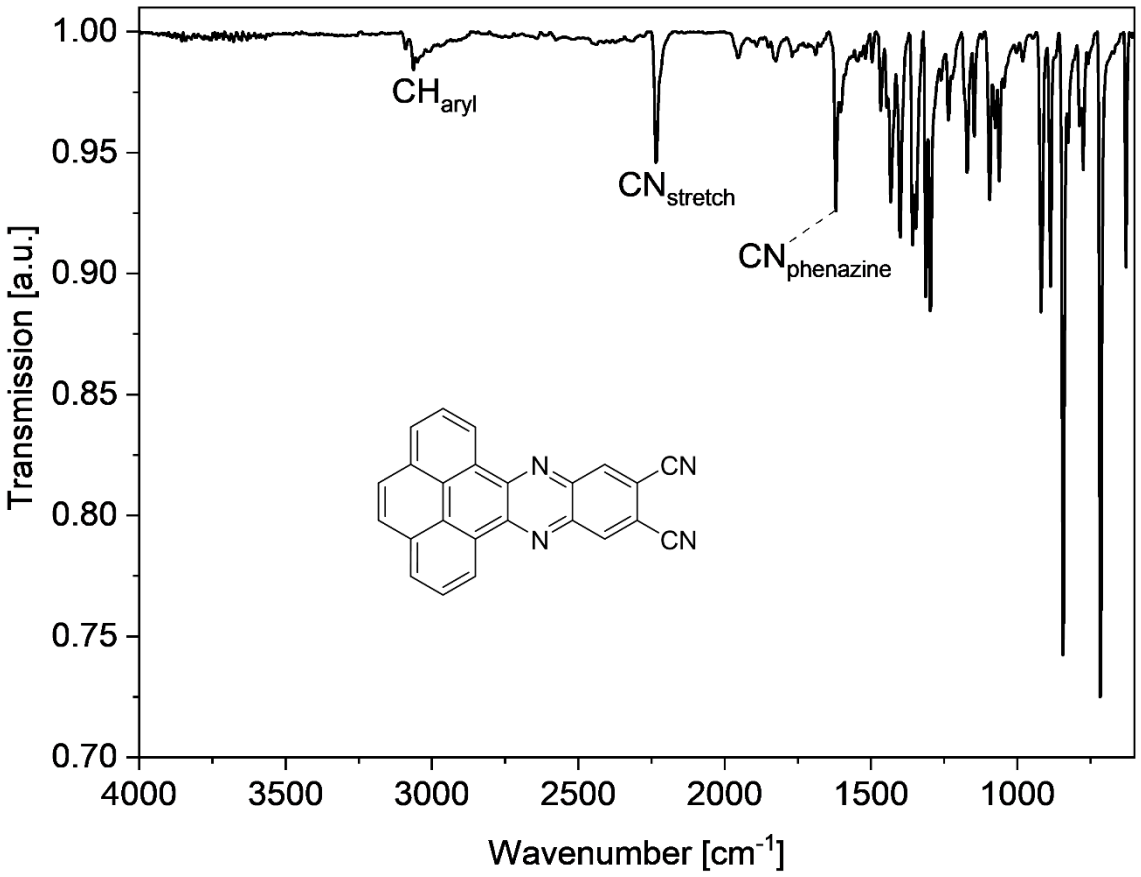

Figure S10. IR spectrum (ATR) of **PPDC**.

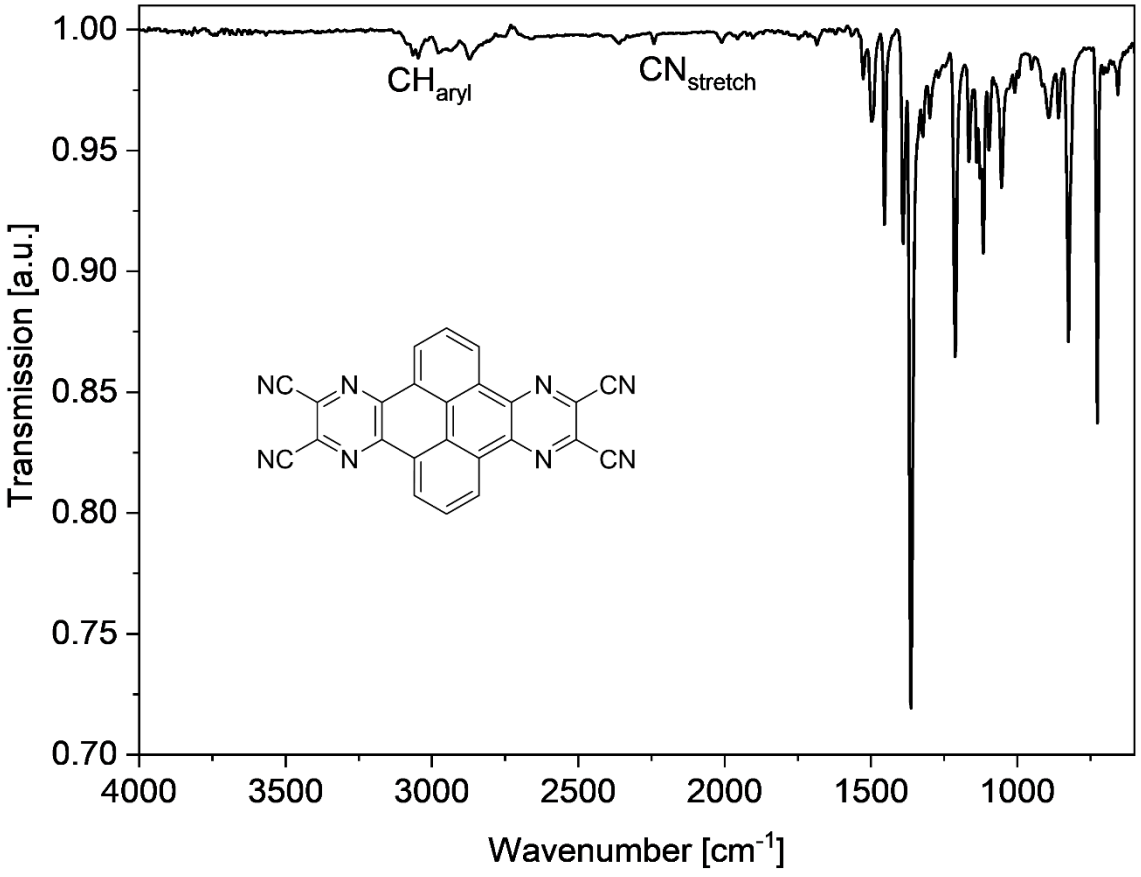

Figure S11. IR spectrum (ATR) of **PPQTC**.

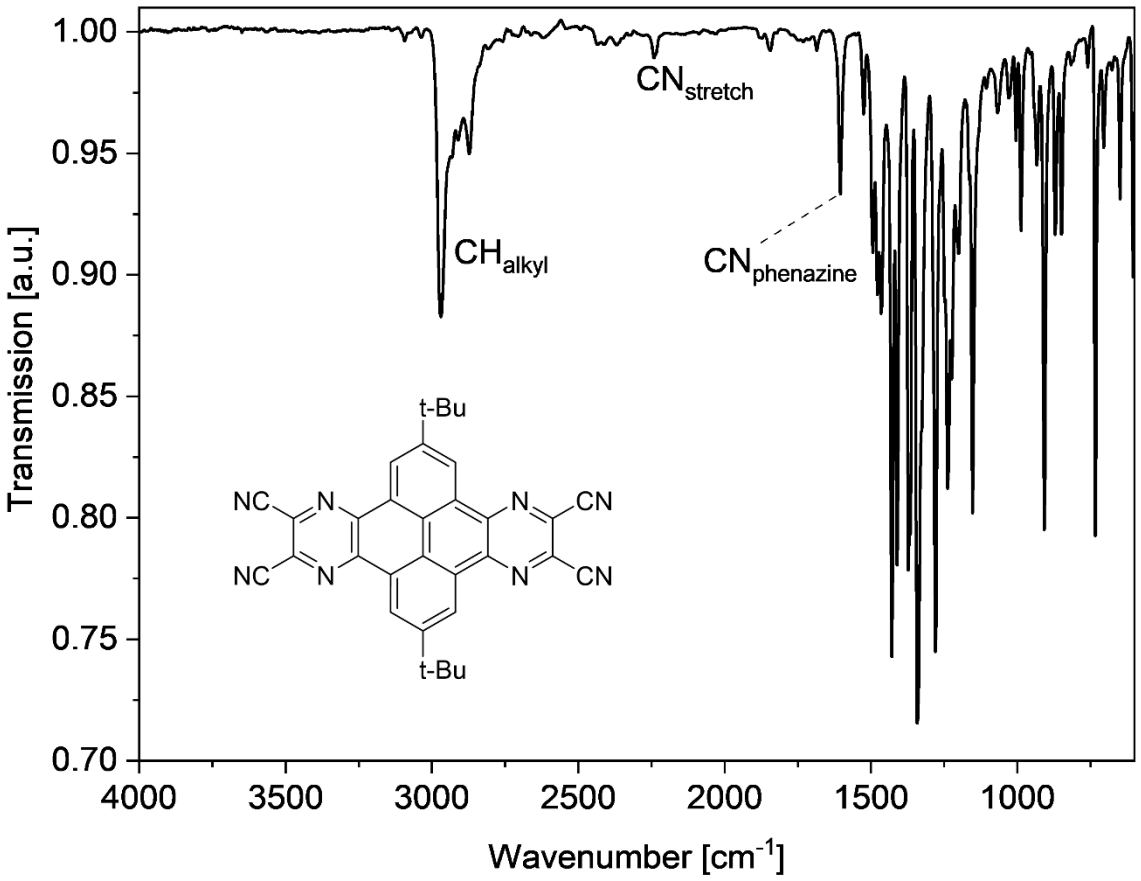

Figure S12. IR spectrum (ATR) of **^{t}Bu-PPQTC**.

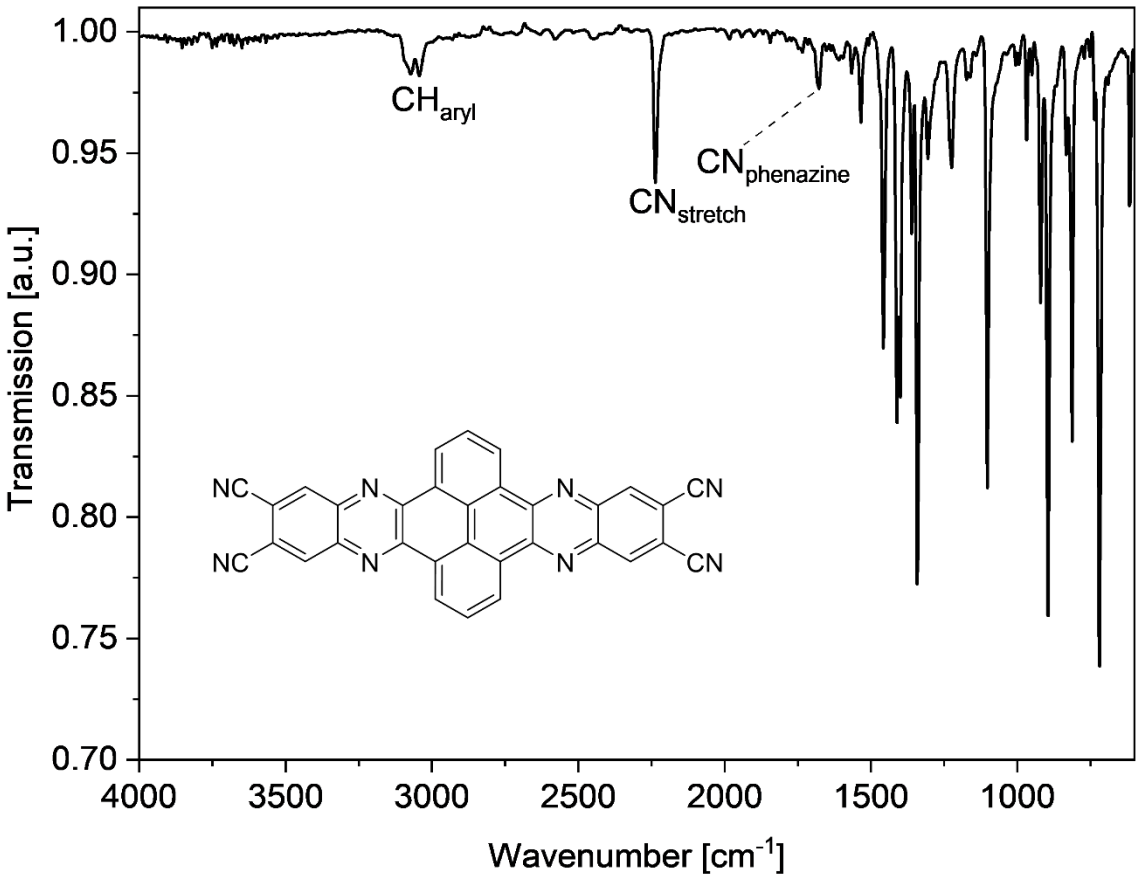

Figure S13. IR spectrum (ATR) of **QPPTC**.

4 Mass Spectra

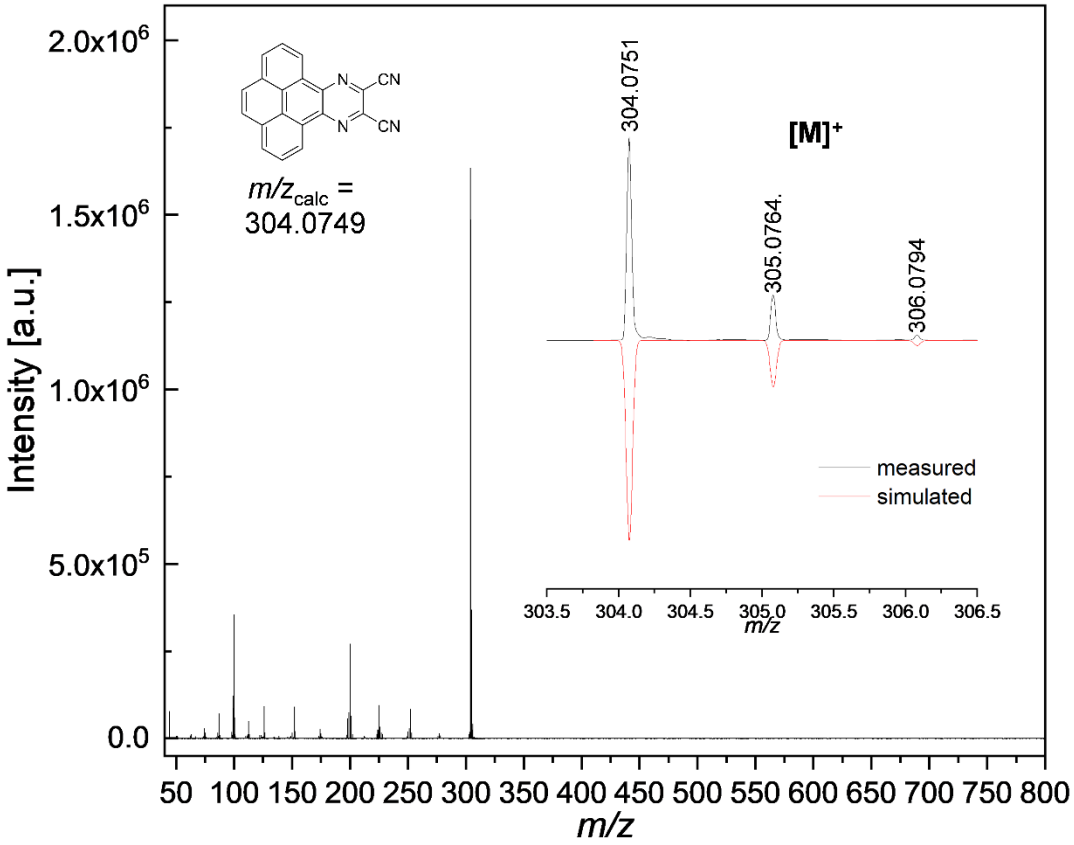

Figure S14. HRMS spectrum (EI+) of **PQDC**.

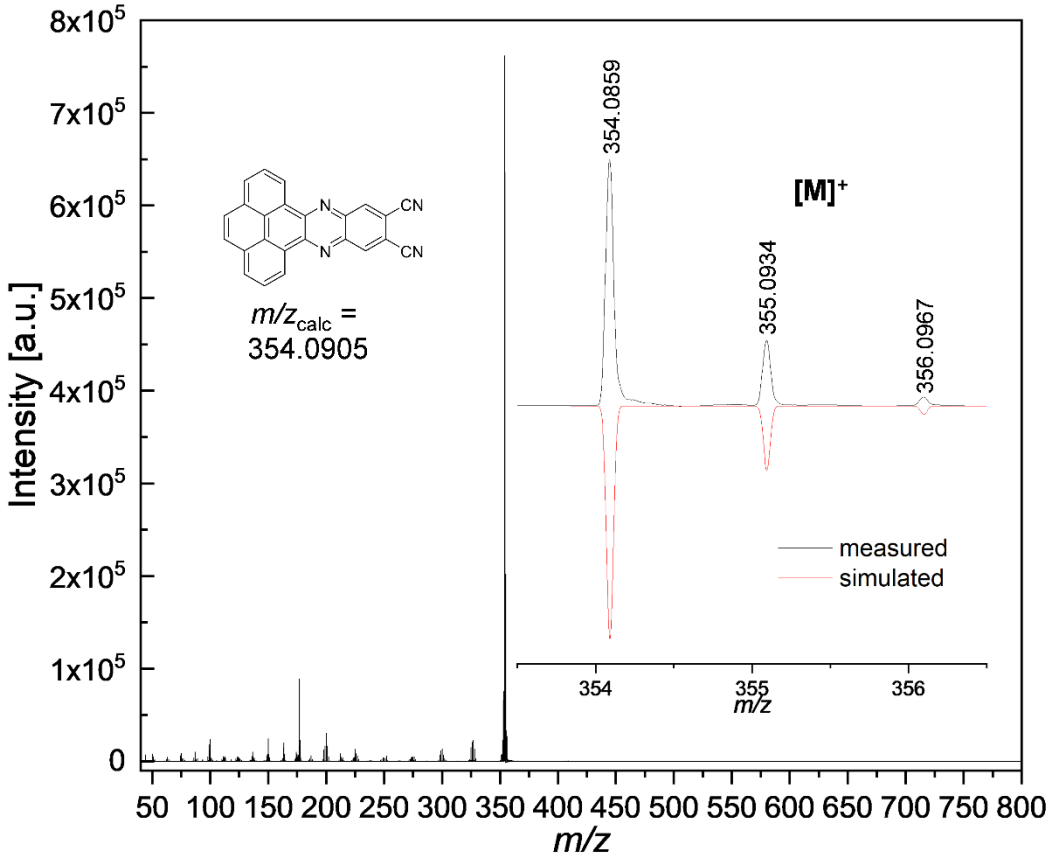

Figure S15. HRMS spectrum (EI+) of **PPDC**.

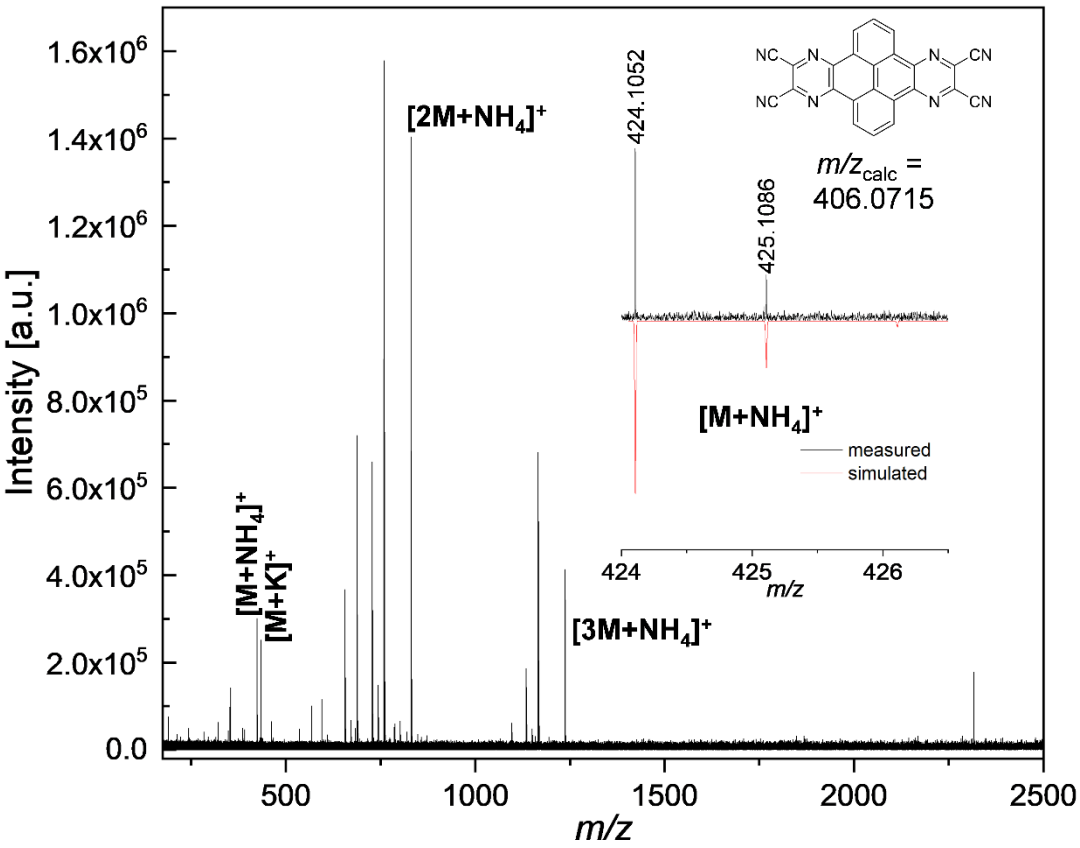

Figure S16. HRMS spectrum (DART+) of **PPQTC**.

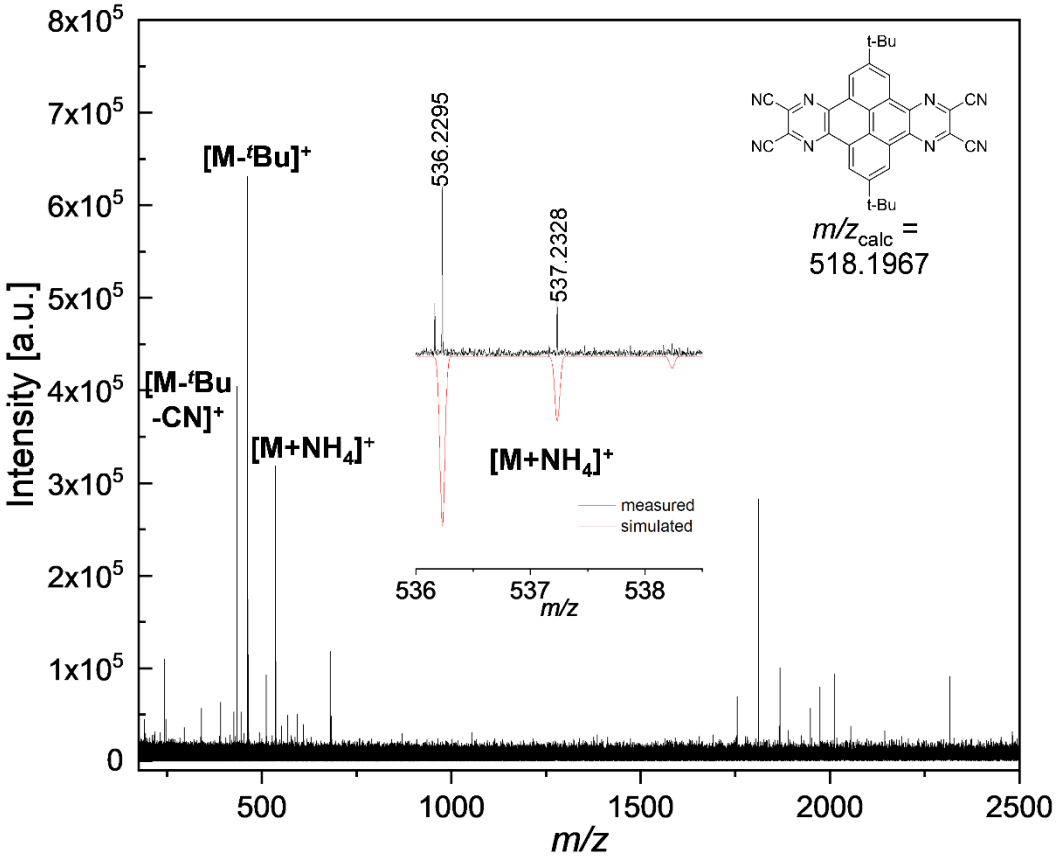

Figure S17. HRMS spectrum (DART+) of **^{t}Bu-PPQTC**.

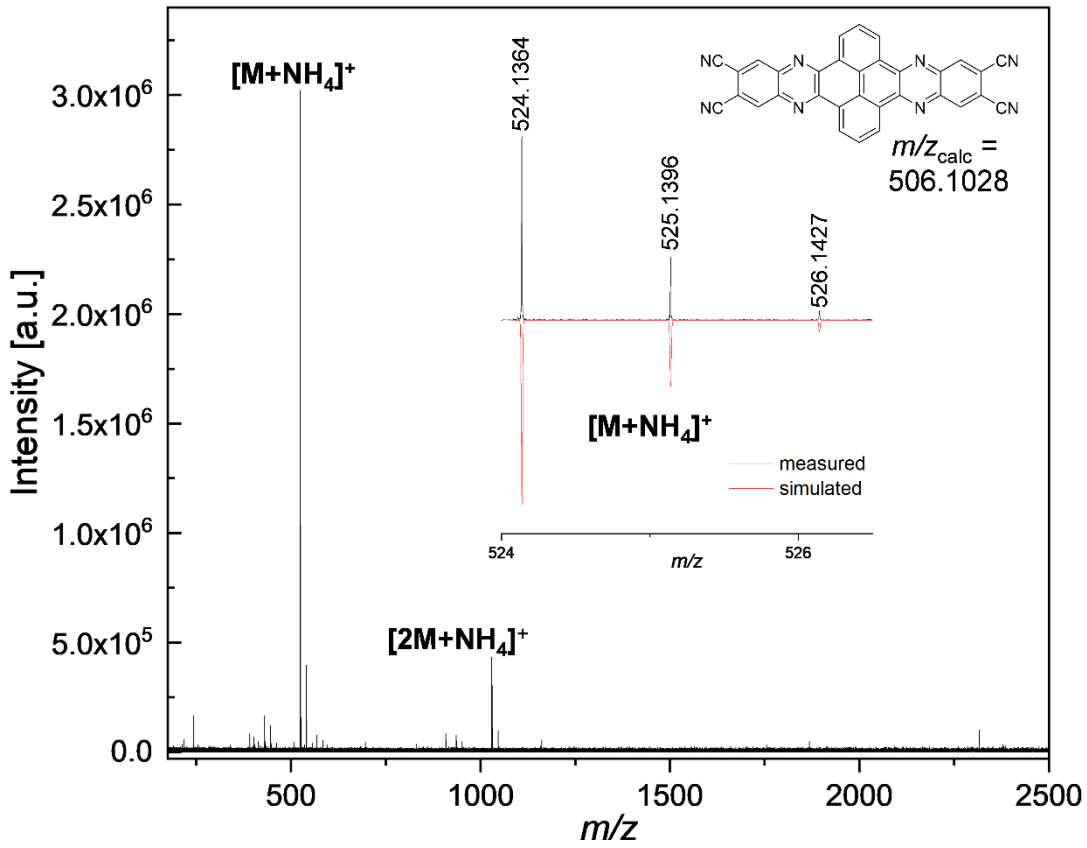

Figure S18. HRMS spectrum (DART+) of **QPPTC**.

5 Thermal Stability of PPQTC

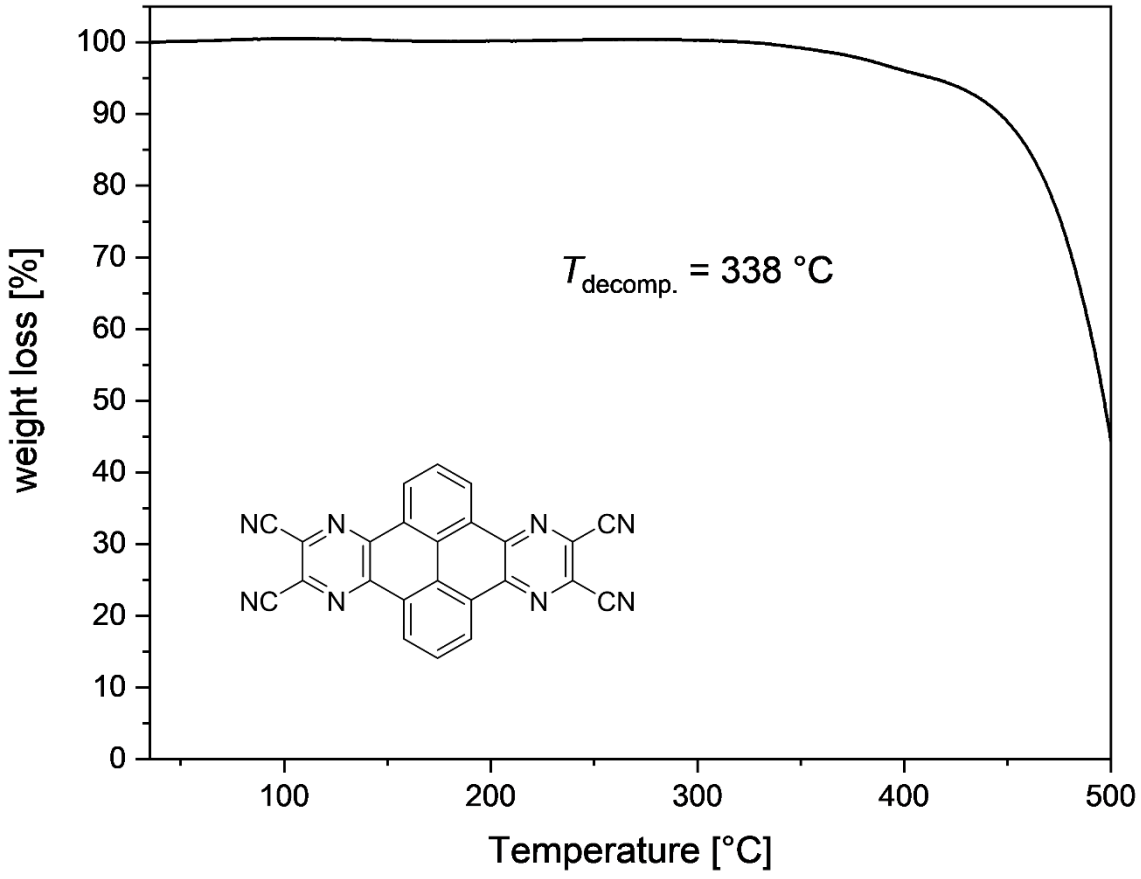

Figure S19. Thermogravimetric Analysis of **PPQTC** measured under N_2 atmosphere with 10 K/min.

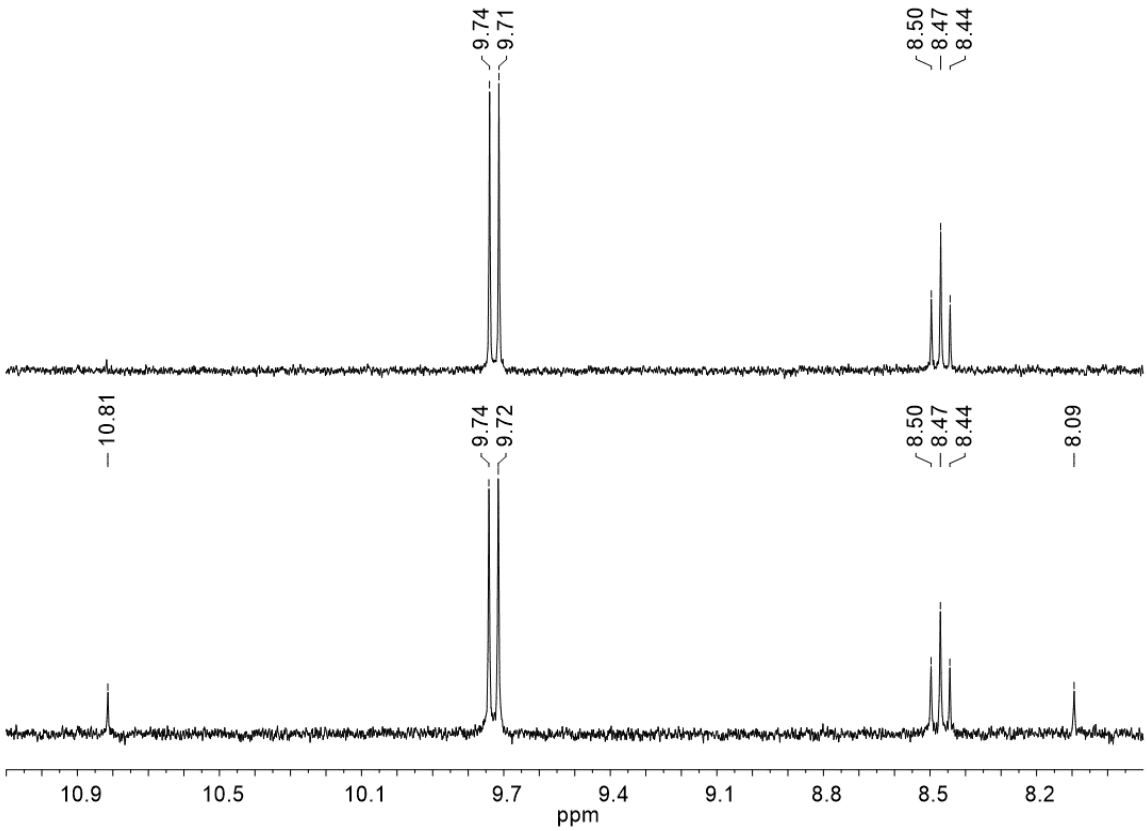

Figure S20. ^{1}H NMR spectra (THF-d8, 300 MHz) of **PPQTC** before (top) and after (bottom) sublimation at a Kugelrohrofen (300 °C, 5×10^{-2} mbar).

6 Crystal Structure Analysis

6.1 Definition of π-π distances

For the determination of face-to-face π-π-distances between two π stacked molecules a centroid was generated from all atoms of the aromatic backbone in the software program 'Mercury'. The distance from this centroid to the plane containing all atoms of the aromatic backbone of the adjacent molecule was then used as the π-π distance.

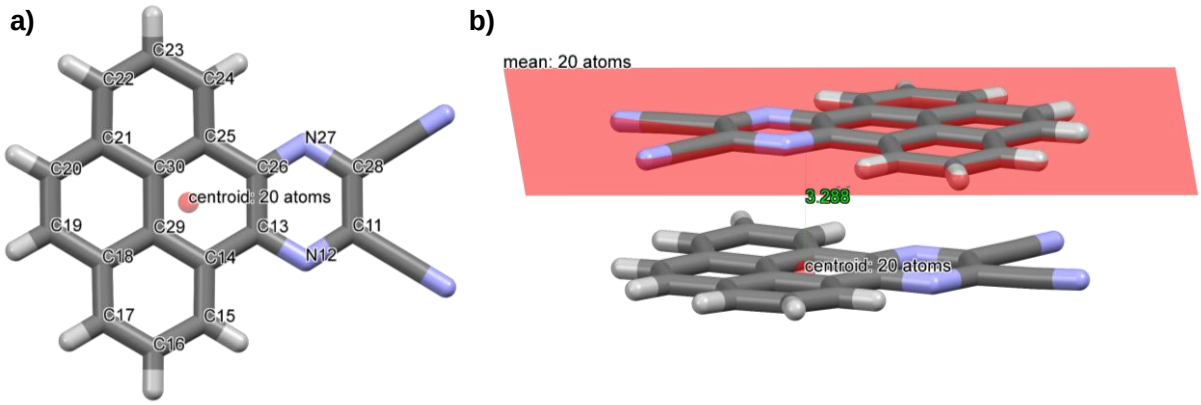

Figure S21. Determination of π-π-distances: a) atoms used for centroid and plane generation. b) distance between a centroid and a plane of two adjacent π stacked **PQDC** molecules.

6.2 Crystal Data

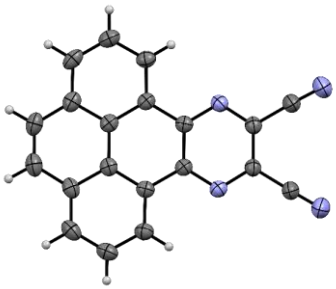

Figure S22. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **PQDC** (polymorph ***α***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S1. Crystal data and structure refinement for **PQDC** (polymorph ***α***).

CCDC	2002728	
Crystallization method	sublimation at a Kugelrohrofen	
Empirical formula	$C_{20}H_8N_4$	
Formula weight	304.30	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	a =9.0334(8) Å	α = 90 deg.
	b = 21.7309(14) Å	β =94.439(7) deg.
	c =7.2212(7) Å	γ = 90 deg.
Volume	1413.3(2) $Å^3$	
Density (calculated)	1.43 g/cm^3	
Absorption coefficient	0.71 mm^{-1}	
Crystal shape	plank	
Crystal size	0.144 x 0.054 x 0.025 mm^3	

Crystal colour	orange
Theta range for data collection	4.1 to 62.1 deg.
Index ranges	$-10 \le h \le 10$, $-24 \le k \le 21$, $-8 \le l \le 5$
Reflections collected	10174
Independent reflections	2167 (R(int) = 0.0181)
Observed reflections	1501 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.33 and 0.77
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2167 / 0 / 217
Goodness-of-fit on F^2	1.05
Final R indices (I>2sigma(I))	R1 = 0.037, wR2 = 0.086
Largest diff. peak and hole	0.12 and -0.17 eÅ^{-3}

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **PQDC** (polymorph ***α***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
N11	0.6648(1)	0.3954(1)	0.3808(2)	0.0344(3)
C12	0.7874(2)	0.4233(1)	0.3345(2)	0.0347(4)
C13	0.9099(2)	0.3908(1)	0.2808(2)	0.0339(4)
N14	0.9140(1)	0.3298(1)	0.2785(2)	0.0336(3)
C15	0.7922(2)	0.3006(1)	0.3276(2)	0.0304(4)
C16	0.7927(2)	0.2339(1)	0.3287(2)	0.0310(4)
C17	0.9165(2)	0.2004(1)	0.2842(2)	0.0371(4)
H17	1.0031	0.2214	0.2519	0.044
C18	0.9141(2)	0.1368(1)	0.2866(2)	0.0421(4)
H18	0.9995	0.1144	0.2573	0.051
C19	0.7890(2)	0.1058(1)	0.3313(2)	0.0423(4)
H19	0.7888	0.0621	0.3311	0.051
C20	0.6622(2)	0.1375(1)	0.3768(2)	0.0374(4)
C21	0.5299(2)	0.1064(1)	0.4235(2)	0.0443(4)
H21	0.5274	0.0627	0.4229	0.053
C22	0.4096(2)	0.1377(1)	0.4681(2)	0.0441(4)
H22	0.3241	0.1157	0.4990	0.053
C23	0.4072(2)	0.2033(1)	0.4702(2)	0.0368(4)
C24	0.2827(2)	0.2369(1)	0.5152(2)	0.0413(4)
H24	0.1967	0.2156	0.5475	0.050
C25	0.2824(2)	0.3000(1)	0.5135(2)	0.0419(4)
H25	0.1961	0.3216	0.5436	0.050
C26	0.4065(2)	0.3325(1)	0.4684(2)	0.0374(4)
H26	0.4053	0.3762	0.4681	0.045
C27	0.5329(2)	0.3011(1)	0.4238(2)	0.0311(4)
C28	0.6653(2)	0.3336(1)	0.3763(2)	0.0299(4)
C29	0.6638(2)	0.2026(1)	0.3767(2)	0.0317(4)
C30	0.5346(2)	0.2361(1)	0.4237(2)	0.0321(4)
C31	0.7903(2)	0.4896(1)	0.3431(2)	0.0430(4)
N31	0.7981(2)	0.5420(1)	0.3509(2)	0.0607(5)
C32	1.0382(2)	0.4229(1)	0.2217(2)	0.0416(4)
N32	1.1369(2)	0.4494(1)	0.1724(2)	0.0605(5)

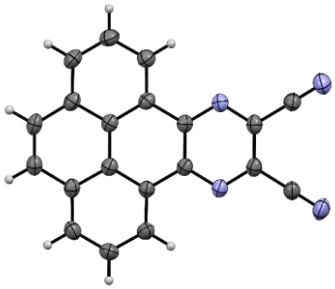

Figure S23. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **PQDC** (polymorph ***β***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S3. Crystal data and structure refinement for **PQDC** (polymorph ***β***).

CCDC	2002729	
Crystallization method	chloroform (slow evaporation)	
Empirical formula	$C_{20}H_8N_4$	
Formula weight	304.30	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a =7.3263(3) Å	α = 90 deg.
	b =9.6562(4) Å	β =98.601(4) deg.
	c = 19.8639(9) Å	γ = 90 deg.
Volume	1389.45(10) Å^3	
Density (calculated)	1.46 g/cm^3	
Absorption coefficient	0.72 mm^{-1}	
Crystal shape	plank	
Crystal size	0.108 x 0.062 x 0.026 mm^3	
Crystal colour	orange	
Theta range for data collection	5.1 to 71.4 deg.	
Index ranges	$-8\leq h\leq 8$, $-11\leq k\leq 11$, $-10\leq l\leq 24$	
Reflections collected	8695	
Independent reflections	2623 (R(int) = 0.0660)	
Observed reflections	1886 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.64 and 0.46	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2623 / 0 / 217	
Goodness-of-fit on F^2	1.01	
Final R indices (I>2sigma(I))	R1 = 0.048, wR2 = 0.126	
Largest diff. peak and hole	0.23 and -0.24 eÅ^{-3}	

Table S4. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **PQDC** (polymorph ***β***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C11	0.6276(2)	0.5803(2)	0.6668(1)	0.0341(4)
N12	0.6715(2)	0.4654(1)	0.6363(1)	0.0337(4)
C13	0.7078(2)	0.4776(2)	0.5723(1)	0.0304(4)
C14	0.7513(2)	0.3534(2)	0.5364(1)	0.0318(4)
C15	0.7487(3)	0.2230(2)	0.5661(1)	0.0390(4)
H15	0.7215	0.2140	0.6112	0.047
C16	0.7860(3)	0.1064(2)	0.5298(1)	0.0443(5)
H16	0.7820	0.0174	0.5500	0.053
C17	0.8287(3)	0.1183(2)	0.4648(1)	0.0412(4)
H17	0.8550	0.0371	0.4409	0.049

C18	0.8340(2)	0.2472(2)	0.4332(1)	0.0342(4)
C19	0.8768(2)	0.2621(2)	0.3652(1)	0.0375(4)
H19	0.9088	0.1823	0.3415	0.045
C20	0.8724(2)	0.3865(2)	0.3343(1)	0.0375(4)
H20	0.9020	0.3931	0.2895	0.045
C21	0.8238(2)	0.5090(2)	0.3683(1)	0.0337(4)
C22	0.8084(3)	0.6381(2)	0.3359(1)	0.0407(4)
H22	0.8343	0.6458	0.2905	0.049
C23	0.7562(3)	0.7543(2)	0.3686(1)	0.0422(5)
H23	0.7441	0.8406	0.3454	0.051
C24	0.7214(2)	0.7457(2)	0.4351(1)	0.0374(4)
H24	0.6862	0.8264	0.4573	0.045
C25	0.7373(2)	0.6204(2)	0.4697(1)	0.0303(4)
C26	0.7013(2)	0.6086(2)	0.5393(1)	0.0305(4)
N27	0.6596(2)	0.7239(1)	0.5715(1)	0.0335(3)
C28	0.6216(2)	0.7095(2)	0.6342(1)	0.0329(4)
C29	0.7922(2)	0.3670(2)	0.4692(1)	0.0312(4)
C30	0.7863(2)	0.4994(2)	0.4361(1)	0.0308(4)
C31	0.5810(2)	0.5659(2)	0.7347(1)	0.0380(4)
N31	0.5400(2)	0.5534(2)	0.7876(1)	0.0505(4)
C32	0.5724(2)	0.8345(2)	0.6679(1)	0.0380(4)
N32	0.5313(2)	0.9328(2)	0.6936(1)	0.0508(5)

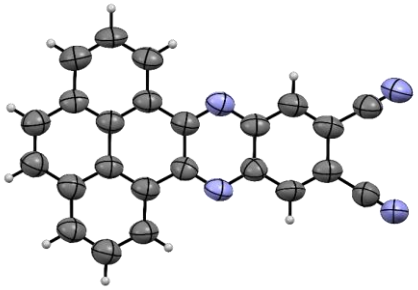

Figure S24. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **PPDC** (polymorph ***α***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S5. Crystal data and structure refinement for **PPDC** (polymorph ***α***).

CCDC	2002730	
Crystallization method	sublimation at a Kugelrohrofen	
Empirical formula	$C_{24}H_{10}N_4$	
Formula weight	354.36	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	a = 12.853(2) Å	α = 90 deg.
	b =7.1688(18) Å	β = 101.541(15) deg.
	c = 18.551(4) Å	γ = 90 deg.
Volume	1674.7(6) $Å^3$	
Density (calculated)	1.40 g/cm^3	
Absorption coefficient	0.68 mm^{-1}	
Crystal shape	plank	
Crystal size	0.061 x 0.033 x 0.013 mm^3	
Crystal colour	orange	
Theta range for data collection	4.9 to 46.1 deg.	
Index ranges	$-12 \le h \le 8$, $-6 \le k \le 6$, $-17 \le l \le 16$	

Reflections collected	7046
Independent reflections	1401 (R(int) = 0.3462)
Observed reflections	568 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	6.58 and 0.30
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1401 / 288 / 253
Goodness-of-fit on F^2	1.34
Final R indices (I>2sigma(I))	R1 = 0.132, wR2 = 0.286
Largest diff. peak and hole	0.46 and -0.33 eÅ^{-3}

Table S6. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **PPDC** (polymorph ***α***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C11	0.1361(9)	0.4614(19)	0.4014(7)	0.080(4)
C12	0.1962(9)	0.3966(19)	0.4666(7)	0.089(4)
H12	0.1650	0.3854	0.5088	0.107
C13	0.3032(9)	0.3470(18)	0.4712(7)	0.072(4)
N14	0.3630(7)	0.2874(15)	0.5353(6)	0.076(3)
C15	0.4634(9)	0.2428(19)	0.5384(7)	0.077(4)
C16	0.5269(9)	0.1686(18)	0.6054(6)	0.074(4)
C17	0.4834(10)	0.147(2)	0.6683(7)	0.083(4)
H17	0.4115	0.1796	0.6671	0.100
C18	0.5456(10)	0.076(2)	0.7326(7)	0.095(5)
H18	0.5158	0.0585	0.7750	0.114
C19	0.6488(10)	0.034(2)	0.7348(8)	0.091(5)
H19	0.6902	-0.0151	0.7789	0.110
C20	0.6970(9)	0.0596(17)	0.6729(7)	0.069(3)
C21	0.8072(10)	0.015(2)	0.6765(8)	0.090(4)
H21	0.8491	-0.0285	0.7215	0.108
C22	0.8521(10)	0.034(2)	0.6164(7)	0.087(4)
H22	0.9248	0.0037	0.6195	0.105
C23	0.7891(9)	0.0985(19)	0.5486(7)	0.082(4)
C24	0.8319(10)	0.1168(19)	0.4846(7)	0.083(4)
H24	0.9040	0.0839	0.4867	0.099
C25	0.7734(10)	0.180(2)	0.4201(8)	0.091(4)
H25	0.8050	0.1914	0.3782	0.109
C26	0.6667(9)	0.2273(19)	0.4151(7)	0.083(4)
H26	0.6255	0.2692	0.3696	0.099
C27	0.6202(9)	0.2128(19)	0.4778(7)	0.075(4)
C28	0.5106(9)	0.2642(17)	0.4723(7)	0.070(4)
N29	0.4533(7)	0.3292(15)	0.4103(6)	0.077(3)
C30	0.3510(9)	0.3720(19)	0.4075(7)	0.075(4)
C31	0.2883(9)	0.4379(18)	0.3422(7)	0.079(4)
H31	0.3190	0.4507	0.2999	0.095
C32	0.1831(9)	0.4849(18)	0.3375(7)	0.073(4)
C33	0.6341(9)	0.1224(18)	0.6088(7)	0.072(4)
C34	0.6823(9)	0.1476(18)	0.5438(6)	0.071(4)
C35	0.0258(11)	0.521(2)	0.3965(8)	0.089(5)
N35	-0.0560(10)	0.571(2)	0.3949(7)	0.112(5)
C36	0.1183(10)	0.559(2)	0.2682(8)	0.084(5)
N36	0.0702(9)	0.614(2)	0.2167(7)	0.111(5)

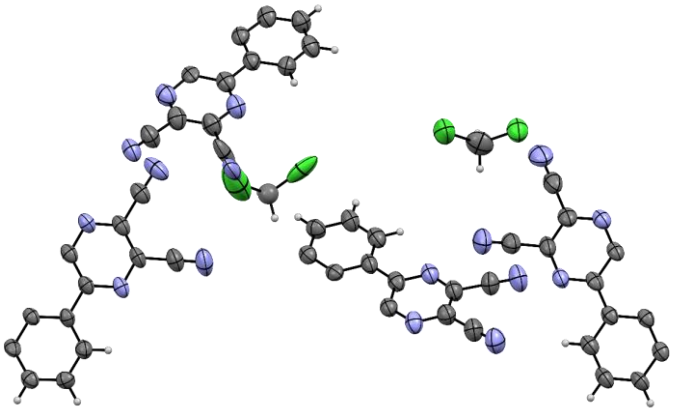

Figure S25. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **PPQTC** (solvate ***α***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S7. Crystal data and structure refinement for **PPQTC** (solvate ***α***).

CCDC	2002731	
Crystallization method	dichloromethane (slow evaporation)	
Empirical formula	$C_{24.50}H_7ClN_8$	
Formula weight	448.83	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	P&^-&B1	
Z	4	
Unit cell dimensions	a =7.4695(5) Å	α =89.134(5) deg.
	b = 12.3050(8) Å	β =88.849(6) deg.
	c = 22.5782(15) Å	γ =81.035(6) deg.
Volume	2049.3(2) $Å^3$	
Density (calculated)	1.46 g/cm^3	
Absorption coefficient	1.92 mm^{-1}	
Crystal shape	plank	
Crystal size	0.079 x 0.041 x 0.020 mm^3	
Crystal colour	yellow	
Theta range for data collection	3.6 to 67.2 deg.	
Index ranges	-8≤h≤8, -14≤k≤14, -26≤l≤25	
Reflections collected	20029	
Independent reflections	6941 (R(int) = 0.0871)	
Observed reflections	2786 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.83 and 0.61	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	20029 / 1265 / 692	
Goodness-of-fit on F^2	1.00	
Final R indices (I>2sigma(I))	R1 = 0.097, wR2 = 0.239	
Largest diff. peak and hole	0.52 and -0.38 $eÅ^{-3}$	

Table S8. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **PPQTC** (solvate ***α***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C111	1.0249(12)	0.5557(7)	0.9976(3)	0.046(2)
C121	1.0278(13)	0.6205(8)	1.0488(4)	0.052(3)
C131	1.0781(13)	0.7243(8)	1.0438(4)	0.052(2)
H131	1.0800	0.7678	1.0782	0.062

C141	1.1255(12)	0.7651(7)	0.9890(4)	0.051(2)
H141	1.1586	0.8364	0.9858	0.061
C151	1.1244(13)	0.7013(8)	0.9390(4)	0.056(3)
H151	1.1576	0.7295	0.9016	0.067
C161	1.0757(12)	0.5972(7)	0.9425(3)	0.045(2)
C171	1.0698(12)	0.5302(7)	0.8903(3)	0.046(2)
N181	1.1133(10)	0.5742(6)	0.8373(3)	0.054(2)
C191	1.1032(13)	0.5125(8)	0.7903(4)	0.057(3)
C201	1.0461(13)	0.4097(8)	0.7936(4)	0.057(2)
N211	1.0067(10)	0.3644(6)	0.8453(3)	0.054(2)
C221	1.0176(12)	0.4264(8)	0.8943(4)	0.050(2)
C231	1.1502(15)	0.5612(9)	0.7338(4)	0.068(3)
N231	1.1873(15)	0.5987(8)	0.6900(4)	0.095(3)
C241	1.0290(14)	0.3461(8)	0.7408(4)	0.063(3)
N241	1.0083(13)	0.3014(8)	0.6985(4)	0.089(3)
C112	0.5543(12)	0.9538(7)	0.4851(4)	0.052(2)
C122	0.6096(13)	0.8528(8)	0.5155(4)	0.054(2)
C132	0.7121(14)	0.7653(8)	0.4860(4)	0.063(3)
H132	0.7487	0.6974	0.5062	0.076
C142	0.7609(14)	0.7774(9)	0.4269(4)	0.067(3)
H142	0.8304	0.7172	0.4069	0.080
C152	0.7104(14)	0.8749(8)	0.3967(4)	0.065(3)
H152	0.7458	0.8816	0.3564	0.078
C162	0.6067(13)	0.9644(8)	0.4254(4)	0.058(2)
C172	0.5509(13)	1.0663(8)	0.3945(4)	0.056(2)
N182	0.6089(11)	1.0772(7)	0.3371(3)	0.063(2)
C192	0.5513(14)	1.1726(8)	0.3102(4)	0.065(3)
C202	0.4361(14)	1.2583(8)	0.3374(4)	0.067(3)
N212	0.3823(11)	1.2491(7)	0.3932(3)	0.063(2)
C222	0.4433(13)	1.1558(8)	0.4230(4)	0.056(2)
C232	0.6203(15)	1.1858(8)	0.2491(4)	0.066(3)
N232	0.6704(14)	1.1973(8)	0.2022(4)	0.089(3)
C242	0.3611(16)	1.3573(9)	0.3046(5)	0.073(3)
N242	0.3030(14)	1.4324(8)	0.2775(4)	0.086(3)
C113	0.4973(12)	1.5304(7)	0.0273(3)	0.049(2)
C123	0.5443(12)	1.6364(8)	0.0278(4)	0.049(2)
C133	0.5359(13)	1.6959(8)	0.0805(4)	0.055(2)
H133	0.5629	1.7688	0.0800	0.066
C143	0.4883(14)	1.6482(9)	0.1334(4)	0.064(3)
H143	0.4870	1.6875	0.1693	0.077
C153	0.4426(13)	1.5433(8)	0.1338(4)	0.058(3)
H153	0.4075	1.5117	0.1700	0.070
C163	0.4473(12)	1.4833(7)	0.0816(4)	0.050(2)
C173	0.3943(12)	1.3755(7)	0.0808(4)	0.052(2)
N183	0.3339(11)	1.3333(7)	0.1316(3)	0.059(2)
C193	0.2886(14)	1.2340(8)	0.1300(4)	0.064(3)
C203	0.3090(13)	1.1704(8)	0.0785(4)	0.062(3)
N213	0.3650(11)	1.2114(7)	0.0270(3)	0.059(2)
C223	0.4046(12)	1.3141(8)	0.0278(4)	0.051(2)
C233	0.2198(16)	1.1894(9)	0.1841(5)	0.071(3)
N233	0.1699(16)	1.1552(9)	0.2274(4)	0.101(4)
C243	0.2632(16)	1.0608(10)	0.0770(5)	0.077(3)
N243	0.2247(15)	0.9741(9)	0.0770(4)	0.102(4)
C114	0.995(4)	0.0344(15)	0.4738(7)	0.056(5)
C124	1.0832(19)	-0.0059(13)	0.4205(6)	0.062(4)
C134	1.0817(19)	0.0565(11)	0.3698(6)	0.072(4)
H134	1.1424	0.0273	0.3348	0.086
C144	0.991(2)	0.1622(13)	0.3707(7)	0.066(4)
H144	0.9887	0.2060	0.3356	0.080
C154	0.902(2)	0.2070(13)	0.4208(6)	0.062(4)
H154	0.8376	0.2800	0.4203	0.075
C164	0.9087(18)	0.1417(10)	0.4726(5)	0.058(3)

C174	0.8208(18)	0.1872(12)	0.5269(5)	0.061(3)
N184	0.7349(16)	0.2935(10)	0.5270(5)	0.077(3)
C194	0.6520(18)	0.3313(10)	0.5766(6)	0.072(4)
C204	0.6495(19)	0.2654(12)	0.6273(6)	0.072(4)
N214	0.7323(17)	0.1637(10)	0.6290(5)	0.076(3)
C224	0.811(2)	0.1192(13)	0.5774(6)	0.053(5)
C234	0.567(2)	0.4495(14)	0.5758(7)	0.091(6)
N234	0.497(3)	0.5257(11)	0.5745(6)	0.107(5)
C244	0.545(5)	0.306(2)	0.6805(11)	0.077(9)
N244	0.455(3)	0.3398(18)	0.7184(8)	0.071(5)
C514	-0.174(2)	0.9449(13)	0.1597(6)	0.098(5)
H51A4	-0.1371	1.0110	0.1773	0.117
H51B4	-0.0654	0.8876	0.1571	0.117
Cl14	-0.3320(10)	0.8982(4)	0.2055(2)	0.150(3)
Cl24	-0.2510(6)	0.9768(3)	0.0904(2)	0.0845(13)
C11B4	-0.975(11)	0.947(4)	0.5146(17)	0.030(15)
C12B4	-1.013(5)	0.935(3)	0.5755(13)	0.035(9)
C13B4	-0.971(6)	0.837(3)	0.6054(15)	0.026(11)
H13B4	-1.0128	0.8298	0.6451	0.032
C14B4	-0.867(6)	0.749(3)	0.5772(13)	0.024(11)
H14B4	-0.8327	0.6810	0.5978	0.029
C15B4	-0.813(4)	0.7610(18)	0.5189(10)	0.016(6)
H15B4	-0.7409	0.7010	0.4994	0.019
C16B4	-0.862(5)	0.860(2)	0.4882(11)	0.020(9)
C17B4	-0.840(7)	0.864(3)	0.4235(12)	0.021(13)
N18B4	-0.712(4)	0.783(2)	0.4004(10)	0.041(9)
C19B4	-0.667(4)	0.8003(19)	0.3431(10)	0.017(7)
C20B4	-0.735(4)	0.8957(18)	0.3112(10)	0.026(7)
N21B4	-0.836(3)	0.9825(18)	0.3366(9)	0.033(7)
C22B4	-0.871(5)	0.970(2)	0.3957(11)	0.023(9)
C23B4	-0.557(11)	0.707(4)	0.313(3)	0.030(17)
N23B4	-0.500(11)	0.641(6)	0.281(4)	0.08(3)
C24B4	-0.715(7)	0.898(3)	0.2465(12)	0.082(14)
N24B4	-0.688(7)	0.892(4)	0.1969(14)	0.107(15)
C51B4	1.044(8)	0.521(6)	0.5405(15)	0.07(2)
H51C4	1.0462	0.5998	0.5472	0.082
H51D4	1.1611	0.4792	0.5534	0.082
Cl1B4	1.022(3)	0.5013(14)	0.4698(10)	0.113(9)
Cl2B4	0.879(5)	0.4815(19)	0.5808(10)	0.223(15)

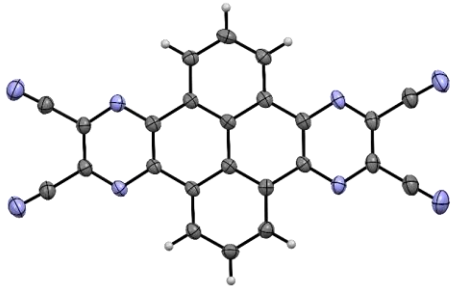

Figure S26. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **PPQTC** (polymorph ***β***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S9. Crystal data and structure refinement for **PPQTC** (polymorph ***β***).

CCDC	2002732
Crystallization method	sublimation at a Kugelrohrofen
Empirical formula	$C_{24}H_6N_8$

Formula weight	406.37
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	orthorhombic
Space group	Pbca
Z	8
Unit cell dimensions	a = 20.6569(10) Å α = 90 deg.
	b =7.1568(3) Å β = 90 deg.
	c = 24.2281(10) Å γ = 90 deg.
Volume	3581.8(3) Å^3
Density (calculated)	1.51 g/cm^3
Absorption coefficient	0.79 mm^{-1}
Crystal shape	needle
Crystal size	0.077 x 0.041 x 0.020 mm^3
Crystal colour	yellow
Theta range for data collection	4.2 to 69.5 deg.
Index ranges	-24≤h≤16, -4≤k≤8, -28≤l≤29
Reflections collected	12730
Independent reflections	3262 (R(int) = 0.0574)
Observed reflections	1708 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.42 and 0.67
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3262 / 0 / 289
Goodness-of-fit on F^2	1.06
Final R indices (I>2sigma(I))	R1 = 0.060, wR2 = 0.109
Largest diff. peak and hole	0.20 and -0.24 eÅ^{-3}

Table S10. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **PPQTC** (polymorph ***β***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C11	0.2459(2)	0.2481(4)	0.5768(1)	0.0238(7)
C12	0.2464(2)	0.3207(4)	0.6313(1)	0.0256(7)
C13	0.1879(2)	0.3536(4)	0.6585(1)	0.0299(8)
H13	0.1882	0.4034	0.6948	0.036
C14	0.1295(2)	0.3143(4)	0.6331(1)	0.0326(8)
H14	0.0901	0.3367	0.6521	0.039
C15	0.1283(2)	0.2426(4)	0.5801(1)	0.0286(7)
H15	0.0880	0.2143	0.5632	0.034
C16	0.1859(2)	0.2115(4)	0.5512(1)	0.0254(7)
C17	0.1854(2)	0.1402(4)	0.4949(1)	0.0271(7)
N18	0.1279(1)	0.0985(3)	0.4717(1)	0.0302(6)
C19	0.1295(2)	0.0328(4)	0.4203(1)	0.0290(7)
C20	0.1878(2)	0.0188(4)	0.3906(1)	0.0300(8)
N21	0.2447(1)	0.0570(3)	0.4131(1)	0.0285(6)
C22	0.2437(2)	0.1138(4)	0.4662(1)	0.0246(7)
C23	0.0696(2)	-0.0335(4)	0.3969(1)	0.0350(8)
N23	0.0236(2)	-0.0980(4)	0.3791(1)	0.0498(8)
C24	0.1867(2)	-0.0425(4)	0.3338(1)	0.0360(8)
N24	0.1833(2)	-0.0911(4)	0.2889(1)	0.0505(8)
C31	0.3064(2)	0.2102(4)	0.5483(1)	0.0247(7)
C32	0.3061(2)	0.1442(4)	0.4933(1)	0.0242(7)
C33	0.3642(2)	0.1068(4)	0.4665(1)	0.0289(7)
H33	0.3637	0.0621	0.4295	0.035
C34	0.4230(2)	0.1341(4)	0.4932(1)	0.0316(8)
H34	0.4625	0.1091	0.4746	0.038
C35	0.4237(2)	0.1978(4)	0.5471(1)	0.0324(8)
H35	0.4640	0.2155	0.5653	0.039

C36	0.3662(2)	0.2364(4)	0.5751(1)	0.0258(7)
C37	0.3666(2)	0.3029(4)	0.6318(1)	0.0270(7)
N38	0.4242(1)	0.3160(3)	0.6578(1)	0.0321(7)
C39	0.4232(2)	0.3886(4)	0.7083(1)	0.0326(8)
C40	0.3658(2)	0.4499(4)	0.7331(1)	0.0313(8)
N41	0.3085(1)	0.4313(3)	0.7089(1)	0.0306(6)
C42	0.3084(2)	0.3533(4)	0.6585(1)	0.0274(7)
C43	0.4845(2)	0.4014(5)	0.7371(1)	0.0426(9)
N43	0.5328(2)	0.4128(5)	0.7601(1)	0.0604(9)
C44	0.3669(2)	0.5371(4)	0.7871(1)	0.0393(8)
N44	0.3701(2)	0.6042(4)	0.8299(1)	0.0532(9)

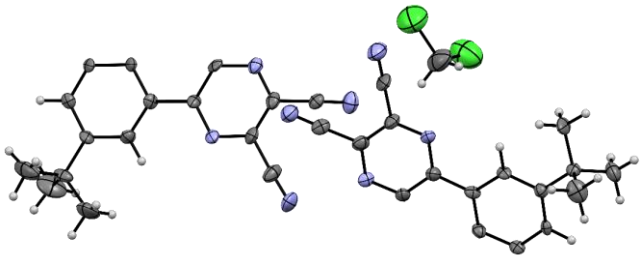

Figure S27. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **^{t}Bu-PPQTC** (solvate ***α***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S11. Crystal data and structure refinement for **^{t}Bu-PPQTC** (solvate ***α***).

CCDC	2002733	
Crystallization method	dichloromethane (slow evaporation)	
Empirical formula	$C_{33}H_{24}Cl_2N_8$	
Formula weight	603.50	
Temperature	170(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a =6.2068(12) Å	α = 90 deg.
	b = 18.102(2) Å	β =93.771(15) deg.
	c = 26.150(5) Å	γ = 90 deg.
Volume	2931.7(9) Å^3	
Density (calculated)	1.37 g/cm^3	
Absorption coefficient	2.30 mm^{-1}	
Crystal shape	needle	
Crystal size	0.080 x 0.020 x 0.015 mm^3	
Crystal colour	orange	
Theta range for data collection	3.4 to 47.8 deg.	
Index ranges	-5≤h≤5, -11≤k≤17, -25≤l≤25	
Reflections collected	10962	
Independent reflections	2695 (R(int) = 0.1902)	
Observed reflections	1221 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.50 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2695 / 440 / 394	
Goodness-of-fit on F^2	1.04	
Final R indices (I>2sigma(I))	R1 = 0.097, wR2 = 0.203	
Largest diff. peak and hole	0.31 and -0.44 eÅ^{-3}	

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **^{t}Bu-PPQTC** (solvate ***α***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C111	1.0390(18)	0.9884(6)	0.5249(4)	0.024(3)
C121	1.2332(17)	1.0155(6)	0.5492(4)	0.021(3)
C131	1.3023(18)	0.9923(6)	0.5978(4)	0.023(3)
H131	1.4311	1.0132	0.6133	0.028
C141	1.1938(18)	0.9405(6)	0.6250(4)	0.025(3)
C151	1.0061(19)	0.9114(6)	0.6007(4)	0.028(3)
H151	0.9286	0.8750	0.6181	0.034
C161	0.9265(18)	0.9339(6)	0.5515(4)	0.023(3)
C181	1.2698(17)	0.9184(6)	0.6786(4)	0.031(3)
C18111	.5110(19)	0.9028(9)	0.6813(5)	0.072(5)
H18A11	.5571	0.8846	0.7156	0.108
H18B11	.5893	0.9483	0.6744	0.108
H18C11	.5421	0.8653	0.6558	0.108
C1821	1.215(3)	0.9800(8)	0.7146(5)	0.075(5)
H18D11	.2779	0.9691	0.7491	0.112
H18E11	.0580	0.9842	0.7153	0.112
H18F11	.2743	1.0267	0.7027	0.112
C1831	1.156(2)	0.8486(7)	0.6969(5)	0.072(5)
H18G11	.2066	0.8377	0.7323	0.108
H18H11	.1885	0.8068	0.6749	0.108
H18I10	.9994	0.8570	0.6951	0.108
C211	0.7272(17)	0.9035(6)	0.5267(4)	0.026(3)
N221	0.6220(14)	0.8521(5)	0.5528(3)	0.026(2)
C231	0.4389(17)	0.8266(6)	0.5297(4)	0.032(3)
C241	0.3576(17)	0.8547(6)	0.4828(4)	0.030(3)
N251	0.4586(15)	0.9067(5)	0.4573(3)	0.029(3)
C261	0.6504(17)	0.9300(6)	0.4785(4)	0.024(3)
C271	0.323(2)	0.7703(6)	0.5567(5)	0.039(4)
N271	0.2275(19)	0.7253(6)	0.5760(4)	0.056(4)
C281	0.1519(18)	0.8278(6)	0.4600(4)	0.027(3)
N281	-0.0106(17)	0.8068(6)	0.4431(4)	0.044(3)
C112	-0.5376(18)	0.4831(6)	0.4760(4)	0.025(3)
C122	-0.7248(18)	0.4390(6)	0.4717(4)	0.023(3)
C132	-0.7945(17)	0.4081(6)	0.4261(4)	0.018(3)
H132	-0.9200	0.3780	0.4251	0.022
C142	-0.6936(18)	0.4181(6)	0.3814(4)	0.025(3)
C152	-0.5127(17)	0.4632(6)	0.3844(4)	0.021(3)
H152	-0.4420	0.4731	0.3540	0.026
C162	-0.4295(17)	0.4951(6)	0.4308(4)	0.023(3)
C182	-0.7708(16)	0.3805(5)	0.3317(4)	0.024(3)
C1812	-0.713(2)	0.2984(6)	0.3358(5)	0.050(4)
H18A2	-0.7605	0.2733	0.3039	0.075
H18B2	-0.7851	0.2763	0.3644	0.075
H18C2	-0.5563	0.2931	0.3420	0.075
C1822	-1.0151(17)	0.3902(7)	0.3222(5)	0.044(4)
H18D2	-1.0647	0.3638	0.2909	0.065
H18E2	-1.0491	0.4429	0.3182	0.065
H18F2	-1.0879	0.3702	0.3513	0.065
C1832	-0.660(2)	0.4123(7)	0.2857(4)	0.045(4)
H18G2	-0.7192	0.3888	0.2541	0.068
H18H2	-0.5041	0.4026	0.2900	0.068
H18I2	-0.6846	0.4657	0.2837	0.068
C212	-0.2383(18)	0.5428(6)	0.4342(4)	0.029(3)
N222	-0.1398(15)	0.5551(5)	0.3903(3)	0.027(2)
C232	0.0376(18)	0.5957(6)	0.3947(4)	0.030(3)
C242	0.1222(18)	0.6217(6)	0.4422(4)	0.033(3)
N252	0.0248(15)	0.6103(5)	0.4854(3)	0.024(2)
C262	-0.1596(18)	0.5719(6)	0.4815(4)	0.027(3)
C272	0.155(2)	0.6098(7)	0.3493(5)	0.038(4)

N272	0.2470(19)	0.6209(7)	0.3141(4)	0.055(4)
C282	0.3255(19)	0.6620(6)	0.4466(5)	0.030(3)
N282	0.4876(17)	0.6914(6)	0.4486(4)	0.042(3)
C31	-0.342(2)	0.7580(10)	0.3399(7)	0.079(6)
H31A	-0.2851	0.7522	0.3760	0.095
H31B	-0.3868	0.7086	0.3270	0.095
Cl1	-0.1403(9)	0.7907(4)	0.3044(2)	0.123(2)
Cl2	-0.5684(9)	0.8167(3)	0.3378(2)	0.117(2)

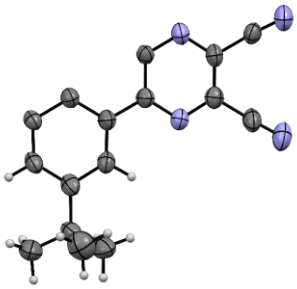

Figure S28. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **^{t}Bu-PPQTC** (polymorph ***β***). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S13. Crystal data and structure refinement for **^{t}Bu-PPQTC** (polymorph ***β***).

CCDC	2002734	
Crystallization method	sublimation at a Kugelrohrofen	
Empirical formula	$C_{32}H_{22}N_8$	
Formula weight	518.57	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	1	
Unit cell dimensions	a =6.1019(11) Å	α =84.348(16) deg.
	b =8.9661(18) Å	β =85.046(15) deg.
	c = 12.679(3) Å	γ =71.586(15) deg.
Volume	653.8(2) Å^3	
Density (calculated)	1.32 g/cm^3	
Absorption coefficient	0.65 mm^{-1}	
Crystal shape	needle	
Crystal size	0.140 x 0.032 x 0.012 mm^3	
Crystal colour	yellow	
Theta range for data collection	5.2 to 53.4 deg.	
Index ranges	-6≤h≤3, -9≤k≤9, -13≤l≤13	
Reflections collected	2968	
Independent reflections	939 (R(int) = 0.2223)	
Observed reflections	375 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.84 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	939 / 168 / 184	
Goodness-of-fit on F^2	0.88	
Final R indices (I>2sigma(I))	R1 = 0.067, wR2 = 0.154	
Largest diff. peak and hole	0.20 and -0.20 eÅ^{-3}	

Table S14. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **^{t}Bu-PPQTC** (polymorph ***β***). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C11	0.0538(14)	0.4683(12)	0.4517(6)	0.047(3)
C12	-0.0737(14)	0.4982(11)	0.3584(6)	0.042(3)
C13	0.0355(15)	0.4315(12)	0.2653(7)	0.051(3)
H13	-0.0496	0.4542	0.2032	0.061
C14	0.2652(14)	0.3323(12)	0.2593(7)	0.050(3)
C15	0.3859(15)	0.3058(12)	0.3513(6)	0.048(3)
H15	0.5426	0.2406	0.3493	0.057
C16	0.2866(15)	0.3708(12)	0.4459(7)	0.047(3)
C18	0.3794(13)	0.2538(12)	0.1577(6)	0.055(2)
C181	0.2537(16)	0.3342(13)	0.0594(7)	0.078(3)
H18A	0.3410	0.2861	-0.0038	0.093
H18B	0.2399	0.4466	0.0542	0.093
H18C	0.0990	0.3221	0.0642	0.093
C182	0.381(2)	0.0820(15)	0.1711(10)	0.093(4)
H18D	0.4609	0.0298	0.2349	0.140
H18E	0.4609	0.0275	0.1088	0.140
H18F	0.2211	0.0785	0.1783	0.140
C183	0.6285(16)	0.2582(15)	0.1394(8)	0.077(4)
H18G	0.6289	0.3679	0.1336	0.116
H18H	0.6976	0.2091	0.0737	0.116
H18I	0.7185	0.2004	0.1993	0.116
C21	0.4180(16)	0.3381(13)	0.5402(8)	0.045(3)
N22	0.6420(13)	0.2524(10)	0.5312(6)	0.048(2)
C23	0.7555(15)	0.2238(11)	0.6210(7)	0.047(3)
C24	0.6516(15)	0.2850(12)	0.7157(7)	0.046(3)
N25	0.4315(12)	0.3727(10)	0.7249(5)	0.052(2)
C26	0.3126(16)	0.4034(13)	0.6368(7)	0.041(3)
C27	0.9975(17)	0.1308(14)	0.6133(7)	0.059(3)
N27	1.1900(14)	0.0645(12)	0.6098(7)	0.074(3)
C28	0.7832(15)	0.2535(12)	0.8094(7)	0.048(3)
N28	0.8964(13)	0.2236(11)	0.8796(6)	0.070(3)

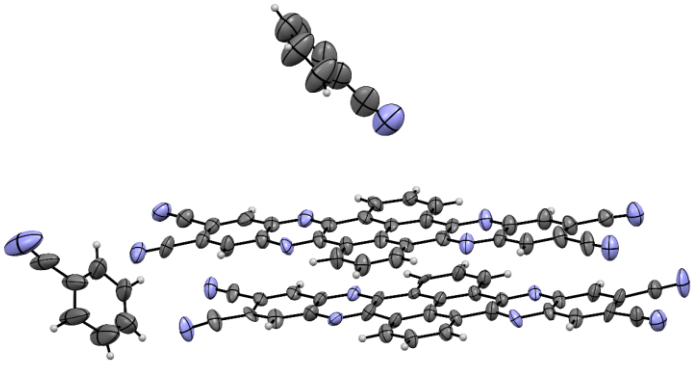

Figure S29. Thermal atomic displacement ellipsoid plot of the asymmetric unit of **QPPTC**. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S15. Crystal data and structure refinement for **QPPTC**.

CCDC	2002735
Crystallization method	benzonitrile (cooling of a hot solution to rt)
Empirical formula	$C_{39}H_{15}N_9$
Formula weight	609.60
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	$P2_1$
Z	4

Unit cell dimensions	a = 12.3586(15) Å	α = 90 deg.
	b = 33.248(4) Å	β =97.48(1) deg.
	c =7.0027(9) Å	γ = 90 deg.
Volume	2852.9(6) Å^3	
Density (calculated)	1.42 g/cm^3	
Absorption coefficient	0.71 mm^{-1}	
Crystal shape	needle	
Crystal size	0.180 x 0.019 x 0.010 mm^3	
Crystal colour	yellow	
Theta range for data collection	5.4 to 52.6 deg.	
Index ranges	$-12 \le h \le 10$, $-32 \le k \le 34$, $-5 \le l \le 7$	
Reflections collected	12828	
Independent reflections	5574 (R(int) = 0.1391)	
Observed reflections	2077 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.73 and 0.62	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5574 / 2311 / 865	
Goodness-of-fit on F^2	1.07	
Final R indices (I>2sigma(I))	R1 = 0.112, wR2 = 0.252	
Absolute structure parameter	-1.9(10)	
Largest diff. peak and hole	0.34 and -0.32 eÅ^{-3}	

Table S16. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **QPPTC**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
N111	0.3441(15)	0.1594(4)	0.564(3)	0.047(6)
C121	0.2852(17)	0.1256(5)	0.578(4)	0.047(7)
C131	0.3343(18)	0.0881(5)	0.561(4)	0.051(8)
H131	0.4093	0.0869	0.5442	0.061
C141	0.2772(17)	0.0535(5)	0.569(4)	0.048(7)
C151	0.1638(17)	0.0552(5)	0.601(4)	0.049(7)
C161	0.1142(18)	0.0912(5)	0.613(4)	0.051(8)
H161	0.0393	0.0921	0.6306	0.061
C171	0.1727(16)	0.1276(5)	0.601(4)	0.038(6)
N181	0.1236(15)	0.1632(4)	0.621(3)	0.050(6)
C191	0.1815(16)	0.1963(5)	0.608(4)	0.039(6)
C201	0.1311(16)	0.2356(5)	0.622(4)	0.038(6)
C211	0.0195(17)	0.2380(6)	0.647(4)	0.053(7)
H211	-0.0212	0.2141	0.6588	0.063
C221	-0.0302(19)	0.2748(6)	0.655(5)	0.053(8)
H221	-0.1062	0.2761	0.6636	0.064
C231	0.0284(16)	0.3100(6)	0.651(4)	0.049(7)
H231	-0.0057	0.3352	0.6660	0.058
C241	0.1403(15)	0.3081(5)	0.625(4)	0.041(6)
C251	0.2029(15)	0.3453(5)	0.615(4)	0.037(6)
N261	0.1521(15)	0.3803(4)	0.627(3)	0.043(6)
C271	0.2135(16)	0.4140(5)	0.621(4)	0.042(7)
C281	0.1628(18)	0.4518(5)	0.635(5)	0.053(8)
H281	0.0874	0.4533	0.6487	0.064
C291	0.2219(17)	0.4859(5)	0.629(4)	0.044(7)
C301	0.3365(17)	0.4842(5)	0.607(4)	0.044(7)
C311	0.3865(18)	0.4482(5)	0.597(4)	0.042(6)
H311	0.4616	0.4471	0.5810	0.050
C321	0.3276(16)	0.4123(5)	0.610(4)	0.038(6)
N331	0.3771(15)	0.3761(5)	0.592(3)	0.045(6)
C341	0.3169(15)	0.3432(5)	0.601(4)	0.039(6)
C351	0.3699(15)	0.3044(5)	0.590(4)	0.038(6)

C361	0.4824(16)	0.3014(6)	0.570(4)	0.045(7)
H361	0.5250	0.3252	0.5709	0.054
C371	0.5311(18)	0.2646(6)	0.549(4)	0.044(7)
H371	0.6063	0.2634	0.5330	0.052
C381	0.4715(17)	0.2296(6)	0.550(4)	0.048(7)
H381	0.5061	0.2044	0.5388	0.057
C391	0.3578(16)	0.2311(5)	0.569(4)	0.044(6)
C401	0.2945(15)	0.1949(5)	0.581(4)	0.035(6)
C411	0.1907(16)	0.2708(4)	0.609(4)	0.039(6)
C421	0.3096(15)	0.2687(4)	0.590(4)	0.033(6)
C431	0.329(2)	0.0148(6)	0.558(4)	0.044(8)
N431	0.367(2)	-0.0166(6)	0.539(4)	0.067(9)
C441	0.105(2)	0.0180(6)	0.606(5)	0.052(9)
N441	0.062(2)	-0.0125(6)	0.612(4)	0.068(8)
C451	0.170(2)	0.5246(6)	0.638(5)	0.055(9)
N451	0.132(2)	0.5561(6)	0.644(4)	0.062(8)
C461	0.397(2)	0.5213(6)	0.608(5)	0.050(8)
N461	0.439(2)	0.5521(6)	0.617(4)	0.062(8)
N112	0.3471(14)	0.1195(4)	0.063(3)	0.036(5)
C122	0.2876(16)	0.0855(5)	0.070(4)	0.038(6)
C132	0.3357(17)	0.0476(5)	0.060(4)	0.043(7)
H132	0.4109	0.0462	0.0459	0.051
C142	0.2798(17)	0.0129(5)	0.071(4)	0.046(7)
C152	0.1641(16)	0.0149(5)	0.088(4)	0.044(7)
C162	0.1166(18)	0.0512(5)	0.105(4)	0.043(7)
H162	0.0413	0.0523	0.1193	0.051
C172	0.1755(16)	0.0876(5)	0.100(4)	0.036(6)
N182	0.1238(14)	0.1235(4)	0.112(3)	0.038(6)
C192	0.1852(15)	0.1564(5)	0.110(4)	0.044(7)
C202	0.1326(15)	0.1954(5)	0.123(4)	0.034(6)
C212	0.0198(15)	0.1978(6)	0.140(4)	0.040(7)
H212	-0.0225	0.1740	0.1416	0.048
C222	-0.0292(18)	0.2353(5)	0.154(4)	0.040(7)
H222	-0.1038	0.2367	0.1725	0.048
C232	0.0287(16)	0.2703(6)	0.140(4)	0.042(7)
H232	-0.0064	0.2956	0.1465	0.050
C242	0.1405(15)	0.2685(5)	0.117(4)	0.039(6)
C252	0.2037(15)	0.3053(5)	0.118(4)	0.039(6)
N262	0.1532(14)	0.3405(4)	0.132(3)	0.037(5)
C272	0.2125(16)	0.3747(5)	0.122(4)	0.043(6)
C282	0.1653(18)	0.4129(5)	0.138(4)	0.043(7)
H282	0.0914	0.4146	0.1616	0.052
C292	0.2218(16)	0.4472(5)	0.121(4)	0.036(6)
C302	0.3373(16)	0.4452(5)	0.109(4)	0.037(6)
C312	0.3853(17)	0.4091(5)	0.095(3)	0.032(6)
H312	0.4604	0.4080	0.0784	0.039
C322	0.3261(15)	0.3729(5)	0.103(4)	0.036(6)
N332	0.3759(14)	0.3371(4)	0.084(3)	0.035(5)
C342	0.3176(15)	0.3036(4)	0.095(4)	0.034(6)
C352	0.3691(14)	0.2647(4)	0.073(4)	0.027(5)
C362	0.4826(15)	0.2618(6)	0.057(4)	0.034(6)
H362	0.5251	0.2856	0.0567	0.041
C372	0.5316(17)	0.2249(5)	0.043(4)	0.046(7)
H372	0.6067	0.2235	0.0270	0.055
C382	0.4723(15)	0.1900(6)	0.051(4)	0.046(7)
H382	0.5073	0.1647	0.0452	0.055
C392	0.3585(15)	0.1917(5)	0.067(4)	0.036(6)
C402	0.2962(14)	0.1543(4)	0.077(4)	0.032(6)
C412	0.1908(15)	0.2310(4)	0.107(4)	0.039(6)
C422	0.3095(15)	0.2291(4)	0.085(4)	0.035(6)
C432	0.332(2)	-0.0255(6)	0.068(4)	0.049(8)
N432	0.376(2)	-0.0558(6)	0.062(5)	0.081(10)

C442	0.108(2)	-0.0225(6)	0.107(5)	0.050(8)
N442	0.0614(19)	-0.0517(6)	0.119(4)	0.057(7)
C452	0.172(2)	0.4861(6)	0.138(5)	0.050(8)
N452	0.1287(19)	0.5167(5)	0.129(4)	0.057(8)
C462	0.396(2)	0.4827(6)	0.100(4)	0.042(7)
N462	0.441(2)	0.5125(6)	0.097(4)	0.056(7)
N50	0.737(3)	0.2939(13)	0.881(6)	0.143(16)
C50	0.746(3)	0.3181(14)	1.000(7)	0.118(13)
C51	0.761(2)	0.3458(12)	1.166(6)	0.115(11)
C52	0.851(3)	0.3673(12)	1.200(6)	0.126(12)
H52	0.9069	0.3658	1.1189	0.152
C53	0.861(3)	0.3922(12)	1.361(6)	0.136(14)
H53	0.9248	0.4080	1.3903	0.163
C54	0.785(3)	0.3947(14)	1.474(6)	0.140(15)
H54	0.7991	0.4080	1.5952	0.168
C55	0.688(4)	0.3787(16)	1.420(7)	0.165(15)
H55	0.6289	0.3830	1.4917	0.198
C56	0.675(3)	0.3551(14)	1.253(6)	0.154(14)
H56	0.6042	0.3457	1.2027	0.185
N60	0.246(3)	0.7021(15)	0.631(5)	0.166(19)
C60	0.252(3)	0.6820(13)	0.497(5)	0.096(11)
C61	0.262(2)	0.6523(11)	0.343(4)	0.092(10)
C62	0.354(2)	0.6322(9)	0.339(5)	0.095(10)
H62	0.4118	0.6343	0.4426	0.114
C63	0.366(3)	0.6079(10)	0.180(5)	0.105(11)
H63	0.4314	0.5931	0.1794	0.126
C64	0.291(3)	0.6049(12)	0.032(5)	0.105(12)
H64	0.3028	0.5907	-0.0812	0.126
C65	0.197(3)	0.6225(15)	0.047(6)	0.173(16)
H65	0.1317	0.6141	-0.0303	0.207
C66	0.194(4)	0.6538(15)	0.180(6)	0.193(17)
H66	0.1454	0.6757	0.1543	0.231

7 Theoretical Calculations

7.1 Electronic Coupling Calculation (DFTB)

The calculation of the electronic couplings requires quantum chemical methods. In this work, the semi-empirical Tight-Binding Density Functional theory (DFTB) method was applied. [25a] This method is derived from density functional theory (DFT) but roughly 2-3 orders of magnitude faster than standard GGA-DFT methods with medium sized basis sets. Therefore, the individual molecules, which contain 46-52 atoms, can be calculated in reasonable computational time, allowing to compute the extensive scans for the dimers containing up to 104 atoms.

For the calculation of the charge transfer couplings, the complex is separated into fragments, corresponding to the individual molecules. For each of the *M* fragments (molecules, indexed as *m*), we compute the molecular orbitals φ_m^i

$$\varphi_m^i = \sum_\mu c_\mu^{i\,m} \chi_\mu \quad .$$

Here, the *i-th* molecular orbital (FO) of fragment *m* is expressed in an atomic-orbital-like basis set χ_μ with expansion coefficients $c_\mu^{i\,m}$. Usually, it is sufficient to consider for each fragment one orbital (FO), which will be the HOMO for a hole transfer and the LUMO for an electron transfer (φ_m^{LUMO} or φ_m^{HOMO}). In special cases, more orbitals (like

HOMO-1 etc.) can also be taken into account. This can be especially relevant, if the energy difference between the orbitals is small. The Hamiltonian matrix is built from the FO coefficients, e.g. for the coupling of the HOMO orbitals one gets

$$H_{mn} = \left\langle \varphi_m^{HOMO} \middle| \hat{H} \middle| \varphi_n^{HOMO} \right\rangle = \sum_{\mu} \sum_{v} c_{\mu}^{HOMO\ m} c_{v}^{HOMO\ n} \bar{H}_{\mu v} \quad .$$

The off-diagonal elements of the Hamiltonian matrix correspond to the electronic couplings between the individual fragments, the diagonal elements are the orbital energies. $\bar{H}_{\mu v}$ is the Hamiltonian in the atomic-orbital basis.

Using the fast, semi-empirical DFTB method to compute $\bar{H}_{\mu v}$ leads to a highly efficient scheme to compute couplings, allowing to treat large systems and investigate a multitude of conformations. In a recent extended benchmark study, it has been shown, that this approximate methodology reproduces the couplings, computed with high level ab initio methods for a large molecular test set, with high accuracy. [25b,c]

Beside the successful benchmark of the coupling calculation, this FO-DFTB approach was also used to perform direct simulations of the charge carrier in different systems e.g. organic semiconductors, DNA and proteins, which reproduced the experimental results. [25d-k]

DFT is known to be an approximate method, which shows excellent performance for many molecular properties like geometries or thermochemistry data, but, on the other hand, is known to exhibit several short comings. The most prominent among these is the self-interaction error of DFT, present in DFT functionals using the generalized gradient approximation (GGA), which leads to a wrong estimate of orbital energies. Compared to ab initio methods, not only the absolute energies are deviant, but often also the relative ordering of the orbitals. This behavior of GGA functionals like BLYP or PBE is - only partially – corrected for when using hybrid functionals like B3LPY.

Typically, the energies of occupied orbitals are too high (by several eV!), and the energy differences between orbitals are too small and/or orbitals are interchanged. The character and shape of the orbitals, however, is preserved. There, in DFT-GGA often the HOMO orbital has a σ-symmetry, while the correct π-orbital can be found as HOMO-1 or HOMO-2. This deficiency is particularly common in large molecules like those considered in this work (in fact, the energy differences between the orbitals is as little as 0.02–0.15 eV). To compute the correct charge transfer couplings, the respective orbitals with the proper symmetry have to be used. This problem also occurs in DFTB, since it is derived from DFT-GGA using a PBE functional. [S8]

To this end, each molecule was placed in the x,y-plane of the coordinate system, and the contribution of the π_z-orbitals on the heavy atoms of the conjugated system to the LUMO, HOMO, …, HOMO-3 was calculated from their LCAO coefficients as $\sum_{\mu}\left(c_{\mu\pi_z}^{i\ m}\right)^2$. The orbital was considered to have π-symmetry if that value exceeded a threshold (0.1). The DFTB+ program was employed and to visualize the orbitals and to calculate the coefficients. [25k]

7.2 Calculation of Reorganization Energies

Reorganization energies for hole and electron transport were calculated by DFT-B3LYP/6-31G*. This method is more accurate than DFTB and is a standard method to calculate reorganization energies. It is a well-known method for

geometry optimization and it has been shown that its result is in very good agreement with experimental data. Pure GGA functionals underestimate lambda, this also holds true for other functionals, such as DFTB and for DFT-PBE, BLYP etc. So, hybrid functionals or range separated functionals have to be used. A standard functional in the literature is therefore B3LYP.[S9]

7.3 Calculated Charge Transfer Integrals

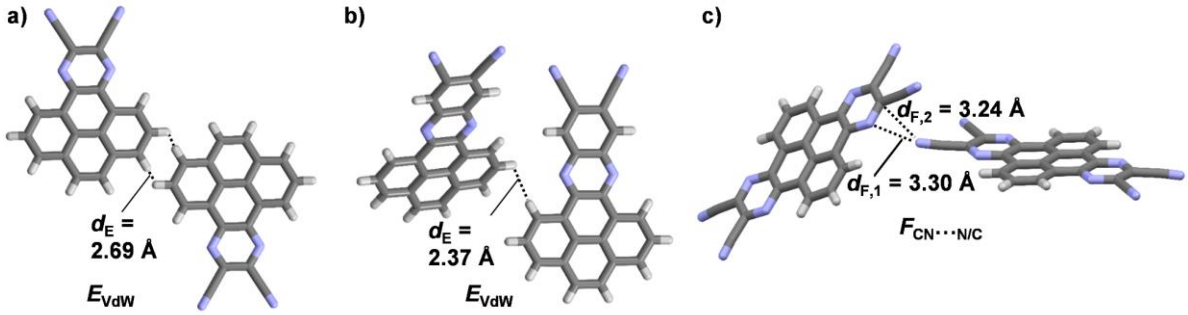

Figure S30. Dimers of a) **PQDC** (polymorph ***β***), b) **PPDC** (polymorph ***α***) and c) **PPQTC** (polymorph ***α***) not shown in the main document with charge transfer integrals significantly larger than 0 (see Tab. S17).

Table S17. List of calculated charge transfer integrals for hole (h) and electron (e) transport calculated by DFTB.

#	cmpd	modification[a]	t_A[a,b] [meV]	t_B[a,b] [meV]	t_C[a,b] [meV]	t_D[a,b] [meV]	t_E[a,b] [meV]	t_F[a,b] [meV]
1	**PQDC**	***α***	**20 (h)** **49 (e)**	2 (h) 3 (e)	3 (h) 3 (e)			
2		***β***	**88 (h)** **113 (e)**	**57 (h)** **252 (e)**	1 (h) 0 (e)	0 (h) 1 (e)	21 (h) 26 (e)	
3	**PPDC**	***α***	**13 (h)** **172 (e)**	**0 (h)** **101 (e)**	0 (h) 0 (e)	1 (h) 7 (e)	15 (h) 2 (e)	
4	**PPQTC**	***α***	**36 (h)** **27 (e)**	**3 (h)** **46 (e)**	1 (h) 1 (e)	13 (h) 2 (e)	8 (h) 20 (e)	7 (h) 15 (e)
5		***β***	**12 (h)** **36 (e)**	7 (h) 5 (e)	7 (h) 0 (e)	1 (h) 13 (e)		
6	**^{t}Bu-PPQTC**	***α***	**53 (h)** **76 (e)**	19 (h) 35 (e)				
7		***β***	**50 (h)** **69 (e)**	4 (h) 7 (e)				
8	**QPPTC**	***α***	**4 (h)** **108 (e)**	0 (h) 5 (e)				

[a] See Figs. 4-8 and Tab. 2 in the main document for assignments and crystallographic parameters.
[b] values for π stacked motifs highlighted bold.

8 References

[S1] P. C. DeRose, E. A. Early, G. W. Kramer, *Rev. Sci. Instrum.* **2007**, *78*, 033107.

[S2] C. Würth, M. Grabolle, J. Pauli, M. Spieles, U. Resch-Genger, *Nat. Protoc.* **2013**, *8*, 1535.

[S3] CrysAlisPro, Agilent Technologies, Oxford (UK) **2011-2014**.

[S4] W. R. Busing, H. A. Levy, *Acta Crystallogr.* **1957**, *10*, 180-182.

[S5] a) G. Sheldrick, SHELXT, University of Göttingen and Bruker AXS GmbH, Karlsruhe (Germany), **2012-2014**. b) M. Ruf, B. C. Noll, Application Note SC-XRD 503, Bruker AXS GmbH, Karlsruhe (Germany), **2014**. c) G. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3-8.

[S6] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, *J. Appl. Crystallogr.* **2007**, *40*, 609-613.

[S7] a) G. Sheldrick, SHELXL-20xx, University of Göttingen and Bruker AXS GmbH, Karlsruhe (Germany), **2012-2014**. b) G. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112-122.

[S8] a) T. Kubař, P. B. Woiczikowski, G. Cuniberti, M. Elstner, *J. Phys. Chem. B* **2008**, *112*, 7937-7947. b) N. Otte, M. Scholten, W. Thiel, *J. Phys. Chem. A,* **2007**, *111*, 5751-5755.

[S9] a) P.E. Schwenn, P.L. Burn, B. J. Powell, *Organic Electronics* **2011**, *12*, 394-403. b) X. Yang, L. Wang, C. Wang, W. Long, Z. Shuai, *Chem. Mater.* **2008**, *20*, 3205-3211. c) D. L. Cheung, A. Troisi, *J. Phys. Chem. C* **2010**,*114*, 20479–20488.