Supplementary Material

1 Measurement results

Supplementary Table 1. Overview of measured and calculated values. Orange markings indicate that the values determined are too low, since for these samples, phosphorescence occurred already in air clearly distorting the outcome.

Host	Deposition	T [°C]	τ [ms]	PLQY raw [%]	PLQY corr. [%]	Abs. [%]	P2L	GPP	Film thickness [nm]
PMMA	sc	20	400	27.7	33.0	57.5	0.10	1.51	2525
PMMA	sc	40	420	25.4	30.8	54.7	0.09	1.57	2325
PMMA	sc	60	428	26.9	33.5	60.9	0.10	1.87	2705
PMMA	sc	80	427	25.1	32.3	56.8	0.09	1.67	2350
PMMA	sc	100	426	25.8	32.9	56.8	0.08	1.67	2320
PMMA	sc	120	429	25.9	32.0	56.8	0.9	1.69	2280
PMMA	dc	20	428	24.5	29.9	64.4	0.12	1.85	3355
PMMA	dc	40	418	23.6	28.2	60.3	0.12	1.65	2925
PMMA	dc	60	416	23.4	28.6	60.1	0.12	1.61	3025
PMMA	dc	80	436	23.6	27.7	65.1	0.12	1.84	3190
PMMA	dc	100	427	23.3	26.5	60.9	0.12	1.69	2820
PMMA	dc	120	428	23.0	26.5	56.4	0.08	1.32	2355
PMMA	bc	20	409	22.7	27.9	43.6	0.09	1.31	1800
PMMA	bc	40	426	23.3	26.4	41.3	0.12	1.66	1860
PMMA	bc	60	412	22.8	26.7	45.8	0.09	1.24	1685
PMMA	bc	80	417	23.9	28.6	50.3	0.11	1.56	2240
PMMA	bc	100	433	23.4	27.6	40.5	0.11	1.72	1240
PMMA	bc	120	433	24.1	28.0	50.4	0.12	1.79	1315
PS	sc	20	452	36.5	37.1	62.4	0.06	1.82	3960
PS	sc	40	474	34.2	35.0	62.4	0.06	2.04	3960
PS	sc	60	460	34.8	35.4	62.6	0.06	1.87	3970
PS	sc	80	484	34.5	39.3	61.1	0.06	2.34	3800
PS	sc	100	474	33.1	34.9	62.7	0.06	2.02	3990
PS	sc	120	445	26.3	27.9	60.0	0.07	1.57	3640
PS	dc	20	422	28.1	34.6	77.8	0.05	1.25	5595
PS	dc	40	428	28.6	33.3	77.6	0.05	1.30	5515
PS	dc	60	429	29.2	33.5	79.0	0.05	1.35	5820
PS	dc	80	433	28.5	32.7	77.9	0.05	1.35	5760
PS	dc	100	456	28.9	31.8	81.4	0.07	1.76	6630
PS	dc	120	427	25.2	28.3	75.8	0.08	1.38	5155
PS	bc	20	423	27.2	33.4	68.5	0.04	1.20	4350

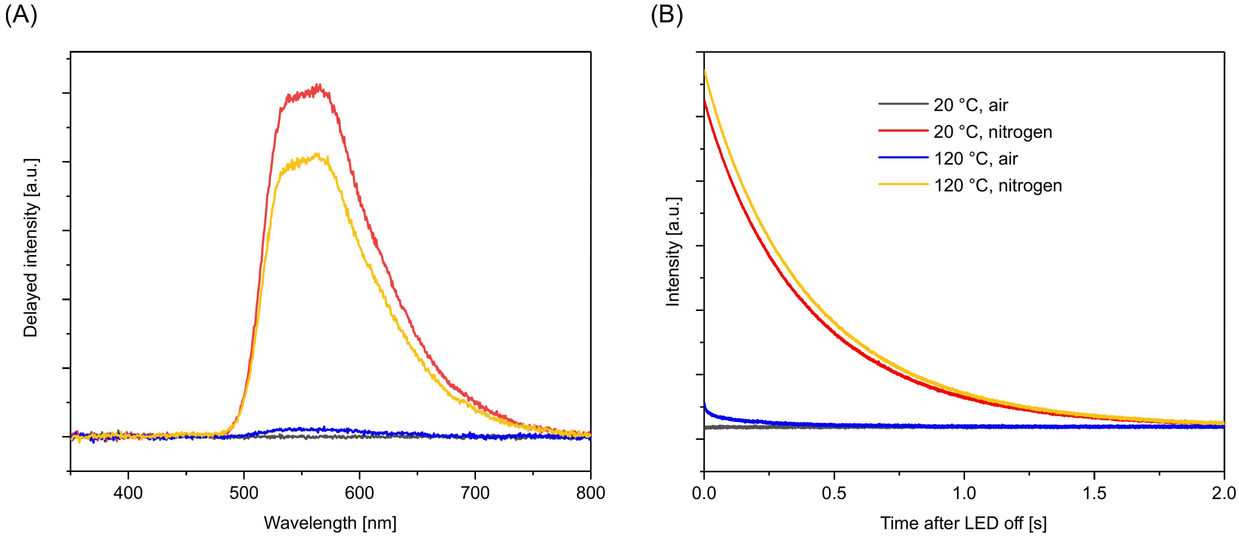
PS	bc	40	450	25.9	30.0	53.3	0.06	1.56	2400
PS	bc	60	463	26.4	30.4	65.2	0.06	1.71	4330
PS	bc	80	470	26.3	30.1	62.8	0.06	1.81	3820
PS	bc	100	446	26.1	28.1	59.9	0.07	1.56	3420
PS	bc	120	444	24.2	27.6	70.6	0.07	1.50	4700
PLA	sc	20	441	32.7	37.5	52.3	0.13	2.44	2305
PLA	sc	40	458	33.1	39.3	53.4	0.12	2.63	2375
PLA	sc	60	454	31.8	38.2	53.2	0.12	2.53	2300
PLA	sc	80	420	23.3	28.0	51.0	0.09	1.46	2225
PLA	sc	100	408	20.1	25.2	47.4	0.08	1.17	2030
PLA	sc	120	406	17.1	20.9	48.7	0.08	0.97	2145
PLA	dc	20	407	24.8	25.4	77.2	0.04	0.69	4155
PLA	dc	40	414	23.7	24.5	75.1	0.03	0.67	4170
PLA	dc	60	423	23.4	24.1	75.3	0.04	0.78	3845
PLA	dc	80	418	22.8	23.5	78.3	0.04	0.76	3945
PLA	dc	100	415	14.4	14.6	76.9	0.05	0.54	4120
PLA	dc	120	409	10.7	11.0	74.7	0.08	0.55	3925
PLA	bc	20	440	28.4	30.4	31.4	0.14	2.15	1275
PLA	bc	40	442	27.8	31.9	45.3	0.13	2.12	2050
PLA	bc	60	446	29.3	32.8	42.6	0.13	2.22	1725
PLA	bc	80	410	21.0	21.3	45.6	0.10	1.14	2035
PLA	bc	100	401	16.4	17.5	43.5	0.09	0.85	2230
PLA	bc	120	397	12.6	13.5	23.0	0.09	0.67	860
ABS	sc	20	426	33.2	39.2	62.8	0.09	1.91	3430
ABS	sc	40	447	31.6	37.5	61.6	0.09	2.08	3290
ABS	sc	60	461	31.6	37.1	61.8	0.09	2.25	3280
ABS	sc	80	450	29.5	35.6	61.0	0.08	2.04	3180
ABS	sc	100	460	32.4	38.5	67.7	0.09	2.30	3835
ABS	sc	120	452	26.7	31.6	61.3	0.08	1.90	3210
ABS	dc	20	433	30.3	36.0	74.4	0.10	1.88	4575
ABS	dc	40	444	29.7	34.4	72.2	0.08	1.81	4365
ABS	dc	60	444	29.0	34.0	69.4	0.06	1.65	3875
ABS	dc	80	450	28.7	33.1	67.4	0.09	1.97	3590
ABS	dc	100	456	28.7	33.1	72.8	0.10	2.05	4360
ABS	dc	120	451	26.2	30.7	74.4	0.09	1.84	4570
ABS	bc	20	436	29.2	34.3	41.3	0.09	1.79	1960
ABS	bc	40	426	27.9	31.3	50.1	0.09	1.58	2365
ABS	bc	60	460	28.7	32.9	71.4	0.10	2.13	4140
ABS	bc	80	441	28.6	31.7	58.3	0.06	1.52	2600
ABS	bc	100	435	27.5	31.1	48.7	0.09	1.66	1785
ABS	bc	120	427	25.9	29.3	55.5	0.08	1.49	1775

Supplementary Table 2. Overview of measured and calculated values for very thin spin-coated samples.

Host	Deposition	T [°C]	τ [ms]	PLQY raw [%]	PLQY corr. [%]	Abs. [%]	P2L	Film thickness [nm]
PMMA	sc	20	387	22.2	25.4	6.2	0.10	225
PMMA	sc	40	384	20.6	22.9	6.3	0.08	220
PMMA	sc	60	390	22.6	24.4	6.2	0.09	210
PMMA	sc	80	378	22.1	24.2	6.1	0.07	210
PMMA	sc	100	378	20.6	21.7	5.9	0.07	210
PMMA	sc	120	386	20.3	22.4	5.8	0.09	205
PS	sc	20	312	15.0	18.2	9.9	0.06	405
PS	sc	40	246	12.7	15.4	8.5	0.04	385
PS	sc	60	256	11.9	14.8	8.0	0.04	395
PS	sc	80	263	12.4	13.8	8.4	0.02	390
PS	sc	100	295	11.9	12.9	8.4	0.04	390
PS	sc	120	264	10.0	10.7	7.5	0.01	385
PLA	sc	20	360	15.6	18.5	11.5	0.12	190
PLA	sc	40	345	15.2	15.7	11.7	0.09	185
PLA	sc	60	334	14.6	15.4	11.0	0.08	180
PLA	sc	80	226	3.5	3.6	9.8	0.06	180
PLA	sc	100	161	2.8	2.9	9.8	0.05	185
PLA	sc	120	240	3.1	3.2	10.1	0.06	180
ABS	sc	20	379	25.8	28.7	10.2	0.08	375
ABS	sc	40	355	24.6	26.3	10.1	0.08	345
ABS	sc	60	364	25.7	26.4	10.2	0.08	340
ABS	sc	80	355	24.2	24.5	9.9	0.08	360
ABS	sc	100	324	21.7	22.4	9.6	0.06	340
ABS	sc	120	320	19.3	20.5	9.3	0.06	350

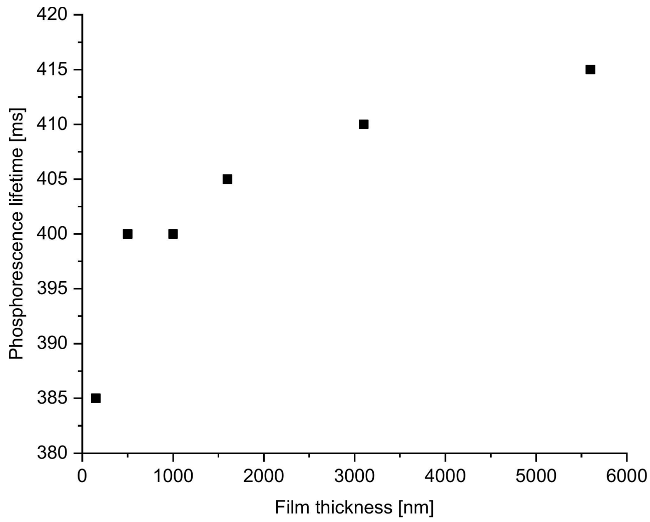
2 Photoluminescence in air and nitrogen

A few samples show phosphorescence already in air (marked in Supplementary Table 1). Usually, the phosphorescence is quenched in the presence of oxygen. This behavior is exemplarily shown in **Supplementary Figure 1**. The graphs show delayed spectra **(A)** as well as decay curves **(B)** of drop-cast PMMA:NPB samples with and without post-treatment. As can be seen, in case of the non-heated sample, there is neither a delayed spectral feature nor a transient visible in air. Only in nitrogen, the phosphorescence is visible. The heated sample shows a minimal intensity in the delayed spectrum and the transient. Using these curves for the determination of the P2L ratio will lead to a little underestimation. Since we compare these values only within the set of 72 samples, this can be neglected.



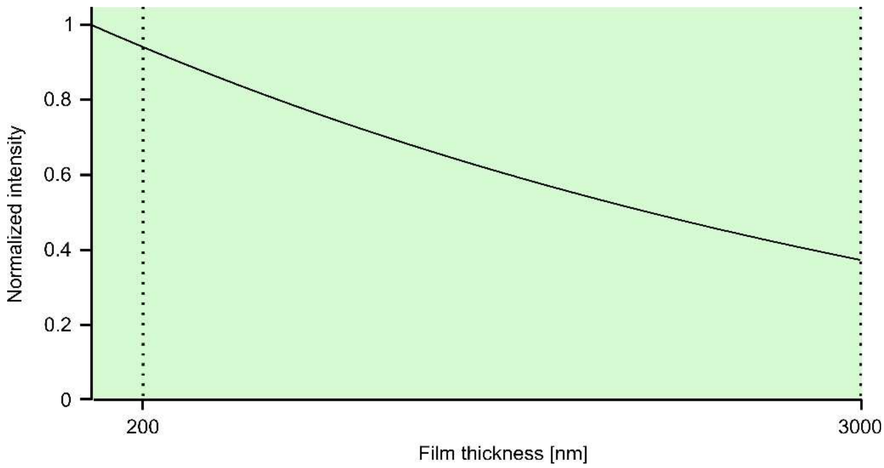
Supplementary Figure 1. (A) Delayed spectra of PMMA:NPB heated at 120 °C (blue and yellow) as well as untreated (grey and red) in ambient air (grey, blue) and nitrogen atmosphere (red, yellow). **(B)** Transient measurements for the same samples.

3 Correlation between film thickness and lifetime, exemplarily tested for PMMA as host material



Supplementary Figure 2. Correlation of film thickness and phosphorescence lifetime for spin-coated PMMA:NPB samples.

The reason behind the correlation between film thickness and phosphorescence lifetime displayed in Supplementary Figure 2 is not yet understood by the authors. We speculate that it could be caused by the profile of the excitation light intensity. Although we use the same excitation light setting for every measurement, huge deviations in film thickness cause the excitation intensity profile to vary significantly between the samples following Beer-Lambert's law. While spin-coated films absorb only about 5 % of the incident light intensity, an absorption of well above 50 % of the drop-cast layers leads to a lower average excitation intensity within these thick films (see **Supplementary Figure 3**). This leads to a significantly reduced exciton density in the far end of the film and, in turn, probably to a strongly reduced annihilation probability which may enhance the exciton lifetime. There are hints that also the solvent plays a role, especially in thin films. These investigations are the subject of currently running experiments and are beyond the scope of this work.



Supplementary Figure 3. Sketch of the excitation light intensity decay inside a sample (indicated by green background) in dependence of the film thickness.

4 PLQY Re-Evaluation

CW emission spectra are recorded in face emission, whereas PLQY is a mixture of face and edge emission. Therefore, the spectra do not look completely identical. The substrate modes suffer from self-absorption and the calculated values have to be corrected afterwards (Ahn TS *et al.* Self-absorption correction for solid-state photoluminescence quantum yields obtained from integrating sphere measurements. Rev Sci Inst (2007) 78:086105. doi: 10.1063/1.2768926):

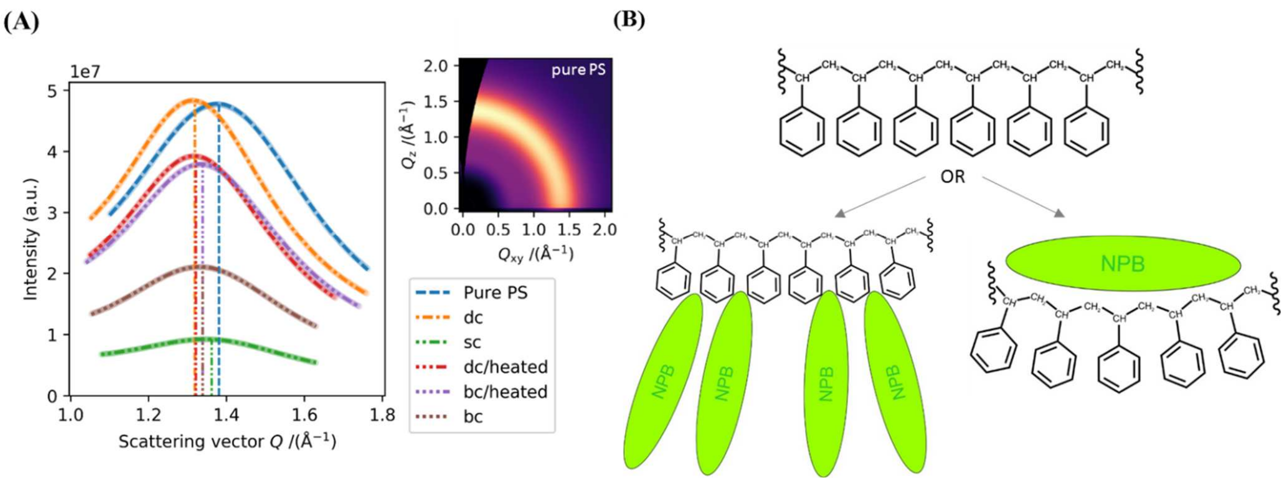
1. Plot PLQY and face-emission spectrum. Ideally, the face emission spectrum should be recorded in air, but since for thick films, sometimes phosphorescence is already visible in air, the spectra obtained in nitrogen atmosphere have been used here.
2. Interpolate both spectra to the same wavelength range. Use only the range of emission, not of the excitation.
3. Chose the right scaling area, where both spectra show signal and where the material will not absorb.
4. Scale the face emission spectrum to match with the PLQY spectrum in this area.
5. Calculate the correction factor:

$$\mathrm{a} = 1 - \frac{\int \text{complete PLQY spectrum}}{\int \text{complete scaled face emission spectrum}}$$

6. Calculate corrected PLQY:

$$\mathrm{PLQY_{corr}} = \frac{\mathrm{PLQY}}{1 - \mathrm{a} + \mathrm{aPLQY}}$$

5 GIWAXS measurements

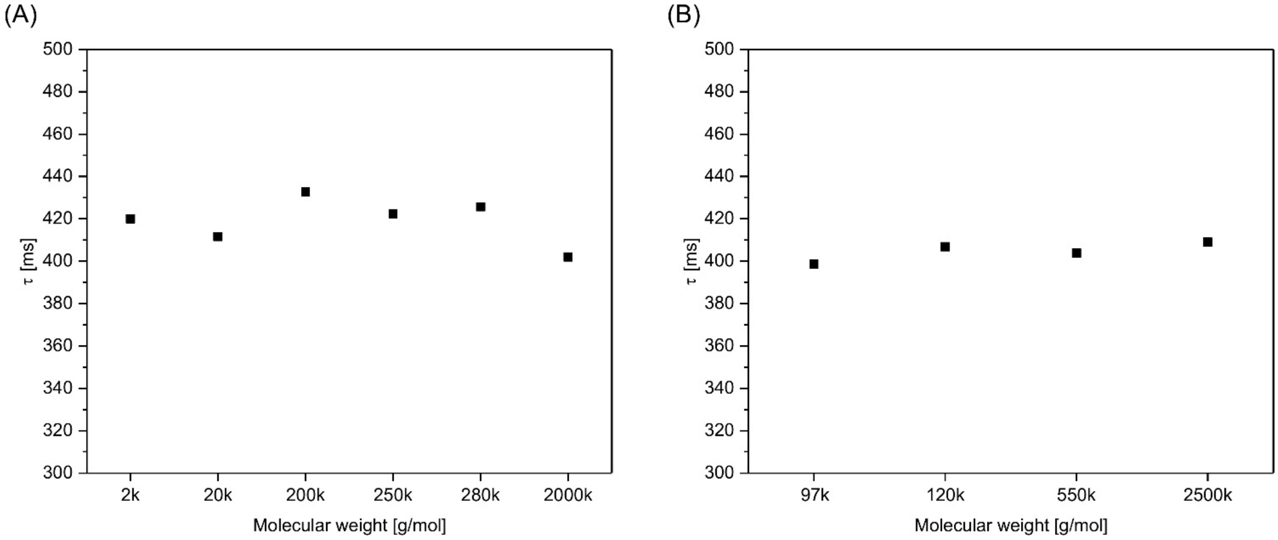


Supplementary Figure 4. Summary of GIWAXS measurements: **(A)** Example data (top right) showing the diffraction pattern of pure PS. The ring with maximum intensity at 1.38 $Å^{-1}$ (see pink graph in A) is also observed in all PS:NPB diffraction data, but with slightly shifted positions for different deposition techniques, including blade-coating (blue), spin-coating (red) and drop-casting (orange and green). For all blend films smaller q-values (blade-coated: 1.34 $Å^{-1}$, spin-coated: 1.36 $Å^{-1}$, drop-cast: 1.32 $Å^{-1}$) are observed. **(B)** sketch of possible interpretation.

Supplementary Table 3: Amplitude, peak width and position of the fitted Lorentzian curves drawn in Supplementary Figure 1.

Sample	A (a.u.)	w /($Å^{-1}$)	x_c /($Å^{-1}$)
pure PS	41034109	0.614	1.381
dc	29621451	0.491	1.319
sc	4943768	0.524	1.362
dc/heated	24563690	0.490	1.322
bc/heated	24479794	0.512	1.339
bc	14373435	0.549	1.339

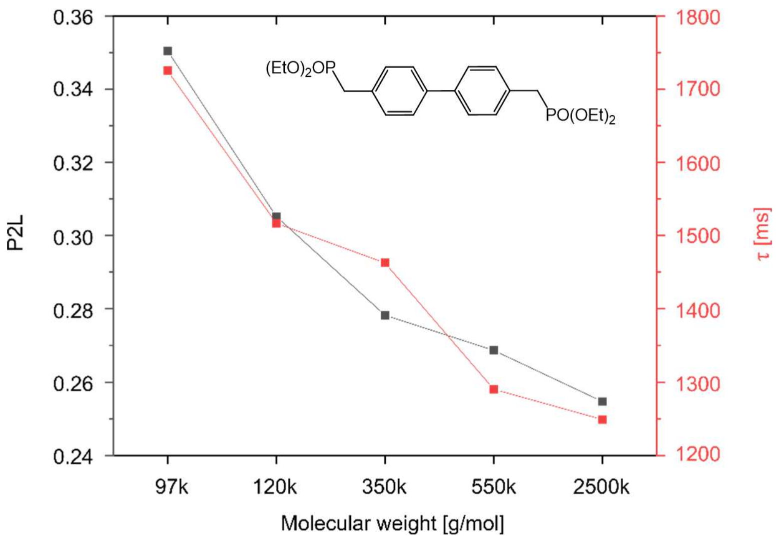
6 Phosphorescence lifetime τ for different PS and PMMA and chain lengths in spin-coated host:NPB samples



Supplementary Figure 5. Correlation of τ for different PS (A) as well as PMMA (B) chain lengths (in MW) in spin-coated host:NPB samples.

The polymers used in this experiment were purchased from Sigma Aldrich.

7 P2L vs. τ for different PMMA chain lengths in drop-cast PMMA:BDPB samples



Supplementary Figure 6. Correlation of P2L and τ for different PMMA chain lengths (in MW) in drop-cast PMMA:BDPB samples. Inset: Chemical structure of BDPB.

8 Surface roughness

Surface roughness was determined using a profilometer (Veeco Dektak 150).

Supplementary Table 4: Surface roughness of unheated and heated samples.

Sample	Deposition	Temperature [°C]	RMS [nm]	Sample	Deposition	Temperature [°C]	RMS [nm]
PMMA:NPB (thin)	sc	20	1.3	PLA:NPB (thin)	sc	20	0.6
		120	1.8			120	6.5
PMMA:NPB (thick)	sc	20	1.1	PLA:NPB (thick)	sc	20	46.3
		120	0.8			120	62.6
PMMA:NPB	dc	20	1.5	PLA:NPB	dc	20	449.5
		120	1.4			120	467.7
PMMA:NPB	bc	20	1.1	PLA:NPB	bc	20	4.4
		120	1.7			120	2.0
PS:NPB (thin)	sc	20	3.3	ABS:NPB (thin)	sc	20	44.8
		120	1.3			120	45.3
PS:NPB (thick)	sc	20	1.1	ABS:NPB (thick)	sc	20	9.4
		120	1.0			120	10.5
PS:NPB	dc	20	1.9	ABS:NPB	dc	20	13.3
		120	0.7			120	15.6
PS:NPB	bc	20	0.5	ABS:NPB	bc	20	10.4
		120	0.9			120	13.6