Journal Name

Electronic Supplementary Information (ESI): Understanding Spontaneous Dissolution of Crystalline Layered Carbon Nitride for Tuneable Photoluminescent Solutions and Glasses

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Figure S1. Thermograms of LiBr·PTI and H₂O·PTI (formed from IF-PTI exposed to atmospheric water¹) run under nitrogen flow gas.



Figure S2. Powder X-ray diffractograms of PTI materials (a) From bottom to top, LiBr·PTI, H₂O·PTI (from ambient absorption of atmospheric water), and IF-PTI. (b) Background removal process for Kapton-tape covered IF-PTI used to prevent atmospheric water uptake and intercalation during XRD measurement. XRD of the amorphous Kapton tape was taken and smoothed (Savitzky–Golay filter). The smoothed Kapton curve was multiplied by a manually fitted coefficient and subtracted from the raw IF-PTI diffractogram.



Figure S3. SEM micrographs of synthesised LiBr·PTI powder.



Figure S4. Structure of relaxed PTI trilayer [black/white] with lithium (purple) and bromine (brown) added in the same layers [LiBr(a)] and adjacent layers [LiBr(x)] along (left) PTI c-axis and PTI (right) a-axis.

Table S1. Relative energies calculated by DFT (see main text for methodology). All values given in eV. Stackingordering of intercalant given in Fig S2, stacking nomenclature of non-intercalated PTI taken from Suter et al.¹

Intercalating Salt	Stacking order	Energy change upon intercalation	Exfoliation energy	Adjacent-layer exfoliation energy	Exfoliation energy exposing cation/anion
None	AA'A	n/a	+0.22	n/a	n/a
	ABA	n/a	+0.19	n/a	n/a
LiBr	а	-0.56	+0.41	+0.23	n/a
	х	-0.42	n/a	n/a	+0.24 / +0.32
KBr	а	+0.84	+0.40	+0.26	n/a
	х	+1.00	n/a	n/a	+0.52 / +0.37
LiCl	а	-0.42	+0.17	+0.23	n/a
	х	-0.32	n/a	n/a	+0.19 / +0.38
КСІ	а	+0.78	+0.48	+0.30	n/a
	х	+1.04	n/a	n/a	+0.50 / +0.36



Figure S5. UV-vis spectra LiBr.PTI and IF-PTI in DMSO. (a) Full wavelength range showing changing optical absorbance behaviour, with decreasing intensity at ~300 nm peak with increasing PTI concentration, with concurrent increasing tail from scatter effects at higher wavelength. (b,c) Zoomed region with all samples of LiBr.PTI and IF-PTI respectively showing scatter tail region. (d) UV-vis absorbance at 350 nm for LiBr.PTI and IF-PTI in DMSO with 1 cm pathlength, corrected for 20× dilution and solvent/cuvette background, normalised for PTI content (i.e. 100% PTI in IF-PTI, 67.0% PTI in LiBr.PTI, Fig S1), in contrast to total loading weight in Main Text Figure 2.



Figure S6. ICP-MS intensity for ⁷Li (left) and ⁷⁹Br (right)

Table S2. Values from ICP-MS measurements. Yield values calculated assuming 33.0 wt% LiBr, from TGA (Fig S1)

LiBr.PTI Loading	[⁷ Li]	[⁷⁹ Br]	[⁶ Li]	[⁸¹ Br]	Li:Br Ratio	Yield
(mg/mL)	(µg/mL)		(µg/mL)		(⁷ Li/ ⁷⁹ Br)	(%)
4.65	2.45	31.89	2.41	29.38	0.877	2.99
10.25	5.64	80.69	5.56	75.97	0.799	3.41
19.75	10.02	133.95	9.95	126.35	0.855	2.95



Figure S7. Supplementary transient absorption spectra (a) TA spectra of 1 mg mL⁻¹ loading LiBr-PTI solution at 350 nm excitation and 1 μ J average pulse energy. (b) TA spectra of 0.5 mg mL⁻¹ loading IF-PTI solution at 400 nm excitation and 0.9 μ J average pulse energy. (c) Normalized probe kinetics of IF-PTI solution at 525 nm emission (400 nm excitation) at various pump powers showing power-independent kinetics. (d) Stretched exponential fit of 1.15 μ J pump power kinetics of IF-PTI solution. Note that fits incorporating 0.9 μ J average pulse power led to poorer fit, but behaviour can be seen to be consistent (c), thus the use just 1.15 μ J for fit in contrast to all pump powers for LiBr-PTI (Main text Fig. 3b).



Figure S8. (a) ⁷Li and (b) ⁷⁹Br NMR of DMSO-d6 solutions of lithium bromide salt (red, top) and LiBr·PTI (blue, bottom).



Figure S9. (a) ⁷Li and (b) ³⁵Cl NMR spectra of DMSO- d_6 solutions of lithium chloride salt (orange, top) and LiCl·PTI (green, bottom). The same parameters were used for the acquisition and processing of NMR data for both LiCl and LiCl·PTI solutions. Integrating the Li signal of LiCl as 1000, gives 5.03 for the Li signal for LiCl·PTI while integrating the Cl signal of LiCl as 1000 gives 7.00 for the Cl signal in LiCl·PTI. Therefore, an excess of Cl over Li in solution (Cl/Li = 1.39) can be deduced. LiCl·PTI was synthesised in the same manner as LiBr·PTI, but using an LiCl/KCl eutectic mixture, as used in Miller *et al.*²



Figure S10. Digital photograph of post-quenched 100:0 and 75:25 DMSO/H2O solutions in cuvettes with the former showing a reflective (poly)crystalline structure and the latter a translucent yellow glass. N.B. Frost from atmospheric water is seen on the exterior of both vials under ambient conditions.



Figure S11. Fluorescence spectra with 260, 310, 360, and 410 nm excitation, normalised to the elastic scatter peak. (Top) 100:0, (middle) 75:25, (bottom) 10:90 DMSO/H2O v/v PTI solutions. Samples measured at room temperature (solid) and immediately after liquid nitrogen quenching (dashed), and after 2 min ambient warming of the cooled glass for 75:25 DMSO/water (dotted).

References

- 1. T. M. Suter, T. S. Miller, J. K. Cockcroft, A. E. Aliev, M. C. Wilding, A. Sella, F. Corà, C. A. Howard and P. F. McMillan, *Chem. Sci.*, 2018, **10**, 2519-2528-2528.
- T. S. Miller, T. M. Suter, A. M. Telford, L. Picco, O. D. Payton, F. Russell-Pavier, P. L. Cullen, A. Sella, M. S. P. Shaffer, J. Nelson, V. Tileli, P. F. McMillan and C. A. Howard, *Nano Lett.*, 2017, **17**, 5891-5896.