

Supplementary Information

Intermolecular lithium bonding between different components upon mixing simultaneously enhances the thermal and electrical properties of an amorphous organic semiconductor material

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S1 Glass transition temperature measurement results

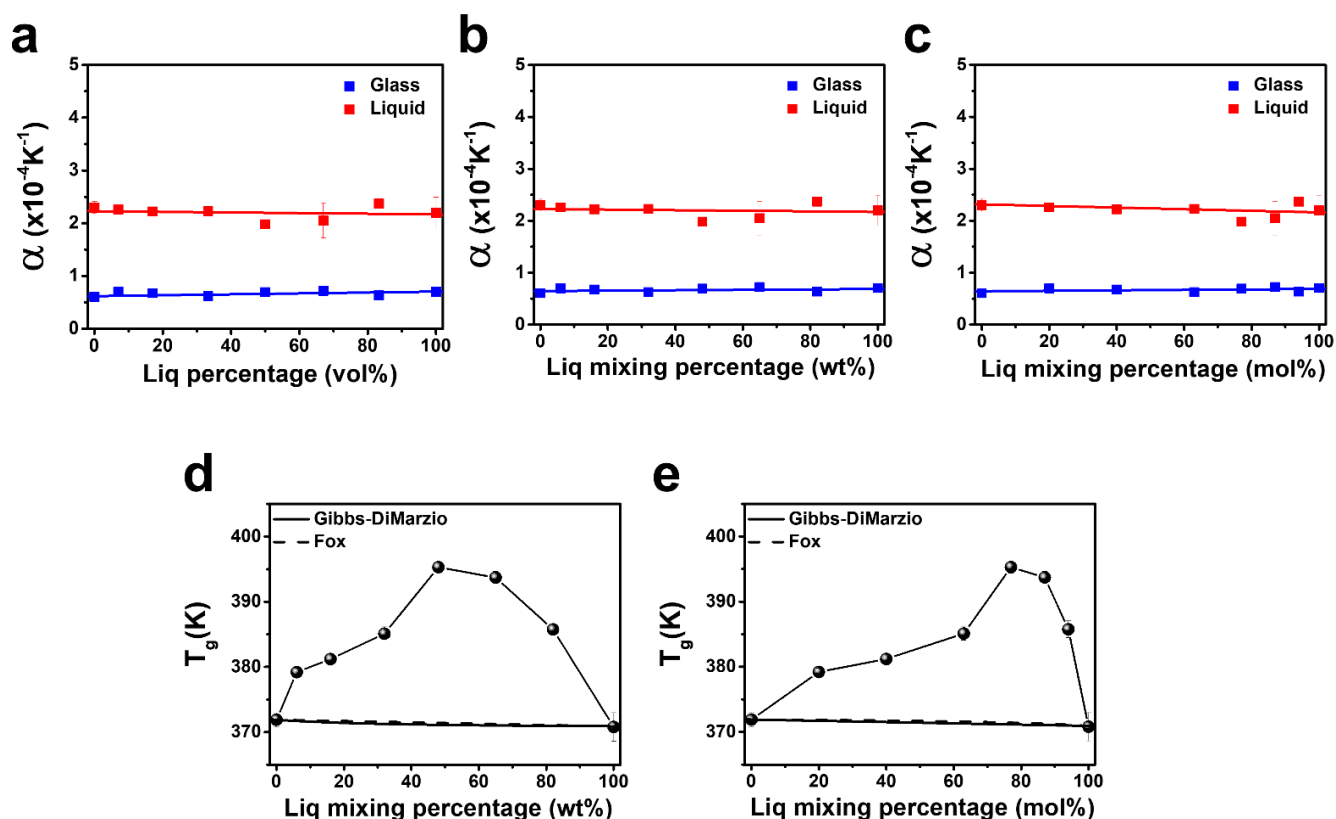


Figure S1. Thermal expansion coefficients of glass and supercooled liquid states of films with varying compositions for (a) volume percentage mixed film, (b) weight percentage mixed film, and (c) mole percentage mixed film. The temperature dependence of thickness is linearly fitted in the supercooled liquid and glass regions, and from the slopes of each lines, the thermal expansion coefficients are calculated using $\alpha = 1/h_{T_g}(dh/dT)$,^{1, 2} where h_{T_g} is the thickness at T_g . The lines represent linear fit to the data. The actual values are listed in Table S1. The glass transition temperature for (d) weight percentage mixed film and (e) mole percentage mixed film is consistent with the T_g for volume percentage mixed film with same component ratio in film.

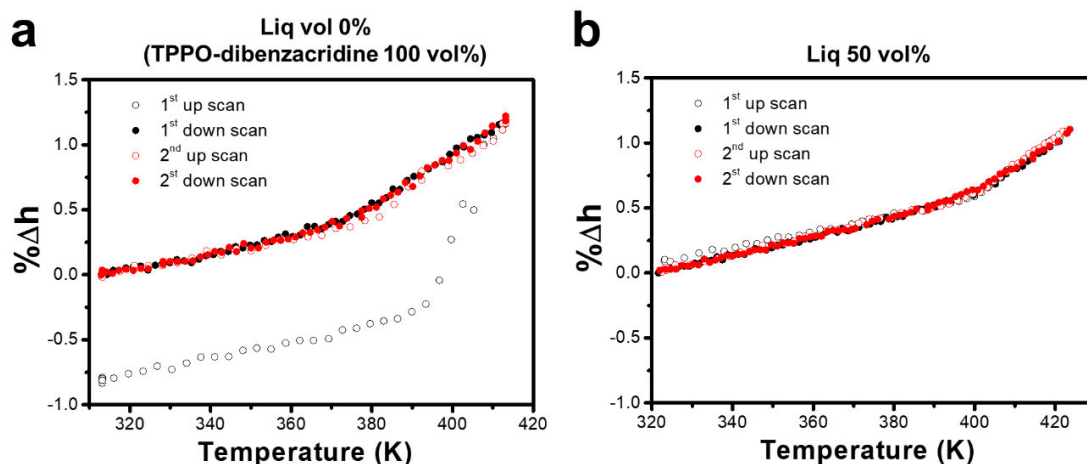


Figure S2. Temperature dependences of percentage thickness change ($\% \Delta h$) for (a) pristine TPPO-dibenzacridine film and (b) 50 vol% Liq mixed Liq: TPPO-dibenzacridine film. For demonstration purposes, only two cycles are shown each. The as-deposited pristine TPPO-dibenzacridine film (1st up scan in **Figure S2a**) shows ultrastable glass behavior of high density whereas 1st up scan of 50 vol% Liq mixed Liq: TPPO-dibenzacridine film tracks consecutive down and up scans which is a typical case for ordinary vapor deposited glasses.^{3,4}

Table S1. Liq mixed TPPO-dibenzacridine T_g and thermal expansion coefficient (α) values.

Liq percentage (vol%)	T_g (K)	Thermal expansion coefficient (α)	
		Liquid ($\times 10^{-4}$) K^{-1}	Glass ($\times 10^{-5}$) K^{-1}
0	371.9 ± 1.1	2.30 ± 0.12	6.06 ± 0.49
7	379.2 ± 0.6	2.26 ± 0.06	7.00 ± 0.47
17	381.2 ± 0.8	2.22 ± 0.02	6.76 ± 0.14
33	385.1 ± 1.0	2.23 ± 0.06	6.24 ± 0.33
50	396.2 ± 1.0	1.98 ± 0.04	6.91 ± 0.21
67	393.7 ± 0.9	2.05 ± 0.33	7.21 ± 0.37
83	385.8 ± 1.3	2.37 ± 0.08	6.33 ± 0.12
100	370.8 ± 2.2	2.20 ± 0.29	7.03 ± 0.56

S2 Density determination and calculation

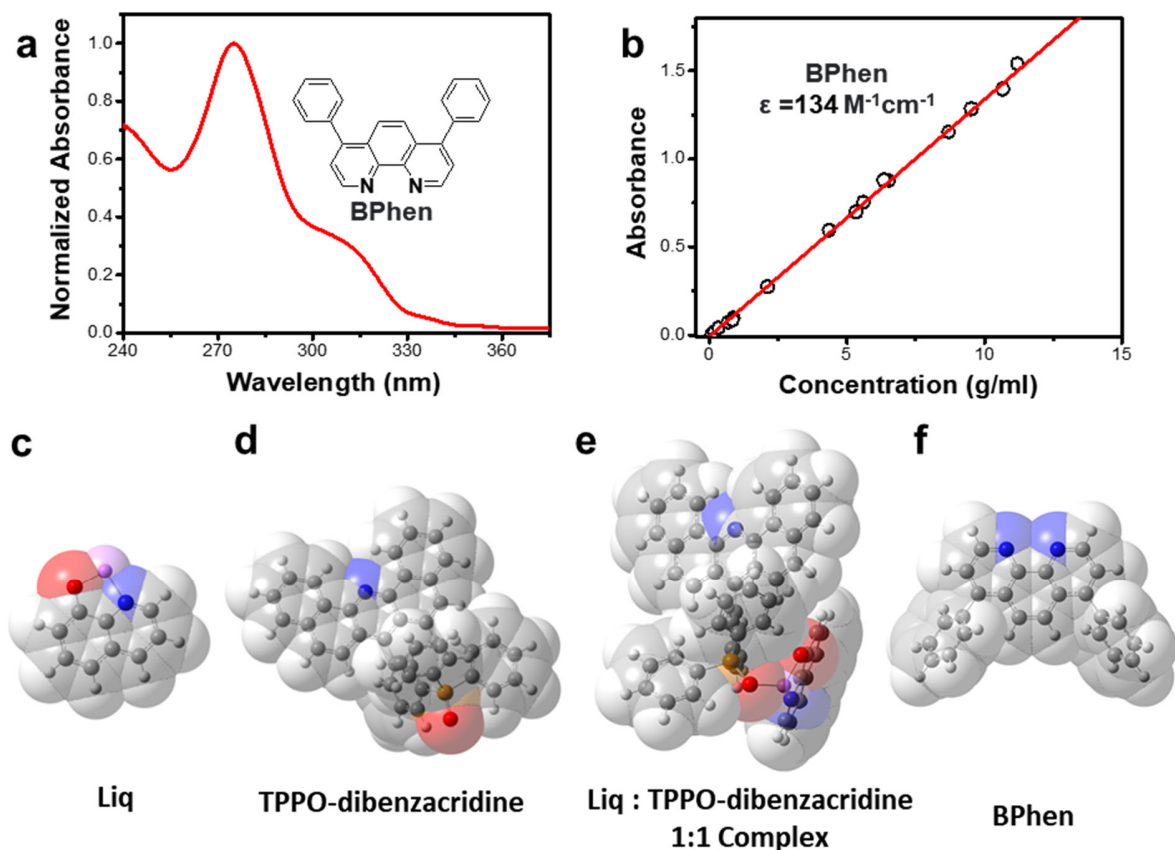


Figure S3. (a) Normalized UV-Vis absorption spectrum of BPhen in chloroform and corresponding (b) concentration dependence of the absorbances. The chemical structure is shown at the inset of (a). (c-f) the solvent-optimized 3D structure of Liq, TPPO-dibenzacridine, Liq:TPPO-dibenzacridine 1:1 complex, and BPhen.

Figure S3 a and b shows the normalized UV-Vis absorption spectra and the corresponding concentration dependence of the absorbances of 4,7-Diphenyl-1,10-Phenanthroline (BPhen) in chloroform. The density of BPhen is estimated to verify the method because the density of BPhen has been reported in the literatures (1.24 g/cm^3). The absorbance is taken at the λ_{max} (247.9 nm), and from the concentration dependence of the absorbance, the extinction coefficients are determined by linearly fitting the data according to the Beer-Lambert law. The thicknesses and area of the physical vapor deposited film of BPhen were determined prior to dissolution in a known amount of chloroform solvent, and the UV-Vis

spectra were recorded. The thickness of the film is measured after annealing the as-deposited film above T_g+20 K for 10 min. From the absorbance measured at λ_{max} , the amount of material in the solution is estimated using each extinction coefficient. By dividing the amount with the original film volume, the density of the deposited film is determined as 1.24 g/cm^3 .

Figure S3 c-f shows the solvent-optimized structure of Liq, TPPO-dibenzacridine, Liq:TPPO-dibenzacridine 1:1 complex, and BPhen for molecular volume calculations. The molecular volume calculation was conducted by the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM), water as a solvent, and the Gepol algorithm. The dielectric constant (ϵ) was 4.7113, which corresponds with the experiment using chloroform. The obtained volumes were divided by the molecular mass for the density estimation and the results are listed in Table S2.

Table S2

		Liq	TPPO-dibenzacridine	Liq: TPPO-dibenzacridine 1:1 Complex	BPhen
Calculated	Molecular Mass (amu)	151.1	555.2	706.2	332.1
	Volume (cm^3/mol)	84.7	447.6	517.6	257.9
	Density(g/cm^3)	1.78	1.24	1.36	1.29
Measured	Volume (cm^3/mol)	92.7	437.2	-	267.8
	Density(g/cm^3)	1.63	1.27	-	1.24

S3 Quantum chemistry calculation results

Table S2. TD-DFT calculation results of Liq with large oscillator strength.

Molecule	Excited state	Oscillator strength	Transition	Percentage (%)	Energy (eV)	Wavelength (nm)
Liq	1	0.027	HOMO → LUMO	98	2.67	464.9
	3	0.046	HOMO-2 → LUMO	15	3.83	323.6
			HOMO → LUMO+2	83		
	8	0.430	HOMO → LUMO+2	14	4.88	254.2
			HOMO-2 → LUMO	76		

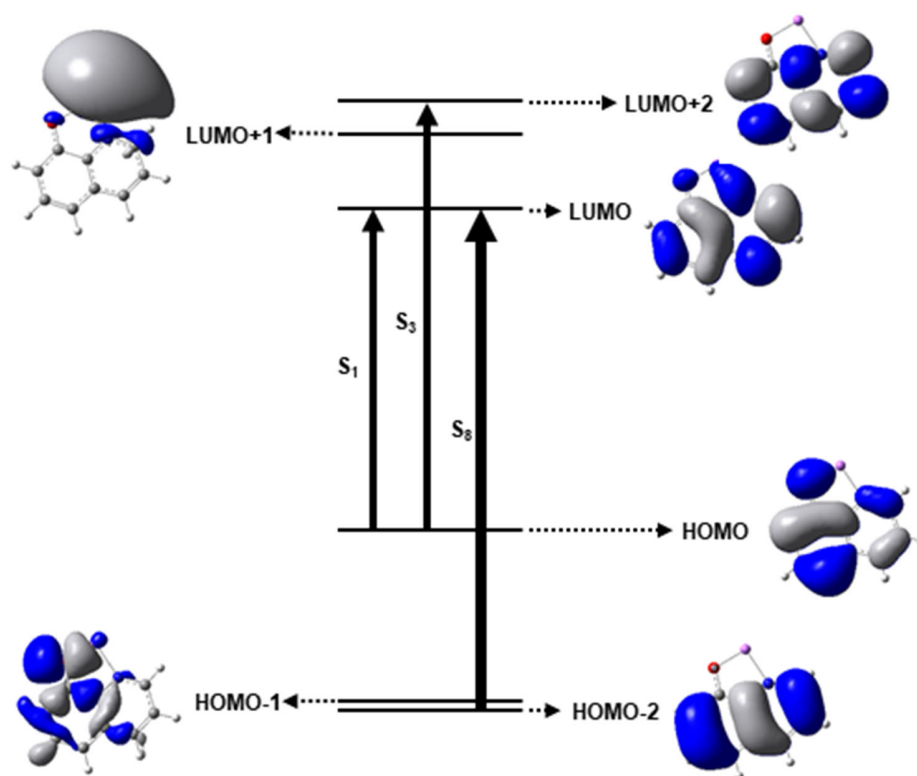


Figure S4. Molecular orbitals and the major excited states of Liq.

Table S3. TD-DFT calculation results of TPPO-dibenzacridine with large oscillator strength.

Molecule	Excited state	Oscillator strength	Transition	Percentage (%)	Energy (eV)	Wavelength (nm)
TPPO-dibenzacridine	3	0.353	HOMO → LUMO+1	53	3.94	314.7
			HOMO-1 → LUMO	12		
			HOMO-2 → LUMO	15		
			HOMO-5 → LUMO	11		
	8	0.416	HOMO → LUMO+2	19	4.27	290.5
			HOMO-2 → LUMO	55		
	35	0.171	HOMO-2 → LUMO+2	23	5.10	243.1
			HOMO-9 → LUMO+1	14		
	57	0.226	HOMO-1 → LUMO+8	11	5.42	228.8
			HOMO-3 → LUMO+4	29		
		HOMO-3 → LUMO+3	23			
61	0.164	HOMO-3 → LUMO+3	66	5.50	225.7	
216	0.300	HOMO-12 → LUMO+8	10	6.85	180.9	

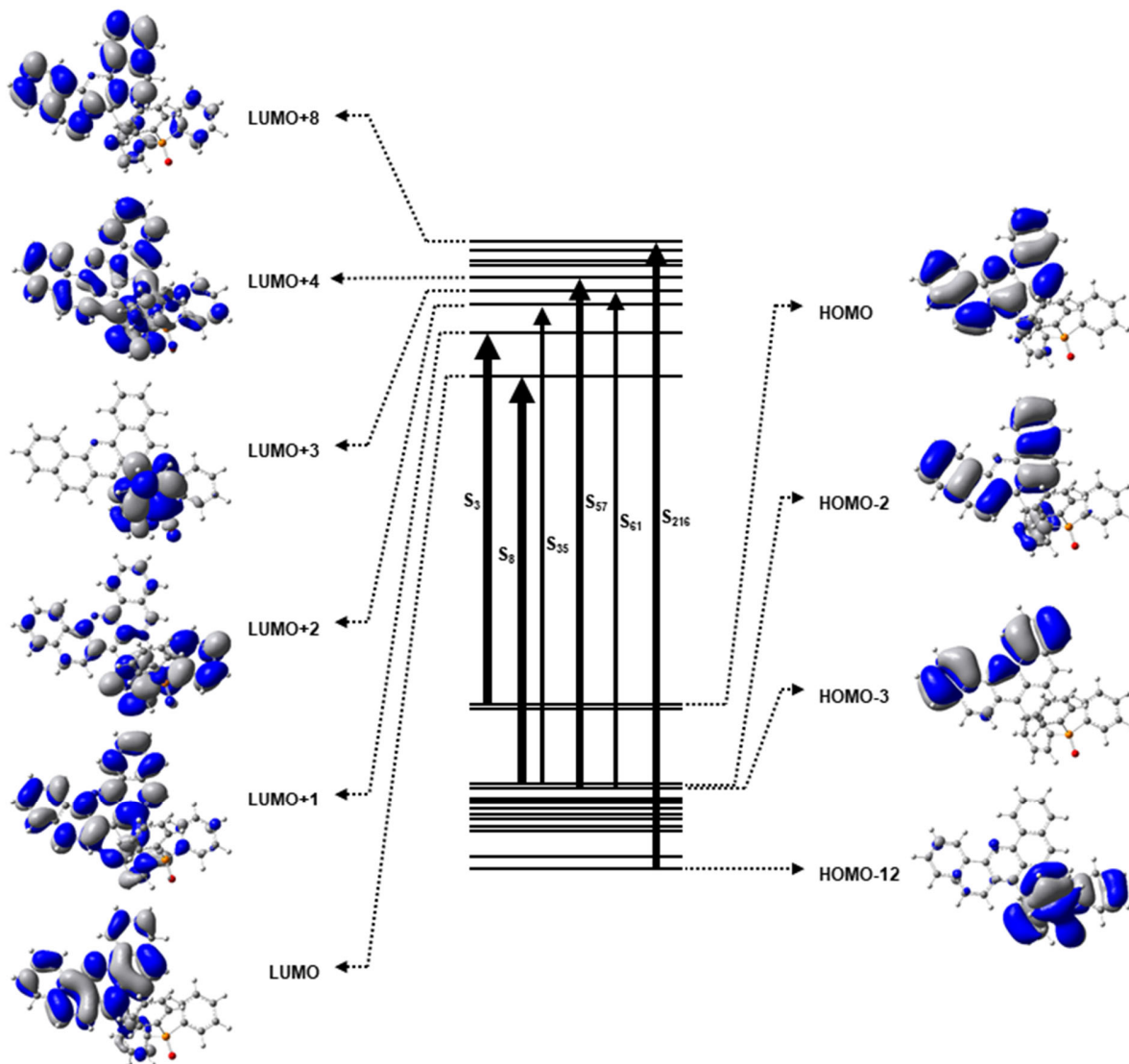


Figure S5. Molecular orbitals and the major excited states of TPPO-dibenzacridine.

Table S4. UV-Vis spectroscopy peak values for the I (243 – 268 nm).

Liq percentage (vol%)	Wavelength (nm)
17	260
23	260
33	259
50	258
67	257
83	257
100	257

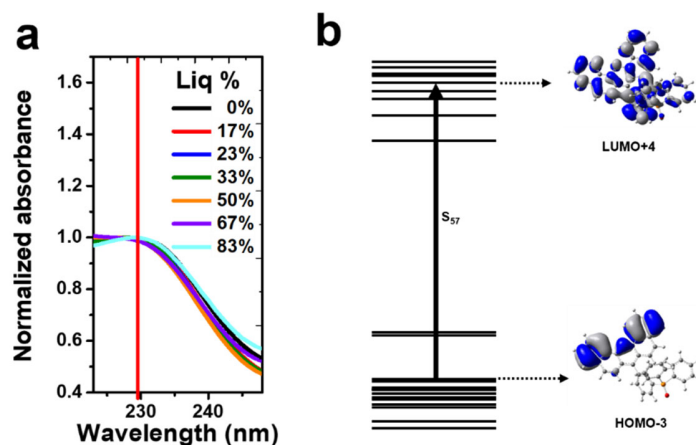


Figure S6. (a) Normalized vol% reconstructed UV-Vis spectra in the 223 – 248 nm range for pristine TPPO-dibenzacridine and Liq mixed films, normalized at 229 nm. (b) The electronic transition of S₅₇ and associated molecular orbitals of TPPO-dibenzacridine. The molecular orbitals associated with the S₅₇ transition are located along the dibenzacridine moiety, where the nitrogen atom supporting the lithium atom of Liq did not interact with the nitrogen of TPPO-dibenzacridine.

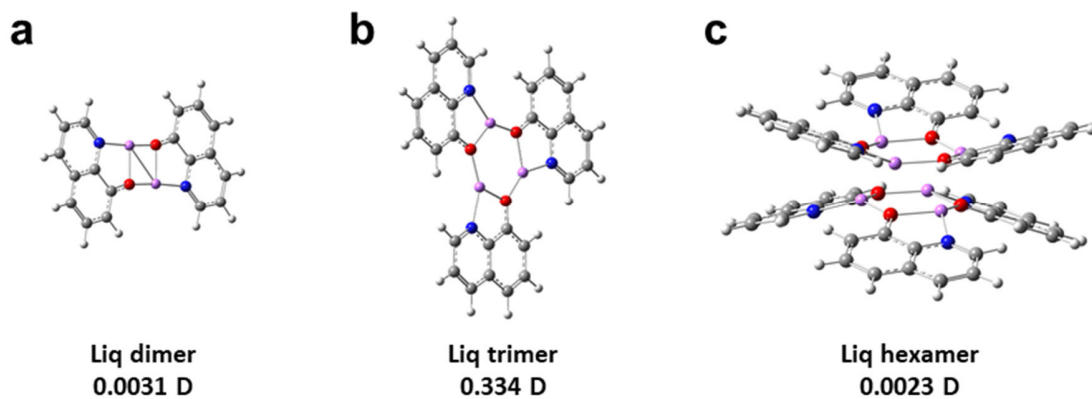


Figure S7. Liq clusters show smaller dipole moments than the Liq monomer (4.73 D).

S4 Estimation of lithium bonded complex in the mixed films

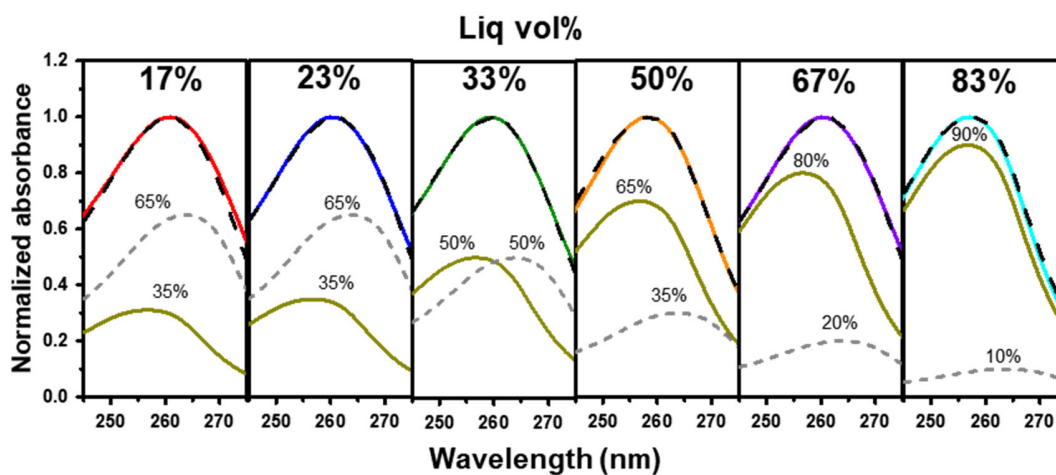


Figure S8 Reconstruction of mixed film peak I (black dash) with complexed Liq peak I (gray dash) and 100% Liq peak I (yellow solid). Red, blue, green, orange, purple, and cyan solid curves are measured peak I of mixed films (Fig 3b).

S5. Validation of mixing ratio

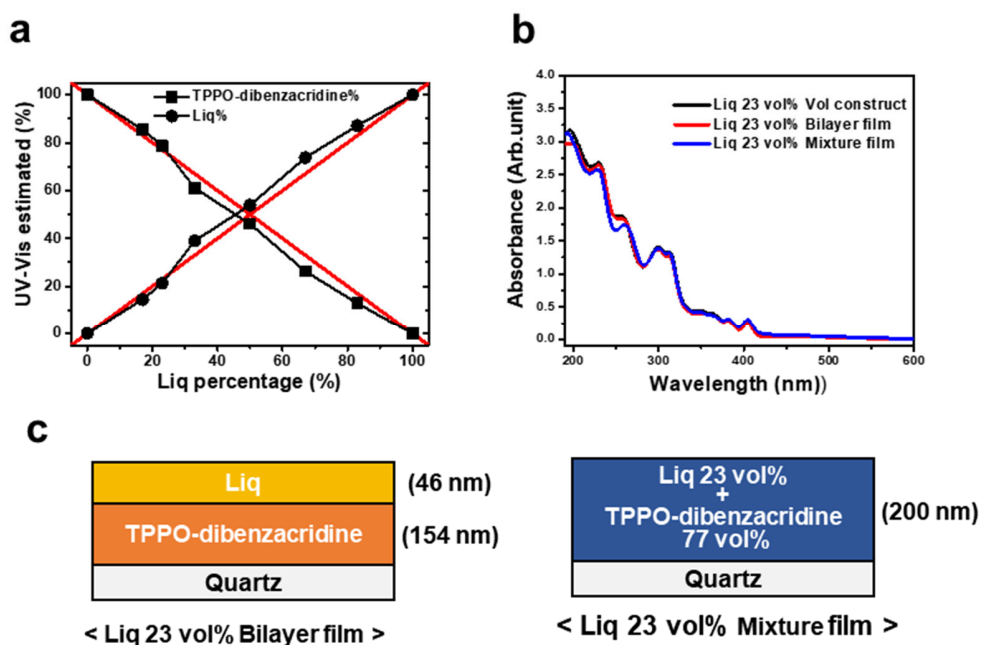


Figure S9. (a) Estimated vol% of Liq (circle) and TPPO-dibenzacridine (square) from measured UV-Vis spectra of mixed films (Figure 3a). (b) The UV-Vis spectra comparison for Liq 23 vol% was constructed from pristine spectra (black), Liq 23 vol% bilayer film (red), and Liq 23 vol% mixture film (blue). (c) The deposition diagram for Liq 23 vol% bilayer film (left) and mixed film (right).

Figure S9a shows the relative amount of each species in the mixed films estimated from the measured UV-vis spectra of mixed films shown in Figure 3a. The relative amounts of Liq (circle) and TPPO-dibenzacridine (square) in films were independently estimated from peak I and peak II, respectively. The red linear lines have either a slope of 1 or -1, and the deviation of the plots from these lines represents the uncertainty in the mixing percentage of the films. The volume constructed spectrum of 23 vol% Liq film shown in Figure S9b is obtained by multiplying the UV-Vis absorbance of pristine Liq and TPPO-dibenzacridine by the ratio of 5:17, respectively which matches with those of measured 23 vol% bilayer and 23 vol% mixed films. The slight mismatch observed in the 243-268 nm range of the mixed film from constructed data and bilayer film can be attributed to the interaction (lithium bonding) between Liq and

TPPO-dibenzacridine. Figure S9 clearly demonstrates the accuracy of the volume ratio control by quartz crystal microbalances upon co-deposition.

Reference

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