Electronic Supplementary Information for

Curved Fractal Structures of Pyridine-Substituted β-Diketone Crystals

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Part I. Materials, methods, and synthesis

Materials. Tetrahydrofuran (THF) was distilled by refluxing with sodium for 3 h before use. All other reagents and solvents were obtained from Aladdin Reagent (Shanghai) and were used as received.

Methods. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. ^{1}H NMR spectra were referenced to the signal for residual protio chloroform at 7.26 ppm and coupling constants are given in hertz. Elemental analysis for C and H was performed by a vario EL cube elemental analyzer. The temperatures of the combustion tube and the reduction tube were 950°C and 550°C, respectively. UV-Vis absorption spectra were recorded on a Beijing Persee TU-1901 UV-vis spectrometer. Photographs were taken by a Cannon 500D digital camera. Micrographs were taken on an Olympus DP72 color camera mounted on a BX51 microscope. Steady-state emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorometer (Japan). Fluorescence lifetime data were acquired with a 1MHz LED laser with the excitation peak at 369 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). Absolute quantum yields were measured with HORIBA Quanta-φ integrating sphere in combination with Horiba FluoroMax-4 spectrofluorometer. Single crystal data were acquired with a Gemini S Ultra Single Crystal Diffractometer. The crystal was kept at 291 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Calculations were performed using the Gaussian 09 suite of programs1 employing density functional theory and B3LYP/6-31G for geometry optimization.

Syntheses

PBDK1

To a dry round-bottom flask 4-methoxyacetophenone (3.00 g, 20 mmol), THF (30 mL), and sodium hydride (60%, 0.8 g, 20 mmol) were introduced successively and the mixture was stirred at room temperature under N_2 for ~10 min. Then ethyl picolinate (1.54 g, 10 mmol) was introduced and the mixture was refluxed under N_2 for ~4 h. After cooling to room temperature, the reaction mixture was quenched by saturated sodium bicarbonate (aq.) and extracted with ethyl acetate. The organic layer was combined and recrystallized to give the product as pale yellow powder crystals (2.42 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.62 (s, 1H), 8.81-8.64 (m, 1H), 8.17 (d, J = 7.9 Hz, 1H), 8.13-8.02 (m, 2H), 7.88 (dtd, J = 11.7, 7.7, 3.8 Hz, 1H), 7.56 (s, 1H), 7.46 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 7.05-6.90 (m, 2H), 3.88 (d, J = 4.8 Hz, 3H). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58, H, 5.13; found: C, 70.61, H, 5.08.

PBDK2. The same procedure as **PBDK1** except that ethyl nicotinate was used as the starting material instead of ethyl picolinate. Yield 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.83 (s, 1H), 9.18 (d, J = 1.9 Hz, 1H), 8.75 (dd, J = 4.8, 1.6 Hz, 1H), 8.36-8.18 (m, 1H), 8.10-7.86 (m, 2H), 7.44 (dd, J = 8.0, 4.8 Hz, 1H), 7.10-6.90 (m, 2H), 6.80 (s, 1H), 3.89 (d, J = 4.4 Hz, 3H). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58, H, 5.13; found: C, 70.63, H, 5.10.

PBDK3. The same procedure as **PBDK1** except that ethyl isonicotinate was used instead of ethyl picolinate. Yield 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.65 (s, 1H), 8.79 (d, J = 6.1 Hz, 2H), 8.08-7.92 (m, 2H), 7.80 (dd, J = 4.6, 1.6 Hz, 2H), 7.08-6.94 (m, 2H), 6.83 (s, 1H), 3.90 (d, J = 4.7 Hz, 3H). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58, H, 5.13; found: C, 70.64, H, 5.07.

Part II. Supplementary figures and tables

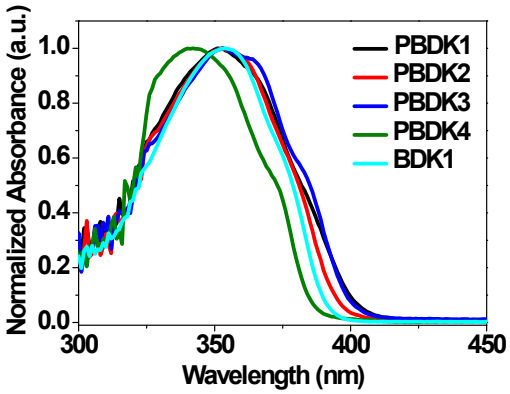

Figure S1. Normalized UV-vis absorption spectra of PBDKs **1**-**4** and the **BDK1** in acetone.

Table S1. UV-vis absorption data of PBDKs **1**-**4** and the **BDK1**.

	λ_{abs} (nm)	ε ($M^{-1}cm^{-1}$)
PBDK 1	352	28,000
PBDK 2	352	27,000
PBDK 3	352	30,000
PBDK 4	342	21,300
BDK1	353	33,000

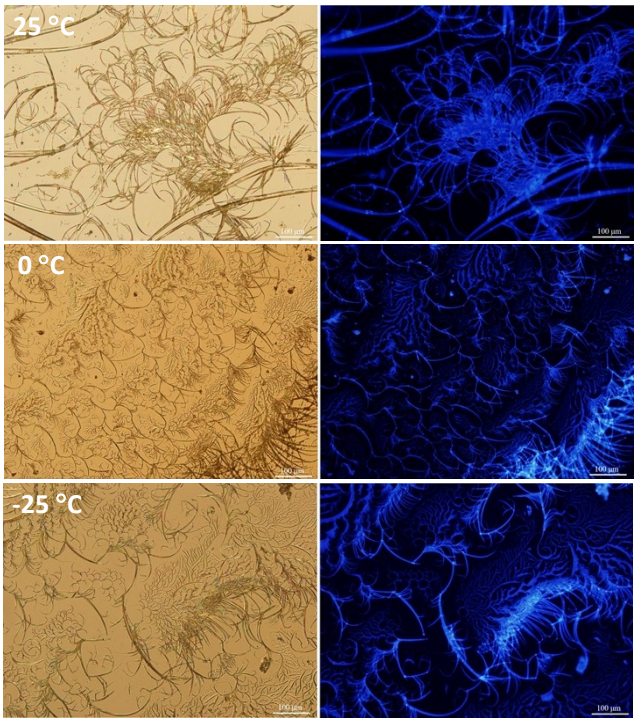

Figure S2. Crystal morphologies (left panel: bright field; right panel: fluorescence mode) of **PBDK1** grown from drop-cast acetone solution at 25, 0 and -20 °C (5 mg/mL). Scale bar: 100 μm.

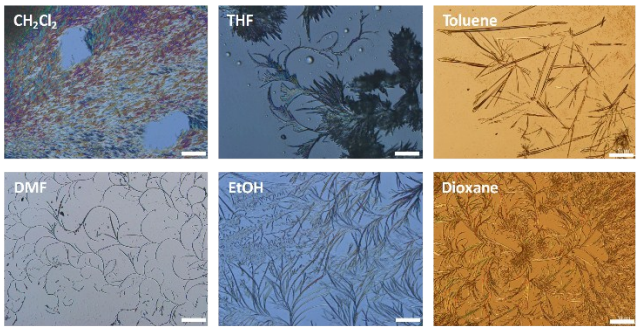

Figure S3. Representative bright-field micrographs of **PBDK1** crystals grown from drop-cast solutions of various solvents (5 mg/mL). Scale bar: 100 μm.

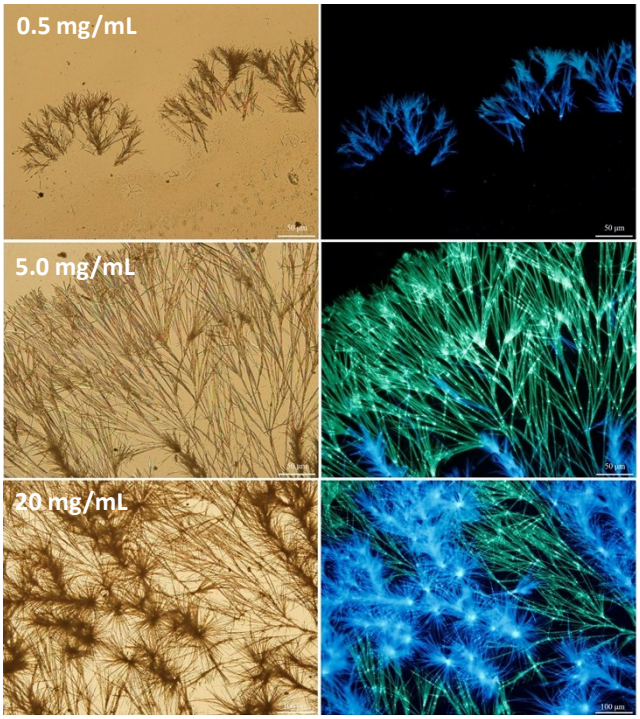

Figure S4. Representative bright-field (left) and fluorescence (right) micrographs of **PBDK2** crystals grown from drop-cast acetone solutions of various concentrations at room temperature. Scale bar: 50 μm.

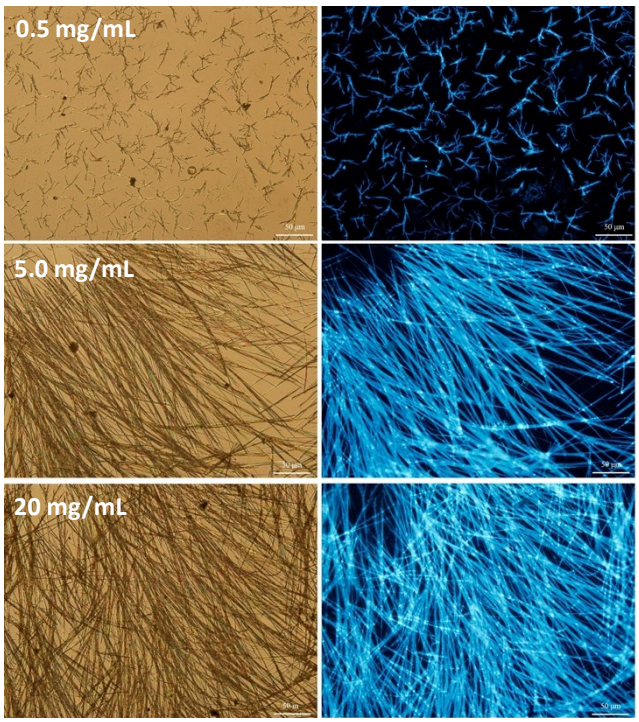

Figure S5. Representative bright-field (left) and fluorescence (right) micrographs of **PBDK3** crystals grown from drop-cast acetone solutions of various concentrations at room temperature. Scale bar: 50 μm.

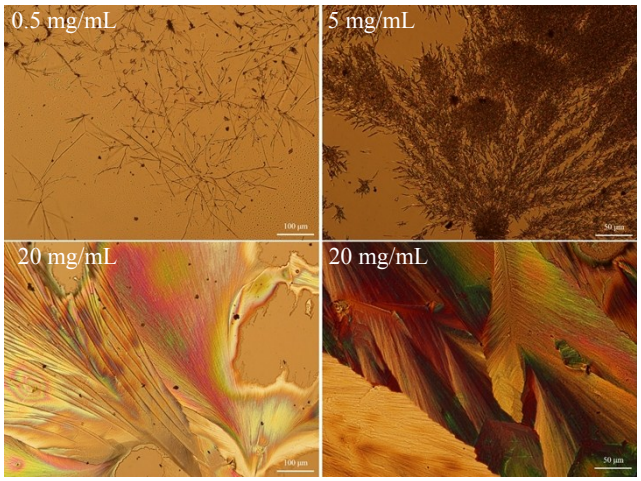

Figure S6. Representative bright-field micrographs of **PBDK4** crystals grown from drop-cast acetone solutions of various concentrations at room temperature.

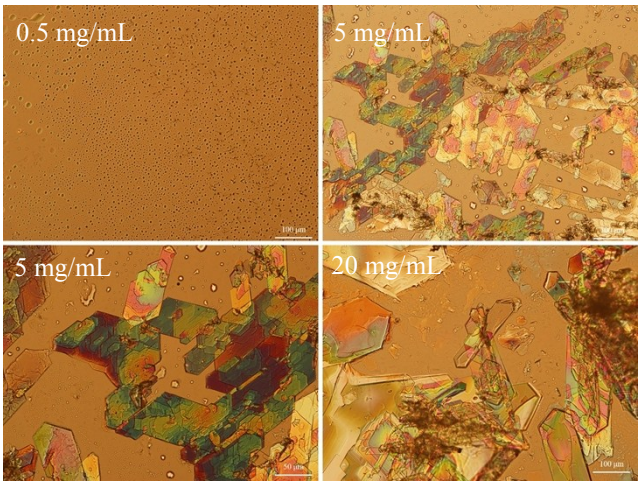

Figure S7. Representative bright-field micrographs of **BDK1** crystals grown from drop-cast acetone solutions of various concentrations at room temperature.

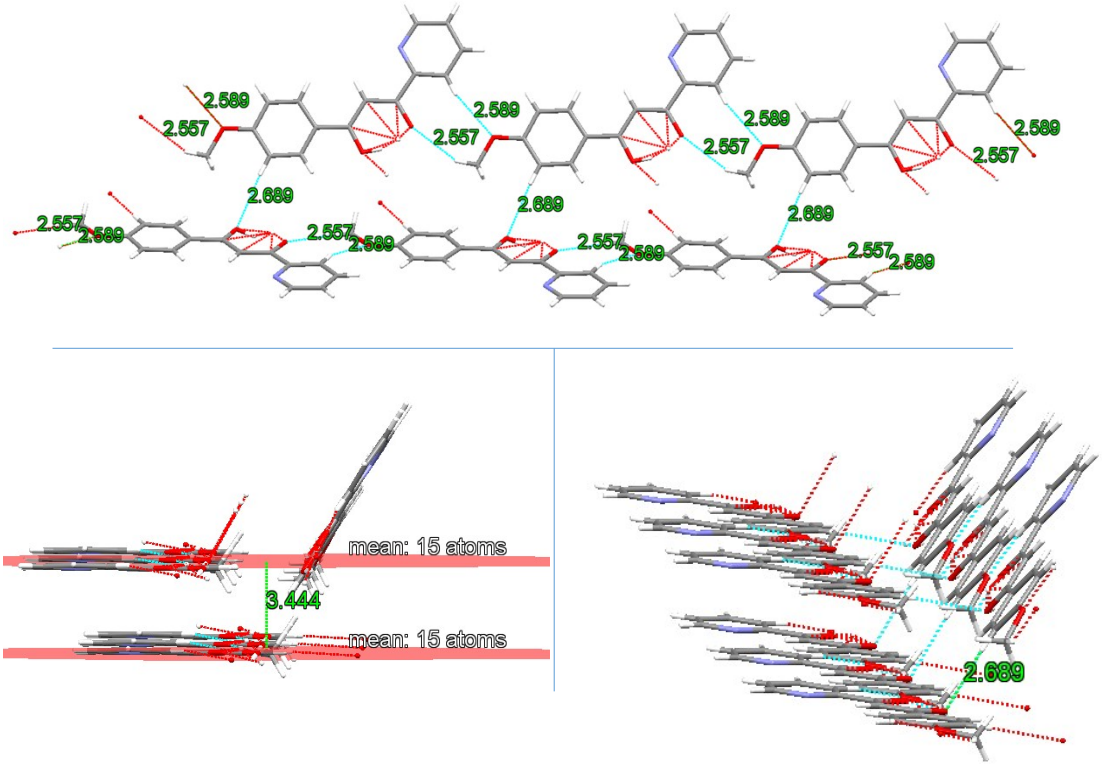

Figure S8. Molecular stacking of **PBDK1** from different views (XRD information extracted in Mercury 3.9).

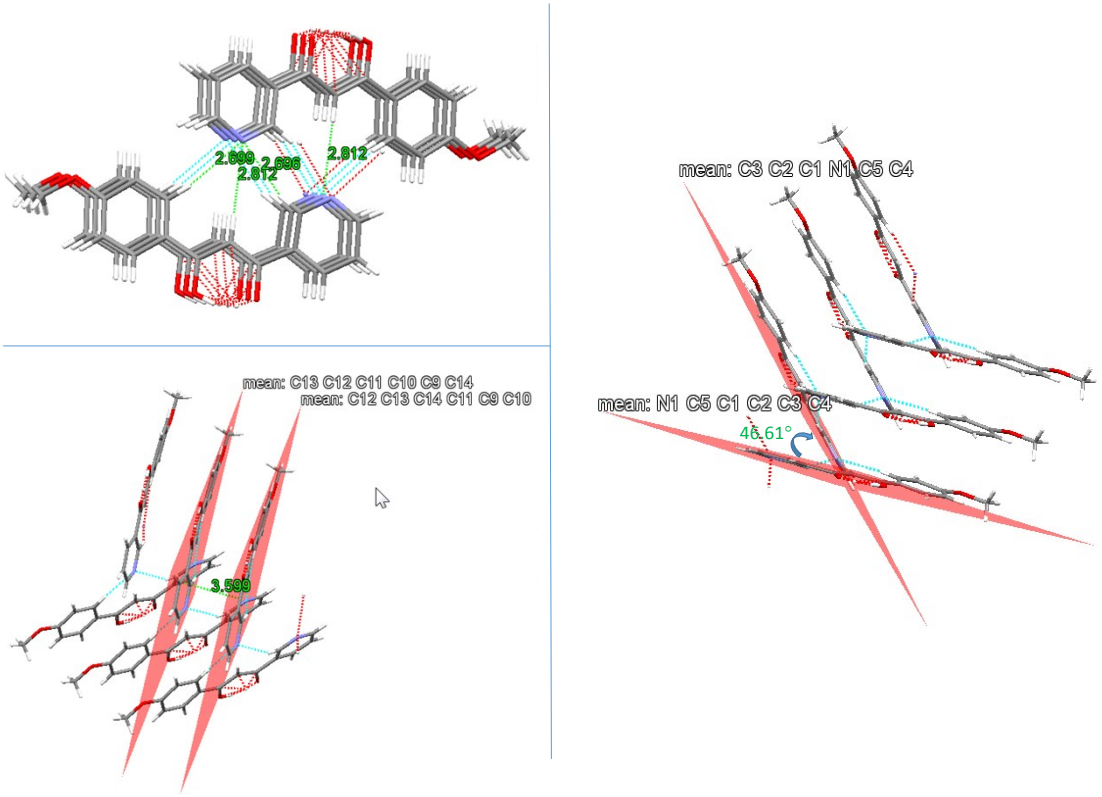

Figure S9. Molecular stacking of **PBDK2** from different views (XRD information extracted in Mercury 3.9).

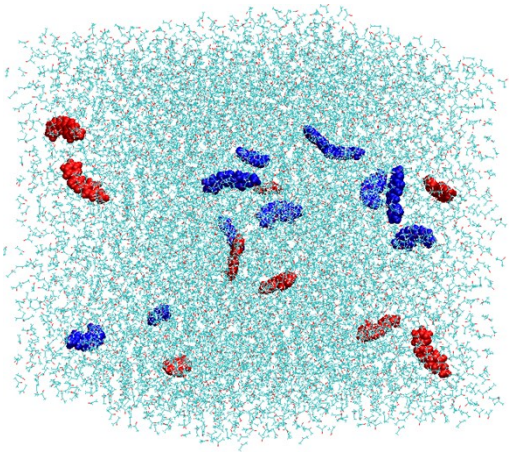

Figure S9. Simulation snapshot of the crystallization process of **PBDK1** in acetone at a concentration of 10 mg/mL at room temperature.

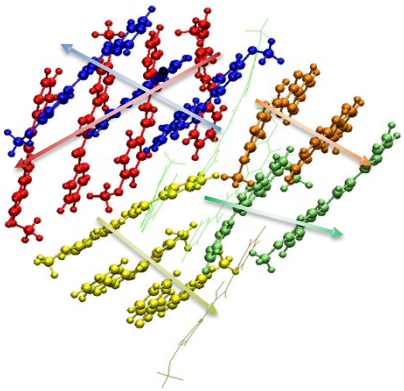

Figure S10. Simulated nucleation process at critical crystallization concentration of **PBDK1** (solvent molecules omitted for clarity and arrows indicating the direction of molecular packing/crystal growth).

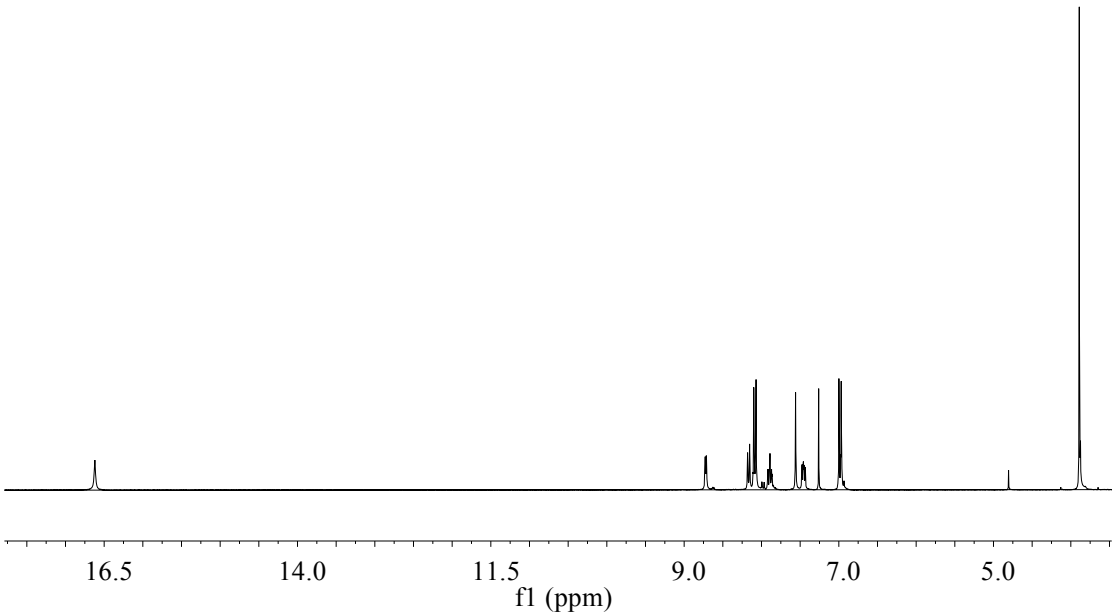

Figure S11. ^{1}H NMR spectrum of **PBDK1** in $CDCl_3$.

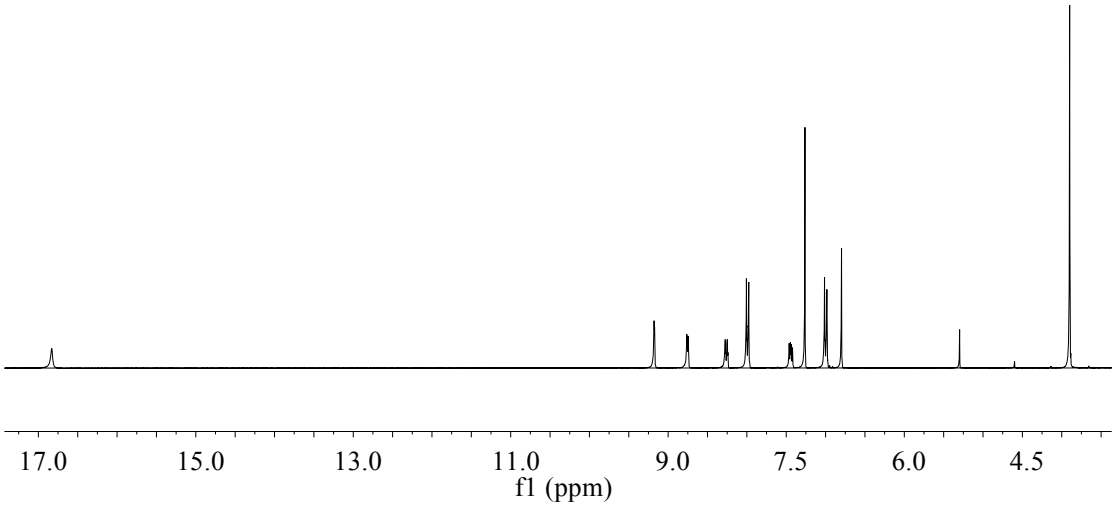

Figure S12. ^{1}H NMR spectrum of **PBDK2** in $CDCl_3$.

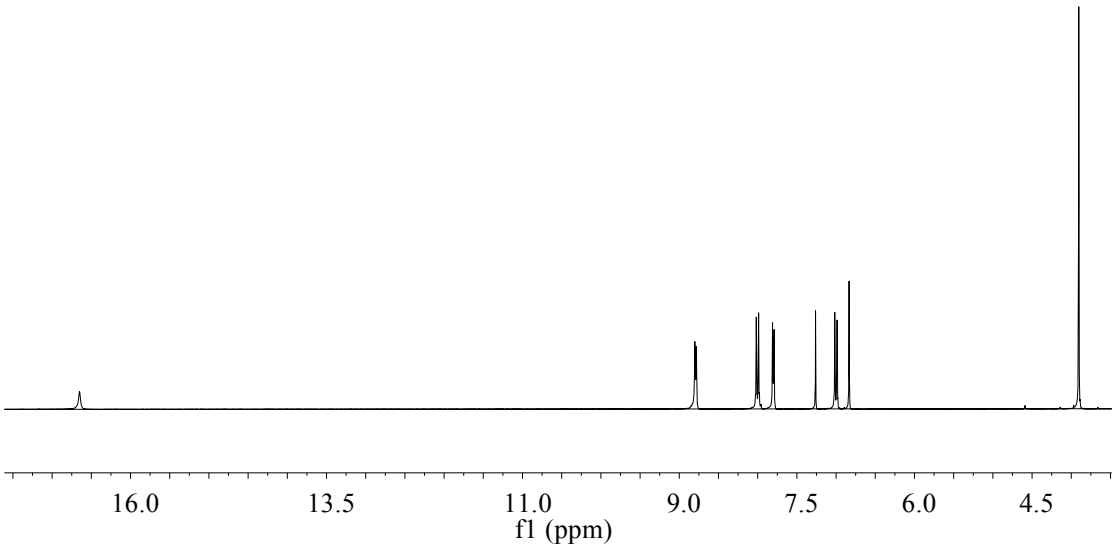

Figure S14. ^{1}H NMR spectrum of **PBDK3** in $CDCl_3$.

Part III. Supporting tables for single crystal data

Table S2 Crystal data and structure refinement for **PBDK1**

Identification code	xtq052401
Empirical formula	$C_{15}H_{13}NO_3$
Formula weight	255.26
Temperature/K	290(2)
Crystal system	Monoclinic
Space group	Cc
a/Å	4.0145(3)
b/Å	26.7097(18)
c/Å	11.7285(10)
α/°	90.00
β/°	94.126(7)
γ/°	90.00
Volume/Å^3	1254.34(17)
Z	4
ρ_{calc}mg/mm^3	1.352
m/mm^{-1}	0.095
F(000)	536.0
Crystal size/mm^3	0.35 × 0.32 × 0.23
2Θ range for data collection	7.02 to 52.74°
Index ranges	-5 ≤ h ≤ 3, -32 ≤ k ≤ 31, -14 ≤ l ≤ 14
Reflections collected	2971
Independent reflections	1852[R(int) = 0.0179]
Data/restraints/parameters	1852/4/180
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0754
Final R indexes [all data]	R_1 = 0.0573, wR_2 = 0.0842
Largest diff. peak/hole / e Å^{-3}	0.09/-0.14
Flack parameter	-1.3(14)

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **PBDK1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*Y*	*z*	U(eq)
O3	-1784(5)	887.6(6)	3530.1(16)	57.2(5)
O2	4123(5)	573.6(7)	8625.7(16)	58.4(5)
O1	4390(5)	971.3(7)	10543.2(18)	62.7(6)
N1	-40(5)	2126.6(8)	10429(2)	55.7(6)
C12	-695(5)	880.5(9)	4655(2)	43.6(7)
C7	1530(6)	1338.9(9)	8941(2)	45.5(7)
C5	1739(6)	1741.8(9)	10884(2)	45.9(6)
C9	1275(6)	926.8(9)	6990(2)	41.1(6)
C6	2593(6)	1335.3(9)	10088(2)	45.5(6)
C11	-1554(6)	1286.9(10)	5299(2)	49.7(7)
C13	1178(6)	491.3(10)	5170(2)	48.4(7)
C15	-746(7)	493.0(11)	2817(2)	58.9(7)
C14	2132(6)	521.8(9)	6328(2)	47.8(7)
C1	-803(8)	2489.7(11)	11138(3)	64.0(8)
C3	1911(7)	2097.9(12)	12748(3)	64.2(8)
C2	112(8)	2493.8(11)	12293(3)	64.0(8)
C8	2344(5)	944.9(9)	8223(2)	43.7(6)
C4	2761(7)	1714.2(10)	12041(2)	56.0(7)
C10	-620(6)	1311.6(9)	6445(2)	47.3(7)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **PBDK1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	67.0(11)	58.5(12)	45.3(11)	-1.6(9)	-1.6(9)	9.7(9)
O2	75.1(14)	48.6(11)	50.0(12)	1.6(11)	-5(1)	13.7(10)
O1	84.2(15)	53.2(13)	49.3(13)	1.6(9)	-5.2(10)	18.3(10)
N1	64.6(15)	49.6(15)	53.0(14)	-2.6(12)	5.1(11)	2.5(12)
C12	42.5(15)	45.6(17)	42.3(16)	2.6(12)	0.4(12)	-4.0(11)
C7	52.4(18)	40.5(15)	43.5(17)	3.3(12)	3.1(13)	1.7(12)
C5	47.6(15)	41.6(16)	48.6(16)	1.3(12)	5.3(12)	-5.8(12)
C9	40.9(14)	40.8(14)	42.4(14)	2.8(11)	7.6(11)	-4.6(11)
C6	44.8(16)	42.1(15)	50.0(17)	0.4(12)	5.8(13)	-3.9(12)
C11	55.9(17)	44.5(16)	48.5(17)	3.7(13)	3.4(14)	11.0(12)
C13	52.4(18)	45.8(16)	47.3(16)	-4.3(12)	5.5(13)	7.4(12)
C15	66.7(19)	64.2(18)	45.1(15)	-4.0(14)	0.0(13)	0.8(15)
C14	53.4(17)	41.3(15)	48.4(16)	4.6(13)	2.2(13)	8.3(12)

C1	74(2)	48.3(17)	71(2)	-0.3(15)	13.4(17)	5.0(14)
C3	76(2)	69(2)	47.5(17)	-6.8(16)	5.5(15)	-8.1(17)
C2	73(2)	54.4(18)	66(2)	-13.7(16)	18.6(16)	-11.1(16)
C8	44.5(17)	40.3(15)	46.1(16)	5.2(12)	1.5(13)	-3.1(11)
C4	61.9(18)	57.9(18)	47.7(17)	0.0(14)	0.8(14)	-4.6(14)
C10	53.9(17)	37.9(14)	50.0(18)	-2.7(12)	4.0(14)	5.1(11)

Table S5 Bond Lengths for **PBDK1.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C12	1.360(3)	C5	C6	1.489(3)
O3	C15	1.426(3)	C5	C4	1.390(3)
O2	C8	1.291(3)	C9	C14	1.389(3)
O1	C6	1.302(3)	C9	C8	1.479(3)
N1	C5	1.340(3)	C9	C10	1.405(3)
N1	C1	1.327(4)	C11	C10	1.370(3)
C12	C11	1.380(3)	C13	C14	1.387(3)
C12	C13	1.395(3)	C1	C2	1.378(4)
C7	C6	1.381(3)	C3	C2	1.367(4)
C7	C8	1.402(3)	C3	C4	1.377(4)

Table S6 Bond Angles for **PBDK1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O3	C15	118.2(2)	O1	C6	C5	115.7(2)
C1	N1	C5	116.8(2)	C7	C6	C5	122.5(2)
O3	C12	C11	116.4(2)	C10	C11	C12	120.8(2)
O3	C12	C13	123.8(2)	C14	C13	C12	118.8(2)
C11	C12	C13	119.8(2)	C13	C14	C9	122.1(2)
C6	C7	C8	120.7(2)	N1	C1	C2	124.3(3)
N1	C5	C6	116.7(2)	C2	C3	C4	119.2(3)
N1	C5	C4	122.7(3)	C3	C2	C1	118.2(3)
C4	C5	C6	120.6(2)	O2	C8	C7	120.2(2)
C14	C9	C8	120.4(2)	O2	C8	C9	116.5(2)
C14	C9	C10	117.6(2)	C7	C8	C9	123.2(2)
C10	C9	C8	122.1(2)	C3	C4	C5	118.7(3)
O1	C6	C7	121.9(2)	C11	C10	C9	120.8(2)

Table S7 Hydrogen Bonds for **PBDK1.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2	O1	0.85(2)	1.73(4)	2.482(3)	147(6)
O1	H1	O2	0.85(2)	1.71(4)	2.482(3)	150(8)

Table S8 Torsion Angles for **PBDK1.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C12	C11	C10	179.0(2)	C14	C9	C8	O2	1.1(3)
O3	C12	C13	C14	-179.5(2)	C14	C9	C8	C7	-179.2(2)
N1	C5	C6	O1	178.4(2)	C14	C9	C10	C11	-0.5(4)
N1	C5	C6	C7	-2.2(3)	C1	N1	C5	C6	-180.0(2)
N1	C5	C4	C3	0.0(4)	C1	N1	C5	C4	0.2(4)
N1	C1	C2	C3	-0.3(5)	C2	C3	C4	C5	-0.3(4)
C12	C11	C10	C9	0.9(4)	C8	C7	C6	O1	0.3(4)
C12	C13	C14	C9	0.1(4)	C8	C7	C6	C5	-179.0(2)
C5	N1	C1	C2	0.0(4)	C8	C9	C14	C13	-180.0(2)
C6	C7	C8	O2	-0.4(4)	C8	C9	C10	C11	179.5(2)
C6	C7	C8	C9	179.9(2)	C4	C5	C6	O1	-1.7(4)
C6	C5	C4	C3	-179.9(2)	C4	C5	C6	C7	177.7(3)
C11	C12	C13	C14	0.2(4)	C4	C3	C2	C1	0.5(5)
C13	C12	C11	C10	-0.7(4)	C10	C9	C14	C13	0.0(4)
C15	O3	C12	C11	175.5(2)	C10	C9	C8	O2	-178.9(2)

C15	O3	C12	C13	-4.8(3)	C10	C9	C8	C7	0.8(3)		

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **PBDK1.**

Atom	***x***	***y***	***z***	**U(eq)**
H7	259	1606	8643	55
H11	-2781	1547	4950	60
H13	1777	216	4744	58
H15A	-1574	555	2041	88
H15C	-1616	180	3069	88
H15B	1649	478	2859	88
H14	3385	263	6672	57
H1A	-2038	2759	10834	77
H3	2554	2088	13525	77
H2A	-480	2759	12751	77
H4	3993	1442	12331	67
H10	-1249	1586	6866	57
H2	5000(150)	680(20)	9260(30)	71
H1	4340(170)	740(20)	10030(50)	71

Table S10 Crystal data and structure refinement for **PBDK2**

Identification code	XTQ052402
Empirical formula	$C_{15}H_{13}NO_3$
Formula weight	255.26
Temperature/K	290(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	21.986(2)
b/Å	3.9115(4)
c/Å	30.020(2)
α/°	90.00
β/°	106.946(9)
γ/°	90.00

Volume/Å^3	2469.6(4)
Z	8
ρ_{calc}mg/mm^3	1.373
m/mm^{-1}	0.791
F(000)	1072.0
Crystal size/mm^3	0.3 × 0.24 × 0.2
2Θ range for data collection	6.16 to 130.14°
Index ranges	-25 ≤ h ≤ 25, -4 ≤ k ≤ 4, -24 ≤ l ≤ 35
Reflections collected	3956
Independent reflections	2096[R(int) = 0.0259]
Data/restraints/parameters	2096/0/174
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0575, wR_2 = 0.1491
Final R indexes [all data]	R_1 = 0.0738, wR_2 = 0.1688
Largest diff. peak/hole / e Å^{-3}	0.19/-0.19

Table S11 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **PBDK2.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O2	1759.0(8)	2239(6)	545.1(5)	81.6(6)
O3	4554.9(8)	-3171(5)	912.7(6)	79.6(6)
O1	1035.0(7)	5035(6)	924.8(5)	80.9(6)
N1	1661.8(9)	8334(6)	2515.0(6)	74.6(6)
C4	1328.3(10)	6397(6)	1719.8(7)	55.9(5)
C6	1486.2(10)	4945(6)	1310.5(7)	57.0(6)
C3	703.2(11)	7245(7)	1687.7(8)	69.3(7)
C5	1782.9(10)	7015(7)	2139.4(7)	65.2(7)
C9	2817.8(10)	781(6)	937.8(7)	53.7(5)
C13	3479.0(11)	-1576(7)	495.9(8)	65.7(6)
C14	2904.5(11)	-221(7)	518.3(8)	64.7(6)
C8	2196(1)	2229(6)	936.1(7)	57.4(5)
C1	1054.3(11)	9119(7)	2468.5(8)	73.4(7)
C7	2078(1)	3569(6)	1337.2(7)	56.1(6)

C11	3894.4(11)	-927(7)	1320.0(8)	67.0(7)
C10	3318.4(10)	403(7)	1337.6(7)	63.2(6)
C12	3969.7(10)	-1904(6)	893.9(7)	60.1(6)
C2	573.2(12)	8628(8)	2072.7(8)	75.2(7)
C15	4661.9(12)	-4246(8)	485.2(9)	81.2(8)

Table S12 Anisotropic Displacement Parameters ($Å^2×10^3$) for **PBDK2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	63.2(9)	123.8(17)	54.8(9)	-13.7(9)	12.8(7)	15.6(10)
O3	60.5(9)	107.5(15)	75.8(10)	-6.6(10)	27.5(8)	10.5(9)
O1	57.1(9)	122.9(17)	59.3(9)	-10.5(10)	11.4(8)	17.1(10)
N1	64.8(12)	104.3(18)	57.3(11)	-9.8(11)	21.7(9)	4.1(11)
C4	52.7(11)	63.3(13)	54.6(11)	5.8(10)	20.3(9)	0.2(10)
C6	55.1(11)	64.5(14)	52.3(11)	2(1)	17.3(9)	-1.7(10)
C3	53.0(12)	91.9(18)	62.4(13)	2.0(13)	15.9(10)	6.7(12)
C5	52.9(11)	87.8(18)	57.8(12)	-3.6(12)	20.4(10)	3.8(11)
C9	56.3(11)	55.9(12)	52.4(11)	-1.4(10)	21.1(9)	-3(1)
C13	69.0(14)	75.9(16)	57.7(12)	-8.5(11)	27.2(11)	2.9(12)
C14	61.1(12)	78.9(16)	53.8(12)	-7.5(11)	16.3(10)	3.0(12)
C8	55.4(11)	63.1(14)	54.7(11)	-1.1(10)	17.3(9)	-2.5(10)
C1	71.5(14)	94(2)	62.4(13)	-2.9(13)	31.9(11)	10.0(14)
C7	53.3(11)	66.9(14)	48.5(10)	-1.4(10)	15.3(9)	0.3(10)
C11	56.5(12)	88.3(18)	56.0(12)	-0.6(12)	16.2(10)	3.8(12)
C10	62.3(12)	79.1(16)	51.7(11)	-1.8(11)	21.9(10)	1.1(12)
C12	54.5(11)	66.0(14)	63.9(12)	-1.1(11)	23.9(10)	0.1(11)
C2	60.8(13)	99(2)	71.9(14)	-0.8(14)	28.5(12)	12.6(13)
C15	74.4(15)	93(2)	86.4(17)	-14.3(15)	38.9(14)	8.5(14)

Table S13 Bond Lengths for **PBDK2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C8	1.282(2)	C3	C2	1.379(3)
O3	C12	1.365(3)	C9	C14	1.384(3)
O3	C15	1.433(3)	C9	C8	1.478(3)
O1	C6	1.287(2)	C9	C10	1.380(3)

N1	C5	1.335(3)	C13	C14	1.390(3)
N1	C1	1.338(3)	C13	C12	1.362(3)
C4	C6	1.484(3)	C8	C7	1.405(3)
C4	C3	1.390(3)	C1	C2	1.354(3)
C4	C5	1.382(3)	C11	C10	1.384(3)
C6	C7	1.389(3)	C11	C12	1.391(3)

Table S14 Bond Angles for **PBDK2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O3	C15	117.92(19)	C12	C13	C14	119.5(2)
C5	N1	C1	116.1(2)	C9	C14	C13	121.4(2)
C3	C4	C6	119.96(19)	O2	C8	C9	116.74(19)
C5	C4	C6	122.70(18)	O2	C8	C7	120.5(2)
C5	C4	C3	117.3(2)	C7	C8	C9	122.78(19)
O1	C6	C4	115.43(18)	N1	C1	C2	124.0(2)
O1	C6	C7	121.75(19)	C6	C7	C8	119.93(19)
C7	C6	C4	122.82(18)	C10	C11	C12	119.6(2)
C2	C3	C4	118.5(2)	C9	C10	C11	120.9(2)
N1	C5	C4	124.6(2)	O3	C12	C11	115.2(2)
C14	C9	C8	118.53(19)	C13	C12	O3	124.5(2)
C10	C9	C14	118.3(2)	C13	C12	C11	120.3(2)
C10	C9	C8	123.13(19)	C1	C2	C3	119.4(2)

Table S15 Hydrogen Bonds for **PBDK2**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2	O1	0.82	1.73	2.467(2)	150.4
O1	H1	O2	0.82	1.73	2.467(2)	148.9

Table S16 Torsion Angles for **PBDK2**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C8	C7	C6	-0.6(4)	C14	C9	C8	C7	-174.8(2)
O1	C	C	C8	0.0(4)	C1	C9	C1	C1	0.4(4)

	6	7			4		0	1	
N1	C 1	C 2	C3	-0.2(5)	C1 4	C1 3	C1 2	O3	-179.4(2)
C4	C 6	C 7	C8	179.9(2)	C1 4	C1 3	C1 2	C1 1	0.7(4)
C4	C 3	C 2	C1	0.0(4)	C8	C9	C1 4	C1 3	179.5(2)
C6	C 4	C 3	C2	-179.2(2)	C8	C9	C1 0	C1 1	-179.1(2)
C6	C 4	C 5	N 1	179.6(2)	C1	N1	C5	C4	-0.7(4)
C3	C 4	C 6	O 1	9.9(3)	C1 0	C9	C1 4	C1 3	0.0(4)
C3	C 4	C 6	C7	-170.0(2)	C1 0	C9	C8	O2	-175.7(2)
C3	C 4	C 5	N 1	0.6(4)	C1 0	C9	C8	C7	4.7(4)
C5	N 1	C 1	C2	0.5(4)	C1 0	C1 1	C1 2	O3	179.8(2)
C5	C 4	C 6	O 1	-169.1(2)	C1 0	C1 1	C1 2	C1 3	-0.4(4)
C5	C 4	C 6	C7	11.0(4)	C1 2	C1 3	C1 4	C9	-0.5(4)
C5	C 4	C 3	C2	-0.2(4)	C1 2	C1 1	C1 0	C9	-0.2(4)
C9	C 8	C 7	C6	178.9(2)	C1 5	O3	C1 2	C1 3	-0.2(4)
C1 4	C 9	C 8	O 2	4.8(3)	C1 5	O3	C1 2	C1 1	179.6(2)

Table S17 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **PBDK2**.

Atom	***x***	***y***	***z***	**U(eq)**
H3	380	6887	1413	83
H5	2203	6473	2162	78
H13	3528	-2255	211	79
H14	2571	18	246	78
H1A	956	10060	2724	88
H7	2396	3534	1620	67

H11	4229	-1165	1592	80
H10	3268	1050	1623	76
H2A	159	9218	2061	90
H15A	4616	-2323	279	122
H15B	4358	-5972	342	122
H15C	5084	-5160	548	122
H2	1438	3118	577	122
H1	1159	4221	717	122

Table S18 Crystal data and structure refinement for **PBDK3**

Identification code	XTQ052403
Empirical formula	$C_{15}H_{13}NO_3$
Formula weight	255.26
Temperature/K	290(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	3.8841(2)
b/Å	11.6062(6)
c/Å	27.6220(12)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1245.19(11)
Z	4
ρ_{calc}mg/mm^3	1.362
m/mm^{-1}	0.784
F(000)	536.0
Crystal size/mm^3	0.35 × 0.24 × 0.2
2Θ range for data collection	6.4 to 138.98°
Index ranges	$-4 \le h \le 2$, $-13 \le k \le 13$, $-33 \le l \le 29$
Reflections collected	4321
Independent reflections	2278[R(int) = 0.0257]
Data/restraints/parameters	2278/2/181
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.1139

Largest diff. peak/hole / e Å^{-3}	0.17/-0.12
Flack parameter	0.0(3)

Table S19 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **PBDK3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	6899(5)	10242.0(12)	588.0(5)	68.0(5)
O3	7640(5)	15606.0(12)	889.6(5)	75.8(5)
O1	4822(6)	8454.7(13)	964.7(5)	78.7(5)
C3	2535(5)	8374.5(16)	1752.4(6)	52.9(4)
C9	6533(5)	12060.9(16)	957.6(6)	46.8(4)
N1	-96(7)	7038.3(16)	2514.6(7)	73.9(5)
C7	4544(5)	10216.1(16)	1366.8(6)	51.9(4)
C8	6020(5)	10808.4(17)	964.2(6)	49.9(4)
C11	5933(6)	13953.7(18)	1300.0(6)	60.4(5)
C14	8036(5)	12567.1(16)	549.7(6)	50.3(4)
C6	4024(5)	9058.8(16)	1346.4(6)	52.9(5)
C10	5528(6)	12779.9(17)	1335.4(6)	55.5(5)
C12	7383(5)	14441.7(17)	887.4(6)	55.4(5)
C13	8447(5)	13739.6(17)	511.1(6)	53.6(5)
C5	19(7)	8173(2)	2533.8(7)	66.1(5)
C4	1282(6)	8873.6(18)	2172.4(6)	59.6(5)
C15	9048(8)	16161(2)	473.1(9)	83.1(8)
C2	2450(8)	7194.5(17)	1722.7(8)	73.4(7)
C1	1104(9)	6578(2)	2107.8(8)	86.3(9)

Table S20 Anisotropic Displacement Parameters (Å^2×10^3) for **PBDK3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	101.1(12)	60.7(8)	42.2(6)	-2.7(6)	15.2(7)	-0.5(8)
O3	101.1(13)	57.7(8)	68.6(9)	-4.1(7)	21.6(9)	-6.5(8)
O1	126.0(15)	59.7(8)	50.3(7)	-5.5(7)	23.2(9)	-4.5(10)

C3	57.8(11)	59.9(9)	41.0(8)	1.4(7)	-1.4(8)	-0.4(9)
C9	45.2(9)	59.3(10)	35.8(8)	1.1(7)	-1.2(7)	0.2(8)
N1	92.3(14)	71.2(11)	58.2(9)	8.9(8)	12.9(10)	-7.7(11)
C7	60.2(11)	58.7(10)	36.9(8)	-1.3(7)	2.7(8)	0.6(9)
C8	52.1(10)	60(1)	37.6(8)	0.3(7)	-1.1(8)	3.6(8)
C11	71.1(13)	65.8(11)	44.4(9)	-7.8(8)	11.2(9)	0.1(10)
C14	53.8(10)	60.5(10)	36.6(7)	-4.0(8)	3.1(8)	-2.0(8)
C6	59.4(11)	59.1(10)	40.1(8)	-0.1(8)	2.4(8)	2.8(9)
C10	63.2(12)	63.3(10)	39.9(8)	-0.1(8)	9.5(8)	-1.1(10)
C12	57.6(11)	58(1)	50.7(9)	-1.6(8)	4.0(9)	-2.3(9)
C13	54.9(11)	64.2(11)	41.6(8)	2.5(8)	3.6(8)	-5.2(9)
C5	74.4(13)	76.2(13)	47.6(9)	2.2(9)	9.8(10)	-1.2(12)
C4	70.5(13)	59.8(10)	48.3(9)	-0.9(8)	9.9(9)	-1.7(10)
C15	100(2)	62.8(12)	86.5(15)	4.2(12)	28.7(16)	-8.4(13)
C2	104.6(19)	58.5(10)	57.3(11)	-2.9(9)	18.8(13)	-4.3(13)
C1	130(3)	58.0(12)	70.9(13)	5.3(11)	24.9(15)	-8.0(15)

Table S21 Bond Lengths for **PBDK3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C8	1.276(2)	N1	C5	1.319(3)
O3	C12	1.355(2)	N1	C1	1.328(3)
O3	C15	1.427(3)	C7	C8	1.428(2)
O1	C6	1.303(2)	C7	C6	1.359(3)
C3	C6	1.491(2)	C11	C10	1.375(3)
C3	C4	1.385(2)	C11	C12	1.392(3)
C3	C2	1.372(3)	C14	C13	1.374(3)
C9	C8	1.467(2)	C12	C13	1.384(3)
C9	C14	1.398(2)	C5	C4	1.377(3)
C9	C10	1.392(2)	C2	C1	1.384(3)

Table S22 Bond Angles for **PBDK3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O3	C15	118.33(16)	C13	C14	C9	121.80(17)
C4	C3	C6	122.92(16)	O1	C6	C3	114.46(16)
C2	C3	C6	119.73(18)	O1	C6	C7	121.99(17)

C2	C3	C4	117.32(18)	C7	C6	C3	123.55(16)
C14	C9	C8	118.87(15)	C11	C10	C9	120.58(17)
C10	C9	C8	123.14(16)	O3	C12	C11	115.58(17)
C10	C9	C14	117.98(17)	O3	C12	C13	124.65(17)
C5	N1	C1	115.05(18)	C13	C12	C11	119.76(17)
C6	C7	C8	120.20(16)	C14	C13	C12	119.34(17)
O2	C8	C9	117.64(16)	N1	C5	C4	124.90(19)
O2	C8	C7	119.58(17)	C5	C4	C3	119.03(18)
C7	C8	C9	122.76(16)	C3	C2	C1	118.6(2)
C10	C11	C12	120.51(17)	N1	C1	C2	125.1(2)

Table S23 Hydrogen Bonds for **PBDK3**.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
O1	H1	O2	0.84(2)	1.64(3)	2.457(2)	163(8)
O2	H2	O1	0.84(2)	1.66(4)	2.457(2)	158(9)

Table S24 Torsion Angles for **PBDK3**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O3	C12	C13	C14	-179.7(2)	C10	C9	C8	O2	176.84(19)
C3	C2	C1	N1	-1.0(5)	C10	C9	C8	C7	-2.1(3)
C9	C14	C13	C12	0.7(3)	C10	C9	C14	C13	-1.7(3)
N1	C5	C4	C3	0.2(4)	C10	C11	C12	O3	179.6(2)
C8	C9	C14	C13	177.01(18)	C10	C11	C12	C13	-0.4(3)
C8	C9	C10	C11	-177.0(2)	C12	C11	C10	C9	-0.6(3)
C8	C7	C6	O1	-0.3(3)	C5	N1	C1	C2	0.9(5)
C8	C7	C6	C3	179.31(18)	C4	C3	C6	O1	-174.8(2)
C11	C12	C13	C14	0.4(3)	C4	C3	C6	C7	5.5(3)
C14	C9	C8	O2	-1.8(3)	C4	C3	C2	C1	0.6(4)

C14	C9	C8	C7	179.25(17)	C15	O3	C12	C11	-178.9(2)
C14	C9	C10	C11	1.6(3)	C15	O3	C12	C13	1.2(4)
C6	C3	C4	C5	-178.6(2)	C2	C3	C6	O1	6.9(3)
C6	C3	C2	C1	179.0(2)	C2	C3	C6	C7	-172.8(2)
C6	C7	C8	O2	-1.1(3)	C2	C3	C4	C5	-0.3(3)
C6	C7	C8	C9	177.80(18)	C1	N1	C5	C4	-0.5(4)

Table S25 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **PBDK3**.

Atom	***x***	***y***	***z***	**U(eq)**
H7	3936	10623	1644	62
H11	5233	14425	1554	73
H14	8778	12097	298	60
H10	4574	12464	1614	67
H13	9431	14058	235	64
H5	-816	8527	2812	79
H4	1294	9670	2210	71
H15A	7588	16021	199	125
H15B	11305	15860	409	125
H15C	9196	16975	531	125
H2A	3280	6817	1450	88
H1A	1033	5780	2080	104
H1	5700(200)	8980(50)	800(20)	129
H2	6400(300)	9550(30)	650(30)	129