Electronic Supplementary Material (ESI) for RSC Advances.

Suplementary information

"*An FT-IR spectroscopic study of the role of hydrogen bonding in the formation of liquid crystallinity for mixtures containing bipyridines and 4-pentyloxybenzoic acid*."

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Contents

Table S1. Transition temperatures and associated enthalpy and entropy changes for *BiPy/5OBA*. Cr: crystal; N: nematic; SmA: smectic A; I: isotropic.

X_{5OBA}	T_{Cr-I}, , T_{Cr-SmA}‡, T_{Cr-N}† /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{SmA-N}, /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{SmA-I} ,T_{N-I} ¥ /℃	ΔH /kJ·mol^{-1}	ΔS/R
0	113	17.57	5.47						
0.1	102	5.03	1.61						
0.2	88	14.02	4.67						
0.3	88	12.98	4.32						
0.4	107	2.37	0.75				(100)	(0.22)	(0.07)
0.5	112‡	1.94	0.61				137	0.24	0.07
0.6	112‡	7.36	2.30				153	4.04	1.14
0.7	120‡	9.85	3.02	155	2.18	0.61	156¥	1.95	0.55
0.8	114†	8.81	2.74				155¥	2.11	0.59
0.9	119†	10.32	3.17				152¥	1.90	0.54
1	125†	21.37	6.46				151¥	1.92	0.54

Table S2. Transition temperatures and associated enthalpy and entropy changes for *EthylBiPy/5OBA*. Cr: crystal; N: nematic; SmA: smectic A; I: isotropic.

X_{5OBA}	T_{Cr-I}, , T_{Cr-SmA}‡, T_{Cr-N}† /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{SmA-N}, /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{N-I} /℃	ΔH /kJ·mol^{-1}	ΔS/R
0	153	23.46	6.62						
0.1	145	14.77	4.25						
0.2	136	6.39	1.88						
0.3	128	4.09	1.23						
0.4	115‡	17.27	5.35	161	1.01	0.28	163	1.01	0.28
0.5	115‡	16.79	5.20	167	1.61	0.44	169	1.61	0.44
0.6	125‡	12.63	3.82	171	1.60	0.43	172	1.60	0.43
0.7	128‡	5.25	1.58	172	2.00	0.54	174	2.13	0.57
0.8	128‡	5.12	1.53	173	1.98	0.53	175	2.41	0.65
0.9	115†	18.09	5.61				162	1.58	0.44
1	125†	21.37	6.46				151	1.92	0.54

Table S3. Transition temperatures and associated enthalpy and entropy changes for *EthaBiPy/5OBA*. Cr: crystal; N: nematic; SmA: smectic A; I: isotropic.

X_{5OBA}	T_{Cr-I}, , T_{Cr-SmA}‡, T_{Cr-N}† /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{SmA-I} ,T_{N-I}¥ /℃	ΔH /kJ·mol^{-1}	ΔS/R
0	112	24.72	7.72			
0.1	109	16.70	5.26			
0.2	105	14.43	4.59			
0.3	93	19.95	6.55			
0.4	92‡	13.61	4.48	106	0.34	0.11
0.5	128‡	4.10	1.23	139	0.15	0.04
0.6	128‡	6.31	1.89	143	2.32	0.67
0.7	129‡	6.64	1.99	151	5.69	1.61
0.8	112‡	13.75	4.29	150	4.11	1.17
0.9	118†	17.55	5.40	148¥	2.21	0.63
1	125†	21.37	6.46	151¥	1.92	0.54

Table S4. Transition temperatures and associated enthalpy and entropy changes for *PropBiPy/5OBA*. Cr: crystal; N: nematic; SmA: smectic A; I: isotropic.

X_{5OBA}	T_{Cr-I}, T_{Cr-N}‡ /°C	ΔH /kJ·mol^{-1}	ΔS/R	T_{N-I}, /°C	ΔH /kJ·mol^{-1}	ΔS/R
0	60	26.87	9.71			
0.1	57	17.53	6.39			
0.2	52	2.88	1.07			
0.3	41	22.61	8.66			
0.4	35	8.80	3.44			
0.5	54	4.28	1.57			
0.6	63	9.97	3.57			
0.7	95‡	3.54	1.16	(94†)		
0.8	112‡	9.68	3.02	(98†)		
0.9	122‡	15.69	4.78	136	1.08	0.32
1	125‡	21.37	6.46	151	1.92	0.54

†From polarised optical microscopy, POM. ( ) indicate monotropic phase.

Table S5. Transition temperatures and associated enthalpy and entropy changes for *ButBiPy/5OBA*. Cr: crystal; N: nematic; SmA: smectic A; I: isotropic.

X_{5OBA}	T_{Cr-I}, T_{Cr-N}‡, T_{Cr-SmA}† /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{SmA-N}, /℃	ΔH /kJ·mol^{-1}	ΔS/R	T_{N-I} /℃	ΔH /kJ·mol^{-1}	ΔS/R
0	116	33.22	10.27						
0.1	112	16.77	5.24						
0.2	106	25.74	8.17						
0.3	95	24.18	7.90						
0.4	106	14.75	4.68						
0.5	119	8.45	2.59				(108)	0.23	0.07
0.6	122‡	9.67	2.94				132	2.34	0.69
0.7	121†	4.88	1.49	130	1.83	0.55	139	1.83	0.54
0.8	107†	13.87	4.39	129			137	2.02	0.59
0.9	116‡	12.28	3.81				142	2.39	0.69
1	125‡	21.37	6.46				151	1.92	0.54

( ) indicate monotropic phases

Table S6. Clearing temperatures, $T_{LC-I}/^{\circ}C$ of the *XBiPy/5OBA* complexes, as a function of the 5OBA molar fraction, x_{5OBA}.

X_{5OBA}	5OBA	Bipy/5OBA	EthylBipy/5OBA	EthaBipy/5OBA	PropBipy/5OBA	ButBipy/5OBA
0						
0.1						
0.2						
0.3						
0.4		100	163	106		
0.5		137	169	139		108
0.6		153	172	143		132
0.7		156	174	151	94	139
0.8		155	175	150	98	137
0.9		152	162	148	136	142
1	151	151	151	151	151	151

Table S7. Relative concentration of supramolecular species estimated for the *1:2-BiPy/5OBA* mixture (in molar percentage, %)

Temperature /ºC	Monomers	Open dimers	Heterocomplex	Closed dimers	Catemer aggregates
180	0.32	22.36	44.83	10.83	21.66
175	5.79	34.64	43.28	16.28	-
170	5.21	19.85	57.59	17.35	-
165	11.06	7.74	52.86	28.34	-
160	11.99	3.41	53.30	31.30	-
155	9.09	9.98	52.98	27.95	-
150	11.28	32.53	32.36	23.83	-
145	6.10	35.40	36.88	21.62	-
140	5.96	27.88	39.90	26.25	-
135	5.21	25.50	47.28	22.01	-
130	3.81	19.84	13.62	32.90	29.83
125	7.16	28.29	5.93	29.99	28.63
120	7.28	25.72	6.94	22.96	37.09
115	3.83	34.25	4.88	20.16	36.87

Table S8. Relative concentration of supramolecular species estimated for the *1:2-EthylBiPy/5OBA* mixture (in molar percentage, %)

Temperature /ºC	Monomers	Open dimers	Heterocomplex	Closed dimers	Catemer aggregates
210	0.70	40.47	28.28	8.81	21.73
205	0.86	40.04	29.88	8.44	20.78
200	8.33	37.13	42.73	2.17	9.64
195	0.68	33.40	57.43	3.46	5.04
190	-	29.91	67.02	1.73	1.34
185	0.05	10.18	65.58	0.00	24.19
180	2.48	18.70	55.16	4.17	19.50
175	0.02	18.06	55.53	3.48	22.90
170	0.88	19.11	61.00	11.43	7.59
165	6.41	20.74	44.95	19.36	8.54
160	1.37	19.54	50.95	28.14	-
155	-	7.26	50.29	21.57	20.88
150	-	10.57	62.60	22.91	3.92
145	0.10	13.76	50.50	9.34	26.30
140	0.03	13.96	38.37	7.12	40.52
135	4.92	25.69	40.24	8.07	21.08

Table S9. Relative concentration of supramolecular species estimated for the 1:2-*EthaBiPy/5OBA* mixture (in molar percentage, %)

Temperature /ºC	Monomers	Open dimers	Heterocomplex	Closed dimers	Catemer aggregates
185	2.13	34.65	43.45	19.76	-
180	0.03	32.27	47.47	20.23	-
175	6.85	23.95	35.85	15.83	17.52
170	2.74	27.51	32.46	23.49	13.80
165	6.16	29.01	27.45	22.30	15.08
160	-	26.98	29.69	17.78	25.55
155	0.11	26.20	33.77	21.28	18.64
145	-	18.08	17.77	31.62	32.53
140	3.30	0.01	32.00	35.98	28.71
135	2.80	0.13	31.39	36.31	29.36
130	3.87	0.10	34.09	0.02	61.91
125	3.13	2.42	26.07	17.69	50.69
115	6.11	1.59	24.60	17.12	50.58

Table S10. Relative concentration of supramolecular species estimated for the 1:2-*PropBiPy/5OBA* mixture (in molar percentage, %)

Temperature /ºC	Monomers	Open dimers	Heterocomplex	Closed dimers	Catemer aggregates
130	0.10	11.09	64.66	15.69	8.47
125	0.22	12.68	62.86	16.80	7.44
120	0.04	9.31	63.23	16.85	10.56
115	-	9.91	63.63	16.73	9.73
110	-	10.85	66.95	17.65	4.56
105	-	-	64.44	21.92	13.64
100	2.69	-	59.22	29.97	8.13
95	0.01	-	42.19	31.91	25.89
90	10.41	0.03	47.97	26.74	14.85
85	4.88	-	49.12	28.09	17.91
80	5.09	0.04	44.51	33.17	17.19
75	-	0.44	60.38	33.38	5.81
70	-	-	88.44	-	11.56
65	5.69	4.89	76.07	-	13.34
60	18.63	6.61	58.81	-	15.95
55	23.36	8.34	53.34	-	14.95
50	27.11	13.49	44.35	-	15.05

Table S11. Relative concentration of supramolecular species estimated for the *1:2-ButBiPy/5OBA* mixture (in molar percentage, %)

Temperature /ºC	Monomers	Open dimers	Heterocomplex	Closed dimers	Catemer aggregates
170	4.03	20.12	52.96	22.90	-
165	8.97	13.54	57.20	15.93	4.36
160	3.45	16.15	60.44	13.68	6.27
155	0.05	17.83	61.44	13.29	7.40
150	0.00	7.70	75.90	9.07	7.34
145	0.76	0.20	68.14	23.91	7.00
140	1.07	0.14	65.86	13.72	19.20
135	-	0.31	55.82	33.94	9.93
130	7.70	0.79	56.13	20.04	15.33
125	4.13	2.46	54.77	18.68	19.96
120	9.47	2.18	60.82	23.74	3.79
115	3.76	-	20.76	36.48	39.00
110	4.13	0.04	22.64	40.62	32.57
105	0.60	-	21.03	46.14	32.23

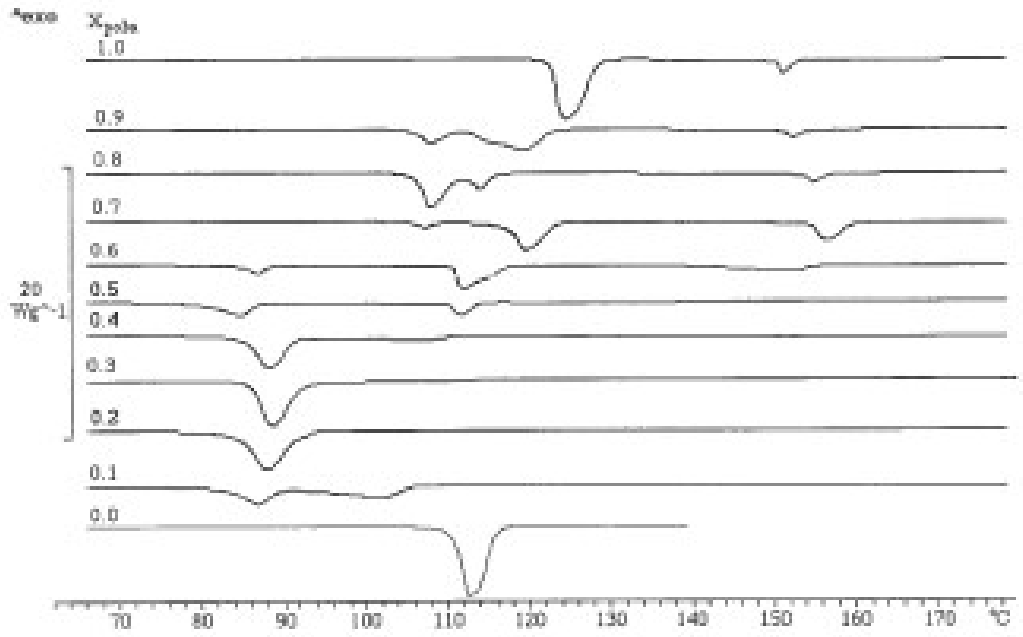

Figure S1. DSC reheating traces collected at 10 ˚C min^{-1} for the *BiPy/5OBA* mixtures.

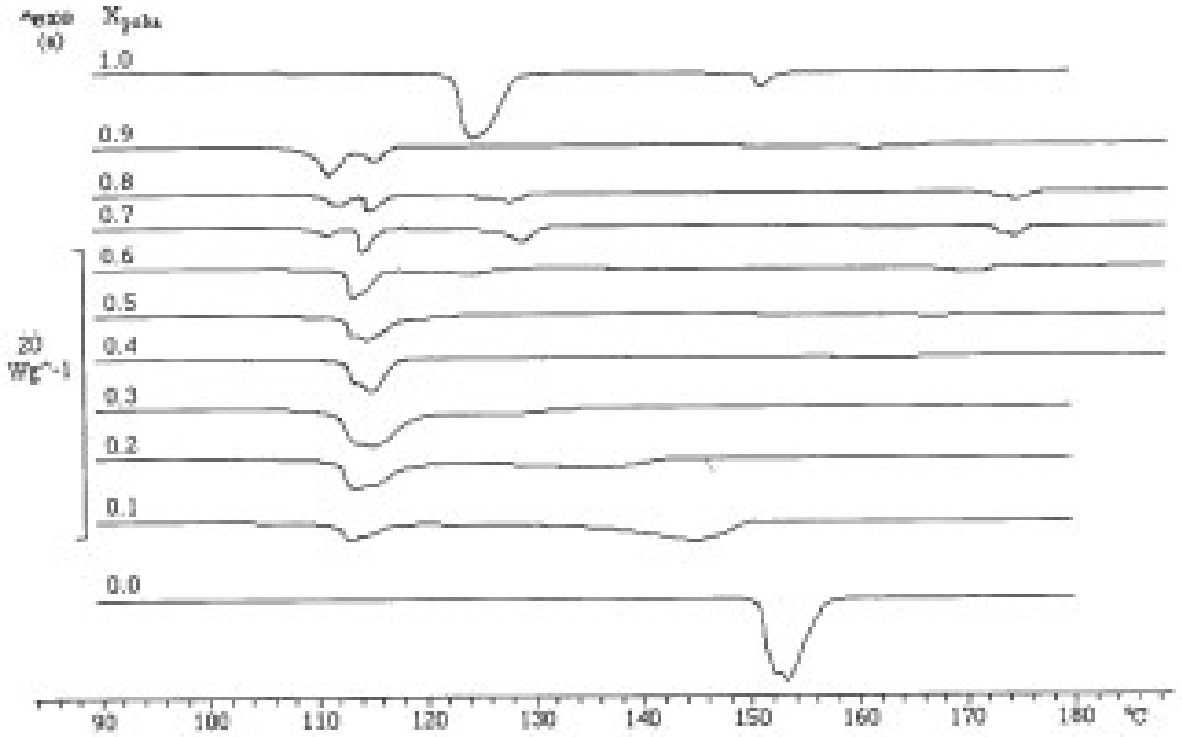

Figure S2. DSC reheating traces collected at 10 ˚C min^{-1} for the *EthylBiPy/5OBA* mixtures.

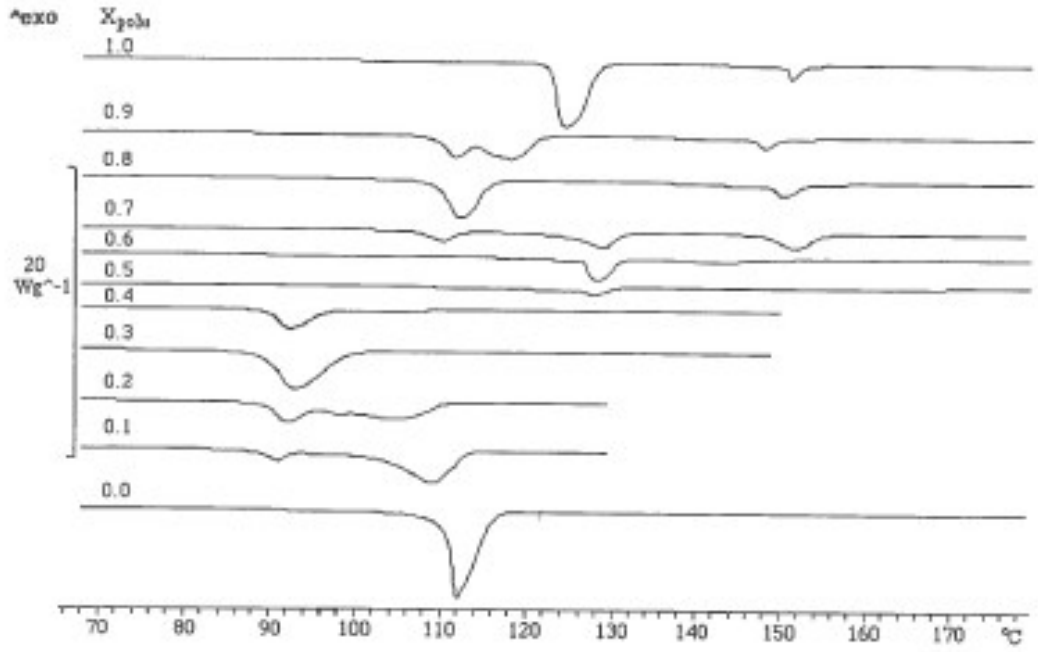

Figure S3. DSC reheating traces collected at 10 ˚C min^{-1} for the *EthaBiPy/5OBA* mixtures.

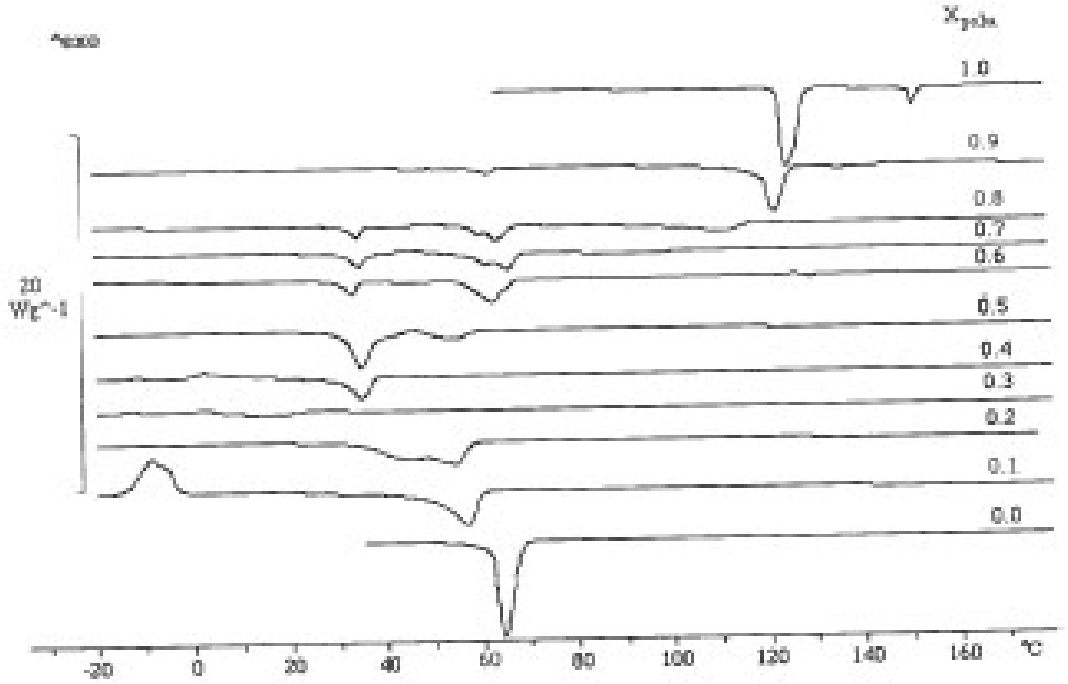

Figure S4. DSC reheating traces collected at 10 ˚C min^{-1} for the *PropBiPy/5OBA* mixtures.

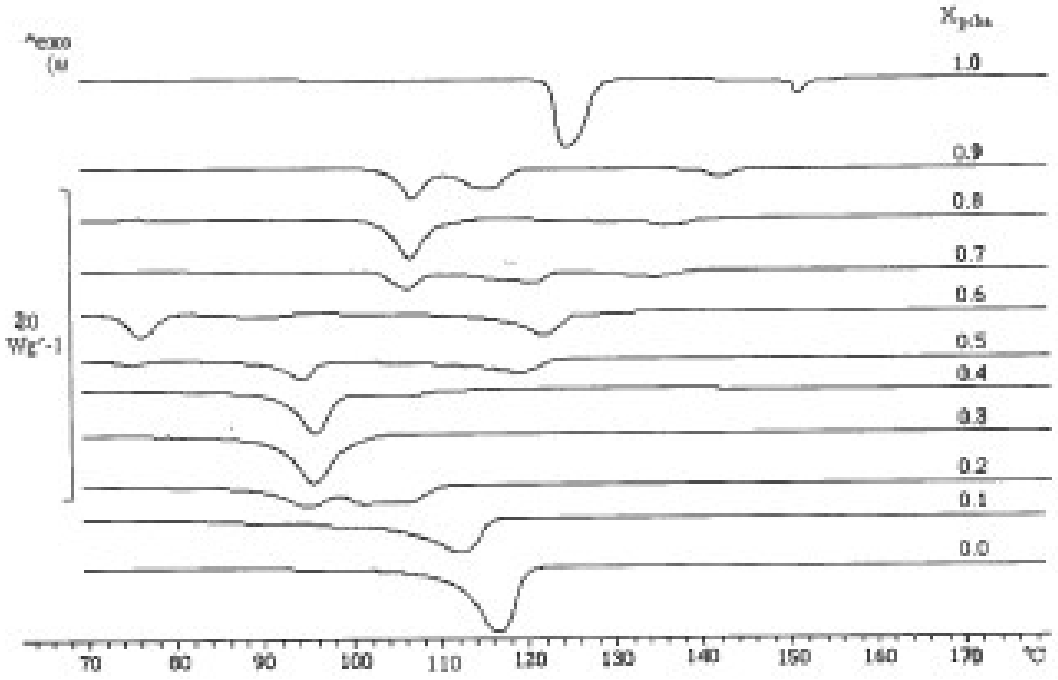

Figure S5. DSC reheating traces collected at 10 ˚C min^{-1} for the *ButBiPy/5OBA* mixtures.