SUPPORTING INFORMATION

<u>Manuscript title:</u> Pyrene-cored blue-light emitting [4]helicenes: synthesis, crystal structures and photophysical properties

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Figure S1¹H-NMR spectra of 6a



Figure S2¹H-NMR spectra of 6b



Figure S4 ¹³C-NMR spectra of 6a



Figure S5¹³C-NMR spectra of **6b**



Figure S6¹³C-NMR spectra of 6c





Figure S8¹H-NMR spectra of 7b



Figure S10 ¹H-NMR spectra of 7d



Figure S12 ¹³C-NMR spectra of 7b



Figure S14 ¹³C-NMR spectra of 7d



Figure S16¹H-NMR spectra of 9



Figure S18¹³C-NMR spectra of 9



Figure S19 TGA curves of 7a-c and 9 at the heating rate of 10 °C min⁻¹ under nitrogen atmosphere.



Figure S20 Packing diagrams for the [4]helicenes 7b, 7c and 9: (I) view parallel to b of 7b, 7c and 9, respectively; (II) view parallel to c of 7b, 7c and 9, respectively, showing the herringbone packing motif.



Figure S21 Normalised emission spectra of 7a-c and 9 recorded in thin neat films.







Figure S22 Cyclic voltammograms (CV) of 7a (a), 7b (b), 7c (c), and 9 (d) recorded from a CH_2Cl_2 solution on a platinum plate electrode at a scan rate of 50 mV s⁻¹.

Parameter	7b	7c	9
Empirical formula	$C_{42}H_{40}O_2$	C44H42	$C_{42}H_{38}O_2$
Formula weight [g mol ⁻¹]	576.78	570.78	574.72
Temperature [K]	123(1)	150(2)	150(2)
Wavelength [Å]	0.71073	0.7749	0.7749
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_{1}/c$	$P \overline{1}$	$P \overline{1}$
Crystal size [mm ³]	$0.30 imes 0.15 imes ext{ }0.15$	$0.09\times0.09~\times~0.02$	$0.25\times0.03~\times~0.01$
<i>a</i> [Å]	17.855(2)	11.3212(6)	10.1438(9)
<i>b</i> [Å]	6.2136(7)	11.3699(6)	20.8219(16)
<i>c</i> [Å]	27.618(3)	25.0897(4)	30.084(3)
α [°]		96.268(4)	72.507(5)
β [°]	104.3513(4)	96.618(4)	85.489(6)
γ [°]		90.287(4)	89879(6)
Volume [Å ³]	2968.5(6)	3188.4(3)	6040.0(9)
Z	4	4	8
Density, calcd [g m ⁻³]	1.290	1.189	1.264
Absorption coefficient [mm ⁻¹]	0.077	0.067	0.076
F(000)	1232	1224	2448
θ range for data collection [°]	0.993 to 27.52	2.25 to 30.00	2.20 to 26.42
Reflections collected	28767	38306	95933
Independent reflections	6774	14294	18813
Observed data $[F^2 > 2\sigma(F^2)]$	5762	10105	12842
R _{int}	0.075	0.0405	0.0809
Restraints/parameters	0398/ 6774	0/814	98/ 1643
Goodness-of-fit on F^2	1.231	1.030	1.061
$R1 [F^2 > 2\sigma(F^2)]$	0.1180	0.0609	0.0752
wR2 (all data)	0.2846	0.1721	0.2123

Table S1 Summary of crystal data of the [4]helicenes 7b, 7c and 9.