Supplementary Information (SI) for ChemComm.

Supporting Information

Tunable thermochromism in N-annulated perylene diimide thin films

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1. Materials and Methods

Materials: All reactants, reagents, solvents, and substrates were purchased from Sigma-Aldrich, Fisher Scientific, Tokyo Chemical Industry (TCI), or Grainger and were used without further purification unless otherwise indicated. Specifically, the polycarbonate substrate (thickness 0.005 in, item # WWG2NJH5) was purchased from Grainger. The N-annulated perylene diimide (PDIN-H) was synthesized in house using previously reported methods,[1] made using reagents and solvents from Sigma Aldrich, TCI, and Fisher Scientific. The inks were made using solvents from Sigma Aldrich, with the branched polyethyleneimine (PEI) also sourced from Sigma Aldrich (product number 408727).

UV-Visible Spectroscopy: All absorption measurements were recorded using an Agilent Technologies Cary 60 optical spectrometer. All solution UV-Visible spectra were measured with 1 cm quartz cuvettes using either tetrahydrofuran (THF), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the solvent. All concentrations are specified within the legends/captions for each spectra. The temperature dependent UV-visible solution spectra were obtained using an external Peltier accessory to heat the solutions.

Digital Photography: All digital images were taken on an iPhone 14 Pro (model number MQ0Q3VC/A; main camera 24 mm, *f*/1.78, 12 MP) using a third party camera application: ProCamera.

Optical & Polarized Optical Microscopy: Images were taken in with and without cross-polarization (90° angle) through an Olympus Optical Microscope (BX53) at 50x magnification with relative digital camera set-up.

Chromaticity Diagrams: All film RGB values were obtained using the Trigit web application,[2] and Origin (equipped with the Chromaticity application) was used to generate all relevant data (XYZ, xyY values) and diagrams.

Ink formulations: PEI was first dispersed in a 1:1 (v/v) solvent blend of ethyl lactate (EL) and 2-methyl tetrahydrofuran (2-MeTHF) to give a stock solution of 200 mg/mL (e.g., 4.0 g PEI diluted to a total volume of 20 mL). Owing to the viscosity of PEI, vigorous shaking with light sonication (10 × 15 s immersions in a sonication bath, with shaking between cycles). was required to achieve a uniform dispersion. Aliquots of this PEI stock were then added to vials containing pre-weighed PDIN-H to obtain the desired PDIN-H loading (e.g., 3.0 mL of the 200 mg/mL PEI stock added to 15 mg PDIN-H to afford 5 mg/mL PDIN-H & 200 mg/mL PEI). The PEI stock solution (not shelf stable) was combined with PDIN-H without delay. Finally PDIN-H/PEI inks were dispersed by shaking or brief sonication (10 × 15 s immersions in a sonication bath, with shaking between cycles). The inks were processed immediately after preparation, as they are not shelf-stable (i.e., will phase separate, one layer being gelatinous and the other liquid). Please refer to the ink engineering sections below for elucidation.

Slot-Die Coating: Slot-die coated films were processed using an Infinity PV TR2RC - Industrial Coater. Parameters: bed speed of 0.4 m/min, a bed temperature of 40 °C, a pump rate of 180 μL/min, and a gap height of 0.2 mm.

2. Solution UV-Visible Spectroscopy

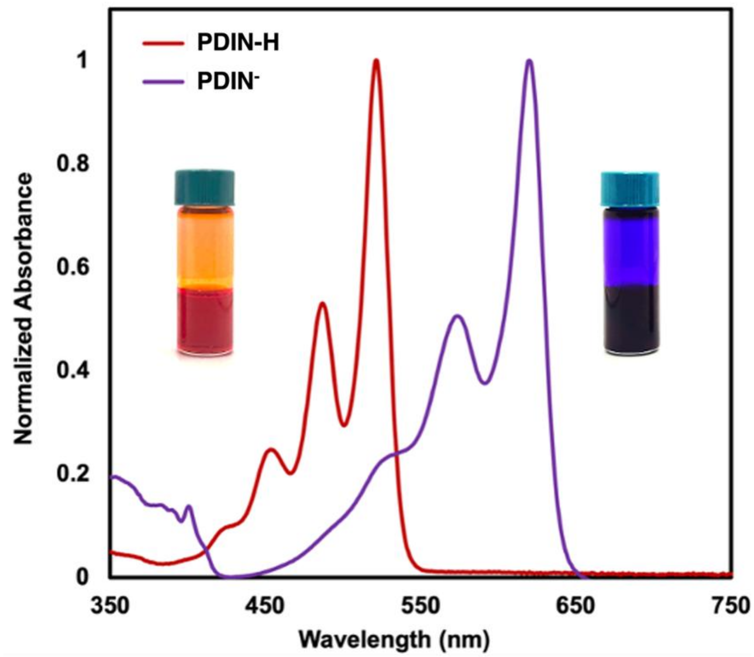

Figure S1. Normalized solution UV-visible spectra of PDIN-H (red trace) in THF and $PDIN^-$ (purple trace) in DBU.

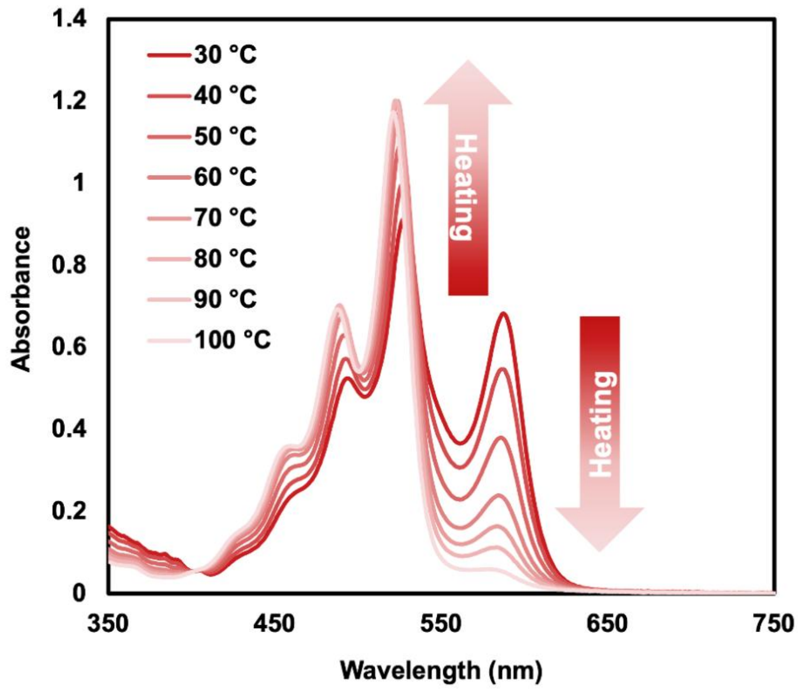

Figure S2. PDIN-H in neat butylamine at 1.8 x 10^{-5} M, heated to 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90 °C, and 100 °C. Each spectrum was recorded immediately upon reaching temperature.

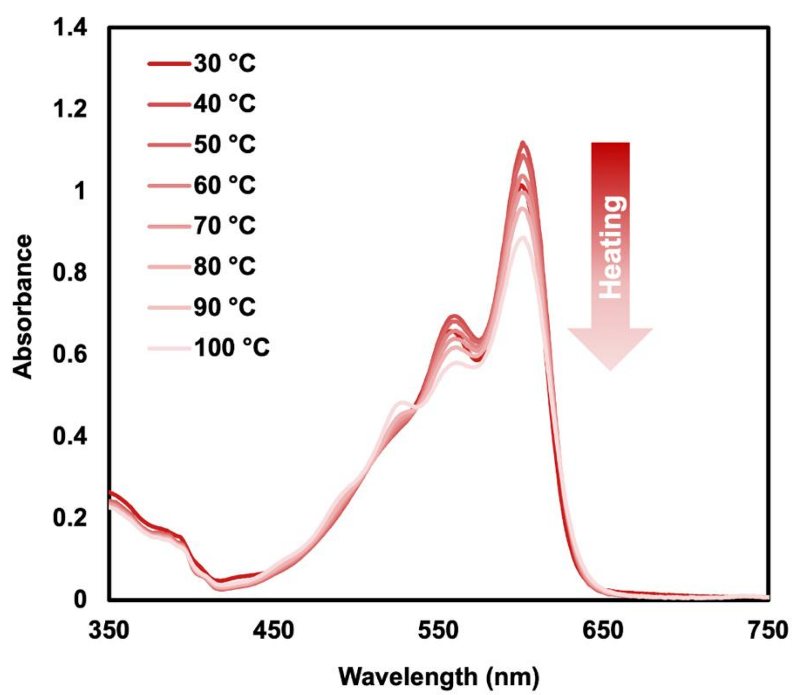

Figure S3. PDIN-H in butylamine and water (1:1) at 1.8 x 10^{-5} M, heated to 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90 °C, and 100 °C. Each spectrum was recorded immediately upon reaching temperature.

3. <u>Processes and Properties of Inks and Films for TTI-5S</u>

Engineering Ink Formulations for Slot-Die Coating of Thin Films

We previously developed and reported a green-solvent blend that provides excellent substrate wetting (for polycarbonate & polyethylene terephthalate) and drying dynamics.[3] The solvent base is composed of a 1:1 mixture of EL and 2-MeTHF. Here, EL provides excellent wetting of our target substrate, polycarbonate, and 2-MeTHF enhances miscibility of PDIN-H and is more volatile than EL. The volatility of the solvent blend is a critical consideration, as EL has a high boiling point of 154°C which can lead to slow drying, resulting pooling of inks post-costing and sub-optimal film uniformity. Therefore, blending with 2-MeTHF (boiling point 78°C) provides a higher volatility base and leads to faster drying times and highly uniform thin-film formation. When necessary, organic-based liquids that harbour amine functional groups are incorporated to the solvent base, which serve to solubilize highly planar π-conjugated organic molecules, such as our N-annulated perylene diimides. In this case, the ratio of the solvents now becomes 1:1:1 using EL, 2-MeTHF, and the organic amine liquid of choice. Previously, green-solvent ink formulations of concentrated PDIN-H in butylamine and water were demonstrated, thus, we opt to use butylamine as the organic amine component where necessary. In terms of film formation technique, we target slot-die coating due to compatibility with roll-to-roll manufacturing systems and scalability (i.e., can fabricate large-area films), which provides proof-of-concept facile fabrication techniques.

Below, neat PDIN-H, neat PEI, and PDIN-H/PEI composite films with the corresponding ink formulations are highlighted to showcase that 1) butylamine was needed to solubilize PDIN-H at 10 mg/mL and thus a 1:1:1 mixture of EL to 2-MeTHF to butylamine was used to make the ink that afforded neat PDIN-H films, 2) PEI exhibits high solubility in the 1:1 mixture of EL & 2-MeTHF and affords transparent and uniform thin films upon coating, and 3) PDIN-H (5 mg/mL) in the presence of PEI (200 mg/mL) can be fully solubilized without needing a third organic amine solvent, as PEI increases miscibility. Additionally, the neat PDIN-H films dry red indicating butylamine leaves the film upon drying, whereas PEI is not volatile and thus remains as a film hence the purple/indigo colour of the PDIN-H/PEI film composite resulting from the presence of deprotonated PDIN-H in the film.

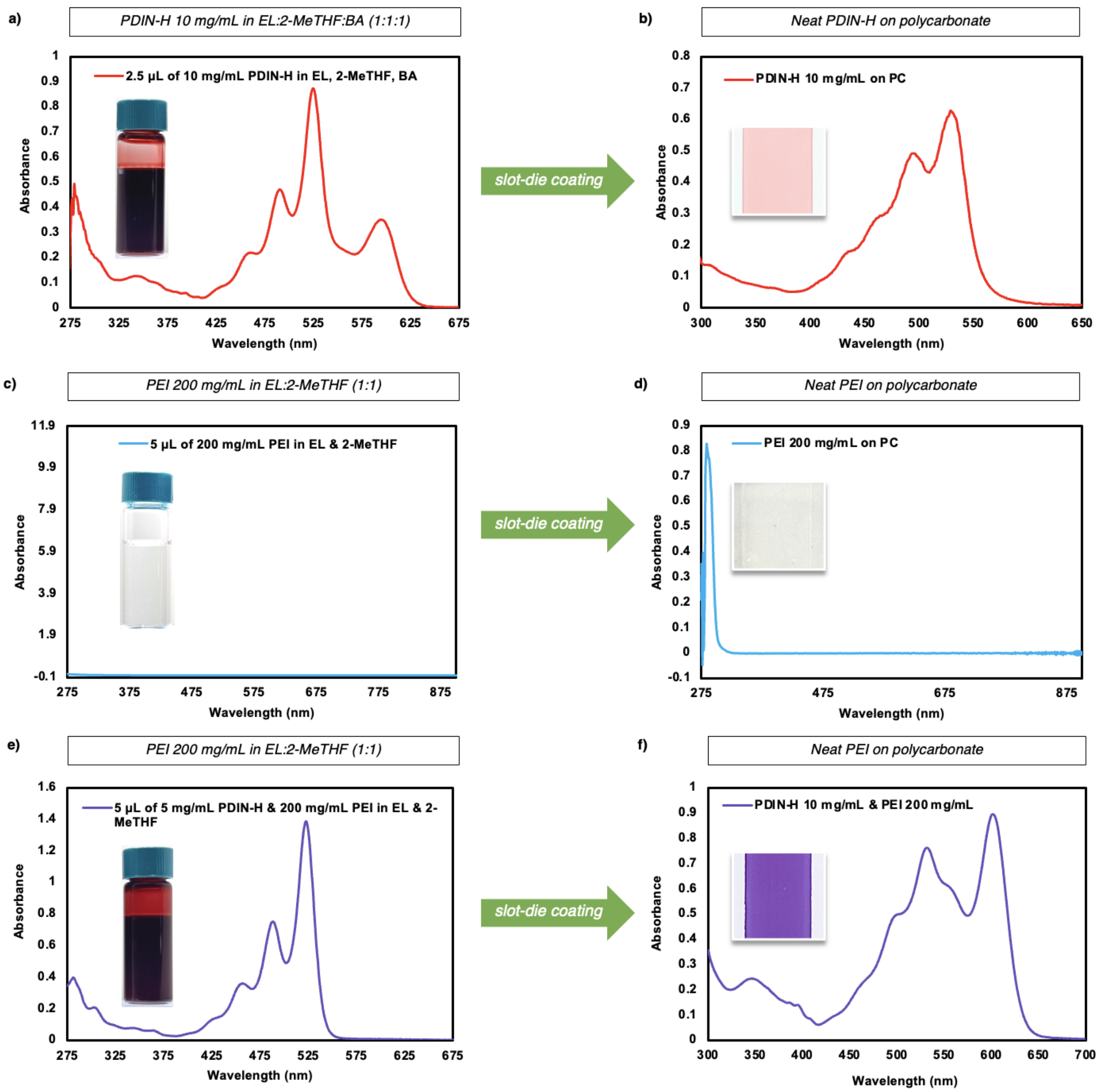

Figure S4. UV-Visible solution spectra with inset digital images of inks: a) PDIN-H in EL, 2-MeTHF, and BA (1:1:1) at 10 mg/mL, b) PEI in EL and 2-MeTHF (1:1) at 200 mg/mL, c) PDIN-H and PEI at 10 mg/mL and 200 mg/mL, respectively, in EL and 2-MeTHF (1:1). UV-visible film spectra with inset digital images of films: d) coated using PDIN-H in EL, 2-MeTHF, and BA (1:1:1) at 10 mg/mL, e) coated using PEI in EL and 2-MeTHF (1:1) at 200 mg/mL, and f) coated using PDIN-H and PEI at 10 mg/mL and 200 mg/mL, respectively, in EL and 2-MeTHF (1:1).

Optical and Polarized Optical Microscopy of Neat PDIN-H & Neat PEI films

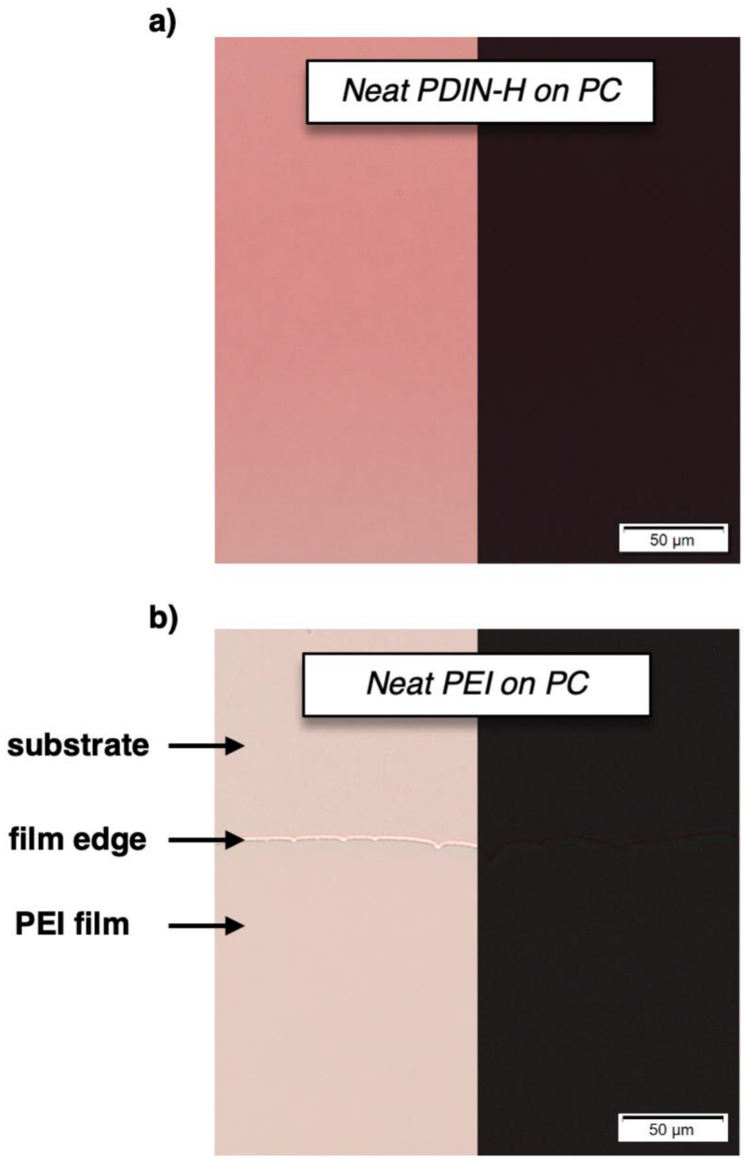

Figure S5. Optical (left) and polarized optical (right) microscopy images of a) neat PDIN-H film coated on polycarbonate using an ink with PDIN-H (10 mg/mL) in EL, 2-MeTHF, and BA (1:1:1), and b) neat PEI film coated on polycarbonate using an ink with PEI (200 mg/mL) in EL & 2-MeTHF (1:1); here, the edge of the PEI film is seen where uncoated polycarbonate is seen at the top of the images and coated PEI on polycarbonate is seen on the bottom section of the images.

Engineering Ink Formulations for Slot-Die Coating of TTI-5S

Engineering ink formulations is critical for resulting film properties. Here, the use of branched PEI (MW = 25,000), being a viscous liquid, requires extensive mixing with the EL & 2-MeTHF solvent blend to become fully dispersed. However, branched PEI is known to undergo air-oxidation which transforms the primary, secondary, and tertiary amine groups to amides and imines, leading to yellow-brown discoloration under heat or UV exposure.[4,5] It was observed that when making inks of PEI in various solvents by aid of sonication, the formulations would sometimes yellow. Knowing that sonication can lead to acoustic cavitation (i.e., the formation of bubbles that grow and collapse) resulting in highly localized areas of extreme temperatures,[6] it is hypothesized that PEI was oxidizing upon extensive sonication. Therefore, the films shown in Figure S5 (**TTI-5S**) were made using inks composed of PDIN-H 5 mg/mL and PEI 200 mg/mL in a 1:1 blend of EL and 2-MeTHF, and used gentle sonication (~15 seconds in sonicator bath, repeated 5-10 times with shaking in between) to fully disperse the components. Additionally, PEI was first solubilized at 200 mg/mL in the 1:1 EL to 2-MeTHF solvent blend by shaking, and the appropriate amount of PDIN-H was then added to this mixture to afford the final ink. Important to note is that these ink formulations can be difficult to reproduce, owing to the heterogeneous mixture involving PEI that is a highly branched, disordered polymer, and we expect that domains within the ink are formed and thus can greatly affect film properties. As such, all films presented within were made from the same batch of stock PEI (200 mg/mL) to avoid issues with alternate rheology of inks, with the exception of the thermal cycling data seen in Figure S8, these films (**TTI-5S**) were made using a different ink batch.. Further studies are required to probe the ink properties and then correlate to the thermochromic properties of the thin films.

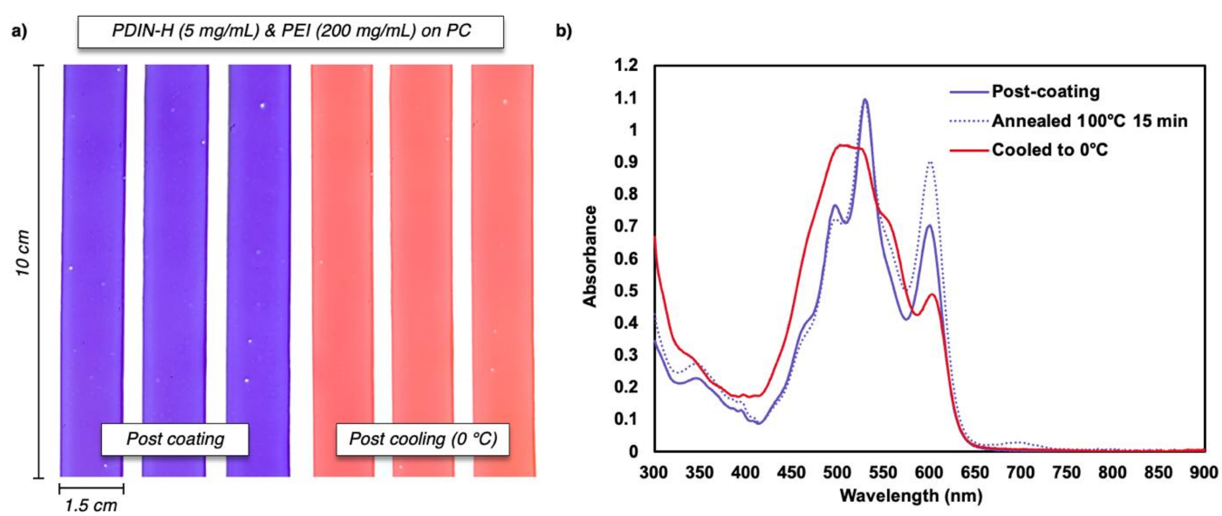

Figure S6. Optical properties of **TTI-5S** films: a) digital photographs of the films post-coating and annealing at 100°C for 15 minutes and post-cooling at 0°C overnight, and b) UV-visible spectra of films immediately post-coating, post annealing, and post-cooling.

Figure S7. Digital photographs of **TTI-5S** films: a) warmed to 20 °C from 0 °C over 30 minutes, b) warmed to 40 °C from 0 °C over 30 minutes, c) warmed to 60 °C from 0 °C over 30 minutes, and d) cooled to ~0 °C from 20 °C over 30 minutes. Warming was done on a hotplate set to the target temperature for temperatures 40 °C and 60 °C and cooling was done by placing the film on a ice pack. For warming to 20 °C, films were set on a benchtop in ambient temperature (20 °C).

Chromaticity Diagrams & Data for TTI-5S Films

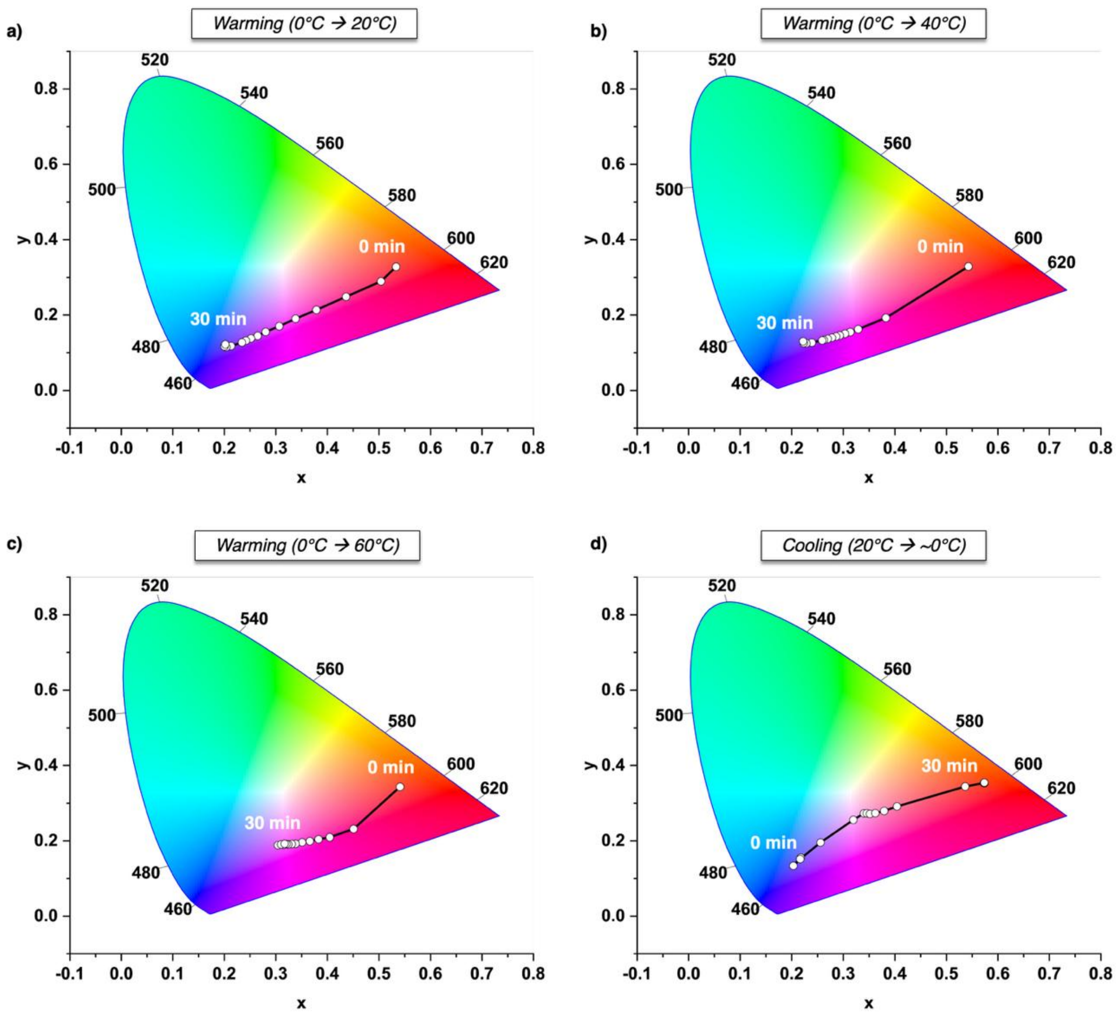

Figure S8. Chromaticity diagram of films made using inks of PDIN-H (5 mg/mL) and PEI (200 mg/mL) that were sonicated (**TTI-5S**) when a) warmed from 0 °C to 20 °C over 30 minutes, b) warmed from 0 °C to 40 °C over 30 minutes, c) warmed from 0 °C to 60 °C over 30 minutes, and d) cooled to ~0 °C (on an ice pack) from 20 °C over 30 minutes.

Table S1. Chromaticity data for **TTI-5S** films warmed from 0°C to 20°C

Time (min)	R	G	B	x	y	Y
0	253.644042	83.1604449	86.165724	0.53398264	0.32718611	0.27748
1	192.230204	48.246135	85.1381976	0.50467772	0.28871771	0.1398
2	161.422794	41.3676471	99.0918175	0.43682915	0.24780896	0.10066
3	141.928922	37.7326546	110.415818	0.37928502	0.21278884	0.08113
4	128.784879	36.0723982	118.978884	0.33864099	0.18938292	0.0716
5	118.02121	34.265083	125.505468	0.30704277	0.16932448	0.06477
6	108.573058	34.0741893	130.695701	0.28069125	0.15469901	0.05944
7	104.589838	33.5058446	136.437594	0.26507398	0.14396174	0.05809
8	97.6784502	33.4013952	137.327489	0.25217128	0.13721975	0.05435
9	93.5602376	33.3988499	140.740008	0.24226753	0.13134062	0.05308
10	90.3014706	33.4885935	143.570607	0.23446096	0.12655632	0.05245
15	79.8365385	36.2098416	150.767345	0.21352955	0.11695186	0.05126
20	73.5710784	39.4098793	154.277621	0.20411118	0.11407762	0.052
25	70.4959465	43.0512821	156.53667	0.20054253	0.11598103	0.0543
30	72.979638	48.0080128	159.321456	0.20212529	0.12132375	0.05994

Table S2. Chromaticity data for **TTI-5S** films warmed from 0°C to 40°C

Time (min)	R	G	B	x	y	Y
0	255	60.0690821	63.4341787	0.54349501	0.32812613	0.27264
1	162.670169	9.00736715	127.869082	0.38317833	0.19151794	0.09411
2	144.977899	7.70881643	140.276812	0.32939321	0.16149192	0.08088
3	139.535145	11.27343	142.823913	0.3139976	0.15401358	0.07713
4	131.803986	13.6306763	141.083937	0.30365302	0.14966724	0.07174
5	127.189372	15.8681159	142.075483	0.2935336	0.14506623	0.06867
6	122.798913	18.2032609	143.025483	0.28675823	0.14243343	0.06627
7	118.595652	20.3163043	143.960628	0.27834735	0.13909684	0.06336
8	114.321618	21.6694444	144.584058	0.27034775	0.13594567	0.06165
9	110.438285	23.9900966	145.044082	0.26255587	0.13303686	0.06013
10	107.979227	24.9520531	145.562681	0.25937973	0.13207379	0.05928
15	97.5363527	31.2169082	148.703744	0.23940749	0.12588688	0.0566
20	90.6012077	36.3043478	150.721498	0.2285553	0.1241535	0.0572
25	88.1504831	40.5352657	153.327053	0.22343382	0.12499735	0.05892
30	86.3797101	44.6493961	154.173551	0.22226377	0.12953615	0.06236

Table S3. Chromaticity data for **TTI-5S** films warmed from 0°C to 60°C

Time (min)	R	G	B	x	y	Y
0	249.168199	90.0670956	77.2115809	0.53632978	0.34070883	0.27994
1	181.461765	19.0917279	127.668382	0.41224926	0.21084069	0.11825
2	170.000184	27.2152574	130.647426	0.38842134	0.20242301	0.10944
3	160.212684	33.3786765	133.301838	0.36587449	0.19469648	0.10257
4	152.456801	38.3715074	135.629228	0.34852677	0.18982762	0.09812
5	149.536397	45.278125	139.582537	0.33597864	0.18919222	0.10132
6	144.16636	47.1428309	140.31875	0.32606929	0.18630101	0.09857
7	141.925368	51.8908088	143.143934	0.3162521	0.18493897	0.10015
8	140.051471	54.6784926	144.239522	0.31302192	0.1864858	0.10228
9	135.365993	54.1422794	143.020221	0.30664254	0.18421549	0.09773
10	134.372794	56.2889706	144.502757	0.30356543	0.18481707	0.09911
15	127.158088	52.7959559	135.758456	0.30593627	0.18582543	0.08718
20	128.263603	53.2270221	136.261949	0.30602248	0.18659856	0.08914
25	128.769301	50.5321691	132.707353	0.31245464	0.18775429	0.08537
30	131.213603	48.1511029	129.655331	0.32271024	0.19132796	0.08525

Table S4. Chromaticity data for **TTI-5S** films cooled from 20°C to ~0°C

Time (min)	R	G	B	x	y	Y
0	92.6897624	76.6204751	178.975584	0.21764689	0.15431616	0.10658
1	63.4970777	50.8319193	143.017534	0.20343596	0.13286888	0.05321
2	76.1244344	61.7669683	150.153846	0.21644496	0.15084847	0.07076
3	89.7820513	66.2261501	128.396116	0.25613142	0.19484292	0.07579
4	104.216535	69.0759804	102.671851	0.31987374	0.25499266	0.08159
5	106.277998	68.1220777	93.0890837	0.34031895	0.27223472	0.07989
6	102.336821	63.9259992	87.3555807	0.34592116	0.27235945	0.07068
7	99.2924208	58.6769419	82.6617647	0.35215632	0.27063786	0.06288
8	99.4285445	55.582862	78.9941554	0.36245404	0.27279412	0.05936
9	102.948812	53.639046	74.5412896	0.37963315	0.27874929	0.05866
10	109.855581	53.0996418	70.2652715	0.4046399	0.29069226	0.0624
15	178.839932	63.6554487	51.7943062	0.53725582	0.34359293	0.13262
20	234.809578	75.1573341	43.3634992	0.5735253	0.3530116	0.22705
25	236.791572	75.8250377	43.0584465	0.57458301	0.35263963	0.23045
30	236.974265	76.0199849	42.9095023	0.57440763	0.35404922	0.23175

Stability of TTI-5S Films

We probed the stability of the **TTI-5S** films in terms of thermal stressing (heating to 200 °C on a hot plate: Figure S7) and thermal cycling (warming to 20 °C from 0 °C, and back over five cycles: Figure S8).

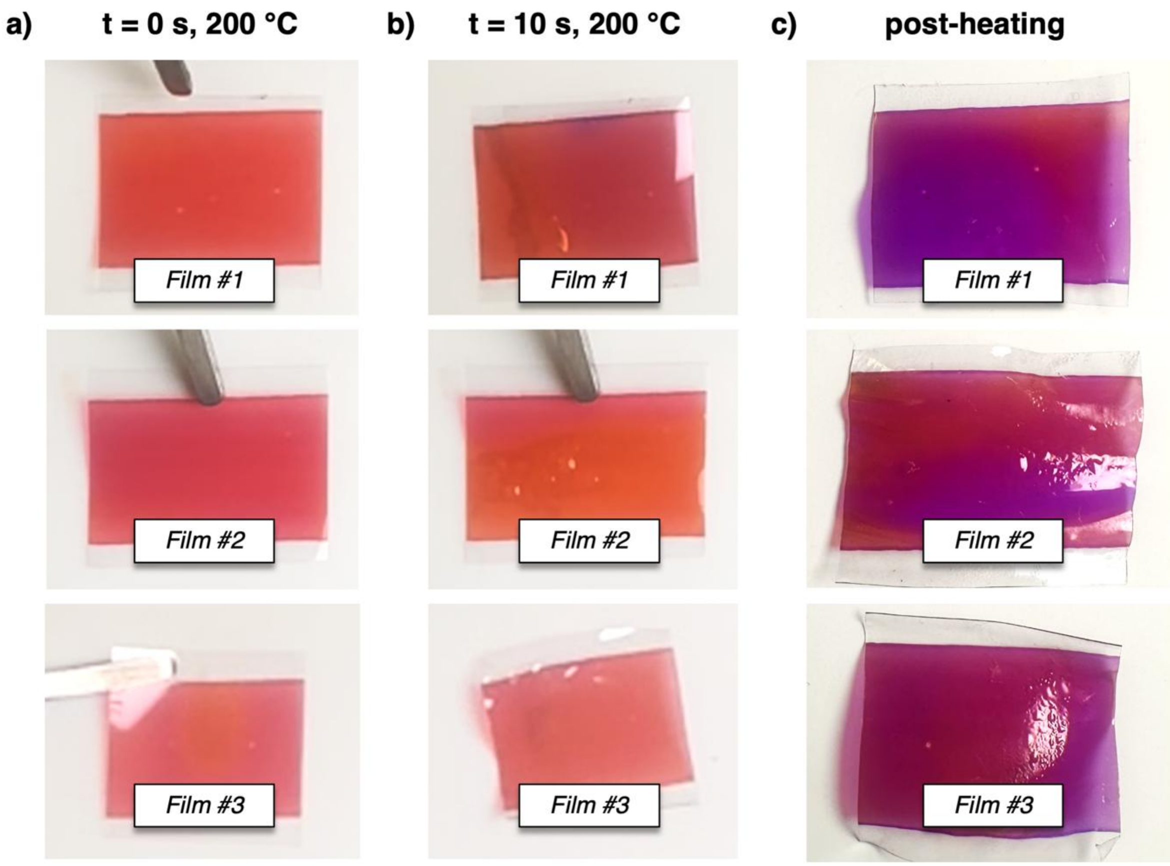

Figure S9. Thermal stress test for **TTI-5S**: a) digital photos of films 1-3 are placed on a hot plate set to 200 °C, b) digital photos of films 1-3 after 10 seconds of being on the hot plate, and c) digital photos of films 1-3 after being removed from the hot plate, which show clear signs of degradation of the polycarbonate substrate.

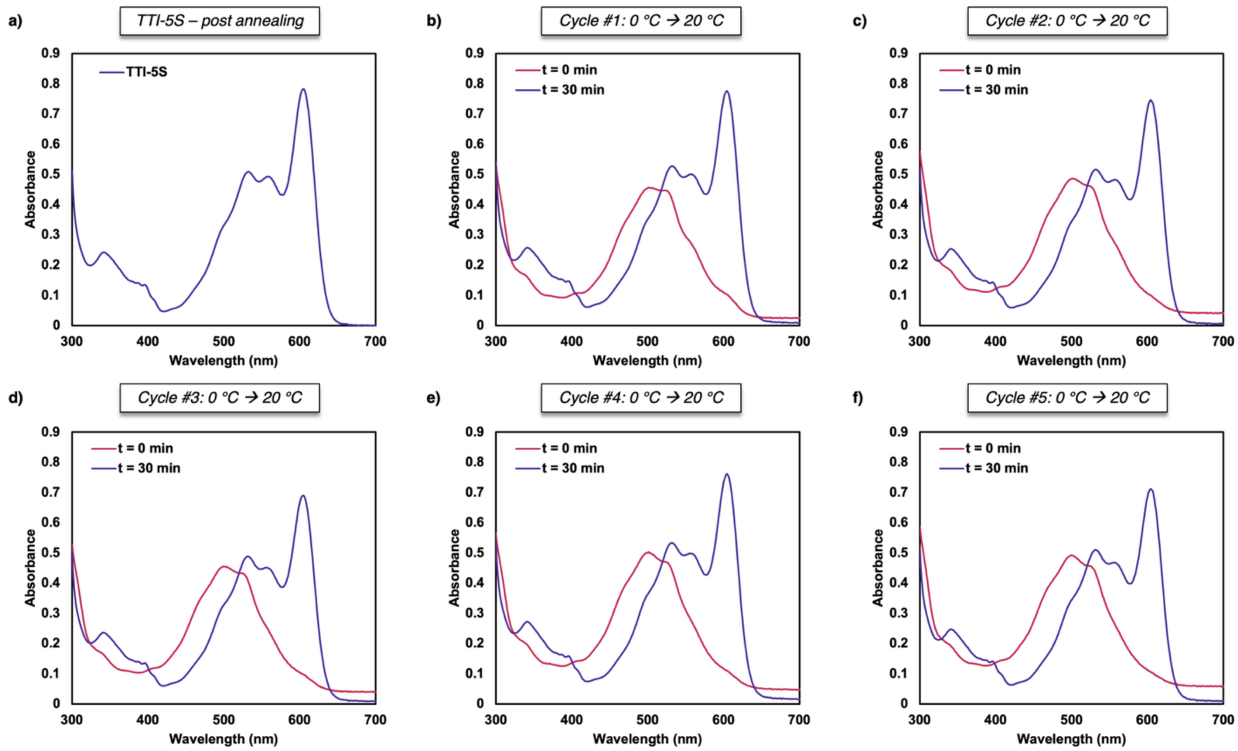

Figure S10. UV-visible absorption spectra of **TTI-5S** films during thermal cycling between 0 °C and 20 °C **(**five cycles**)**. a) As-coated film after annealing at 100 °C for 15 min and b-f) cycles 1-5, recorded after cooling at 0 °C for 15 min and subsequent warming to 20 °C for 30 minutes.

4. Processes and Properties of Inks and Films for TTI-5, TTI-10, and TTI-15

Engineering Ink Formulations for Slot-Die Coating of Thin Films

To increase the PDIN-H:PEI ratio for subsequent TTI profiling, we raised the PDIN-H loading in the inks. However, it was observed that at 10 mg/mL and above PDIN-H does not fully dissolve in the blend of PEI (200 mg/mL) with EL and 2-MeTHF (1:1). Additionally, while sonication did help disperse some of the PDIN-H, at 10 mg/mL and above PDIN-H is not fully miscible in this blend and crystallites persist. Therefore, due to this aspect and the negative impact sonication can have on the structural integrity of PEI, we sought to study TTI films made from inks that were not sonicated using PDIN-H loadings of 5 mg/mL (TTI-5), 10 mg/mL (TTI-10), and 15 mg/mL (TTI-15), keeping PEI constant at 200 mg/mL and the solvent blend of EL to 2-MeTHF consistent at a ratio of 1:1. Here, all inks were simply shaken vigorously, and coated as is. Additionally, to further preserve PEI integrity, annealing of these films was omitted.

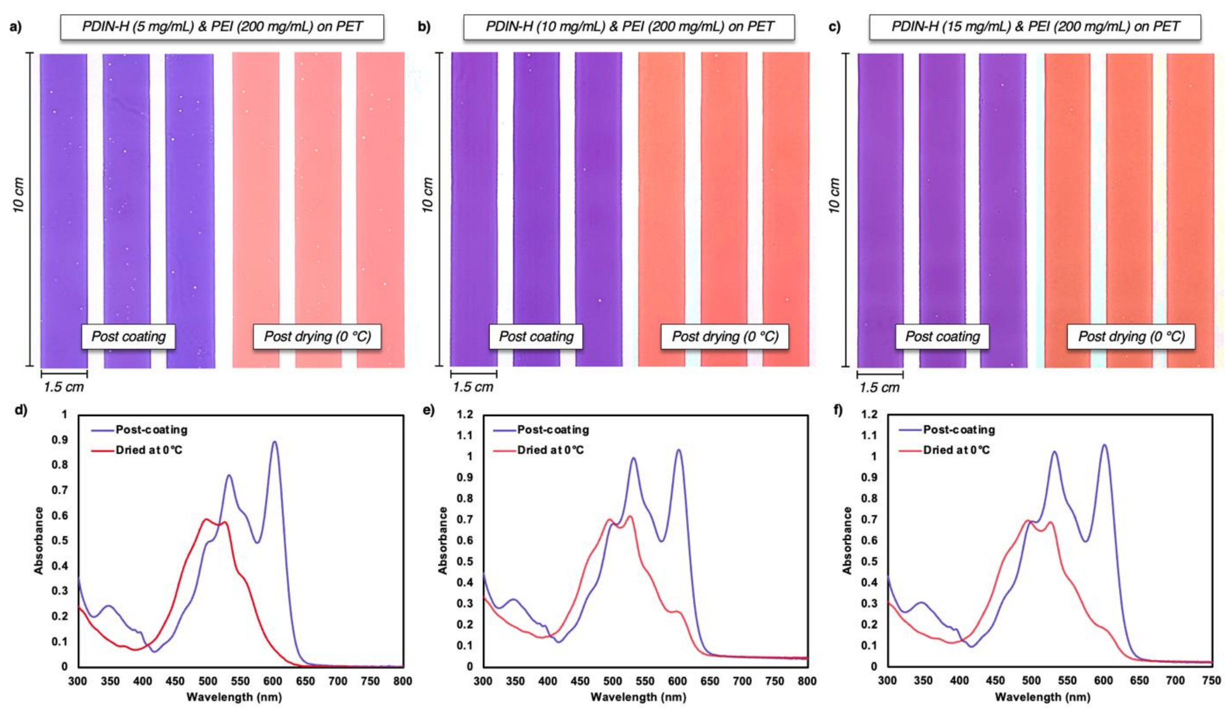

Figure S11. Optical properties of **TTI-5**, **TTI-10**, and **TTI-15** films: a) digital photographs of the **TTI-5** films post-coating and post-cooling at 0°C overnight, b) digital photographs of the **TTI-10** films post-coating and post-cooling at 0°C overnight, c) digital photographs of the **TTI-15** films post-coating and post-cooling at 0°C overnight, d) UV-visible spectra of **TTI-5** films post-coating and post-cooling, e) UV-visible spectra of **TTI-10** films post-coating and post-cooling, and f) UV-visible spectra of **TTI-15** films post-coating and post-cooling.

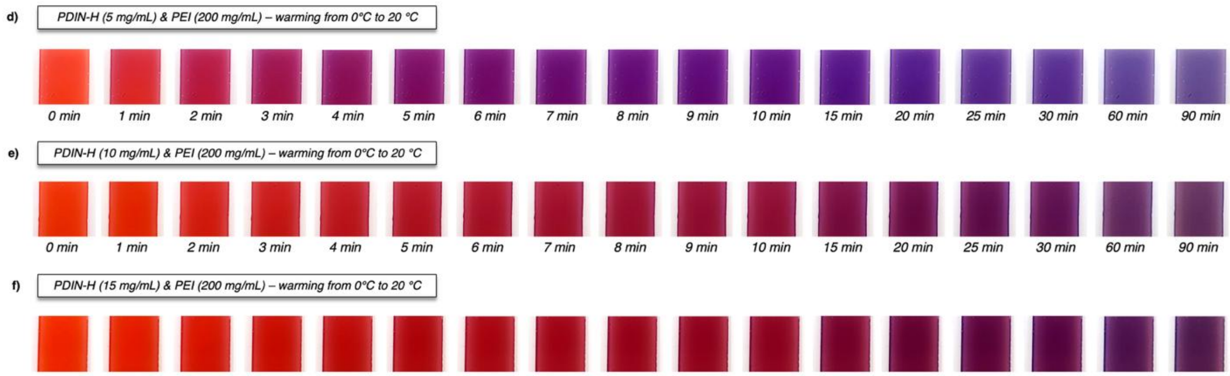

Figure S12. Digital photographs of a) **TTI-5** films warmed to 20 °C from 0 °C over time, b) **TTI-10** films warmed to 20 °C from 0 °C over time, and c) **TTI-15** films warmed to 20 °C from 0 °C over time. Films were warmed on a benchtop under ambient conditions (20 °C).

Optical and Polarized Optical Microscopy of TTI-5, TTI-10, and TTI-15 films

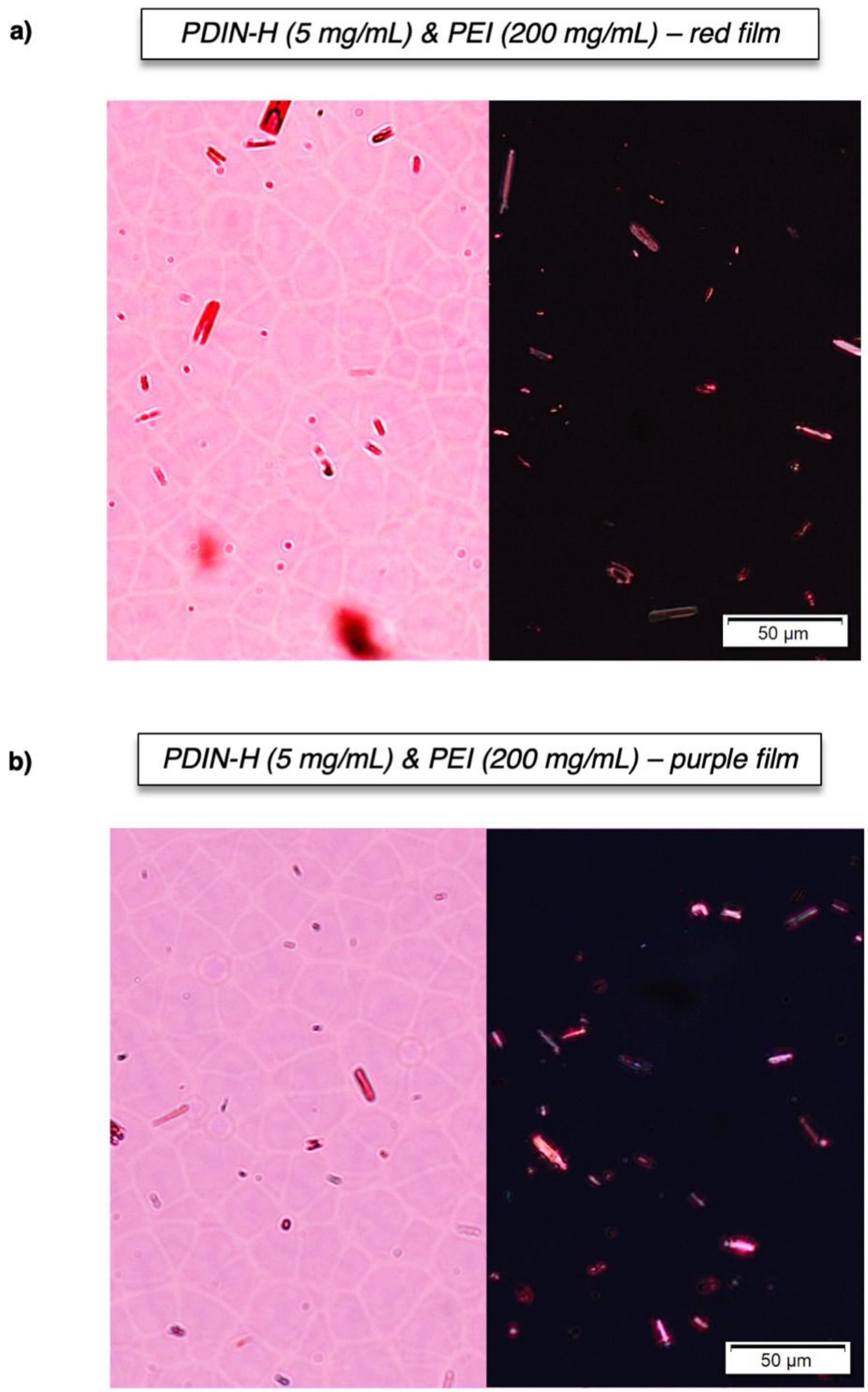

Figure S13. Optical (left) and polarized optical (right) microscopy images of **TTI-5** films a) cooled to 0°C (red film), and b) warmed to 20°C for 90 minutes (purple film).

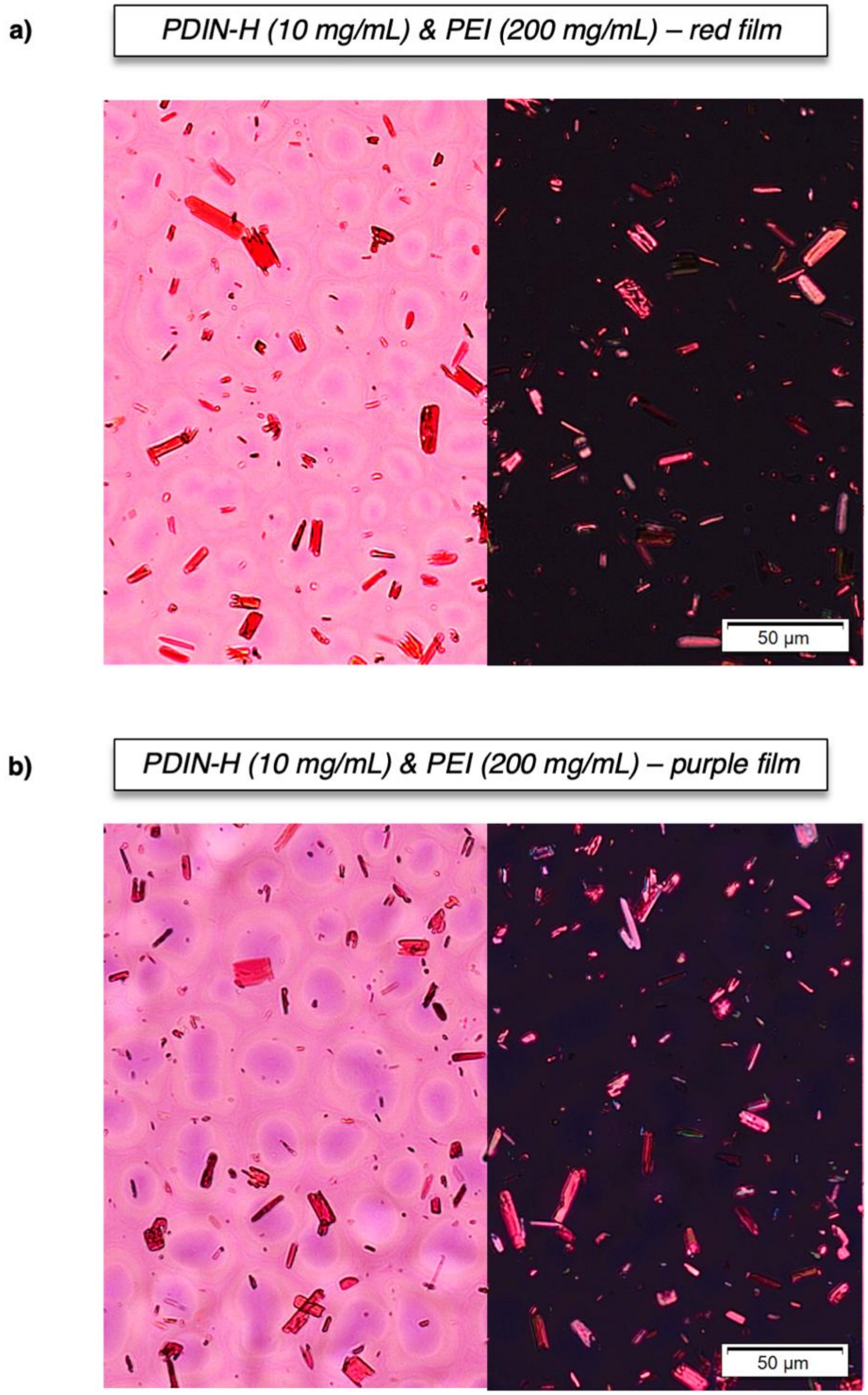

Figure S14. Optical (left) and polarized optical (right) microscopy images of **TTI-10** films a) cooled to 0°C (red film), and b) warmed to 20°C for 90 minutes (purple film).

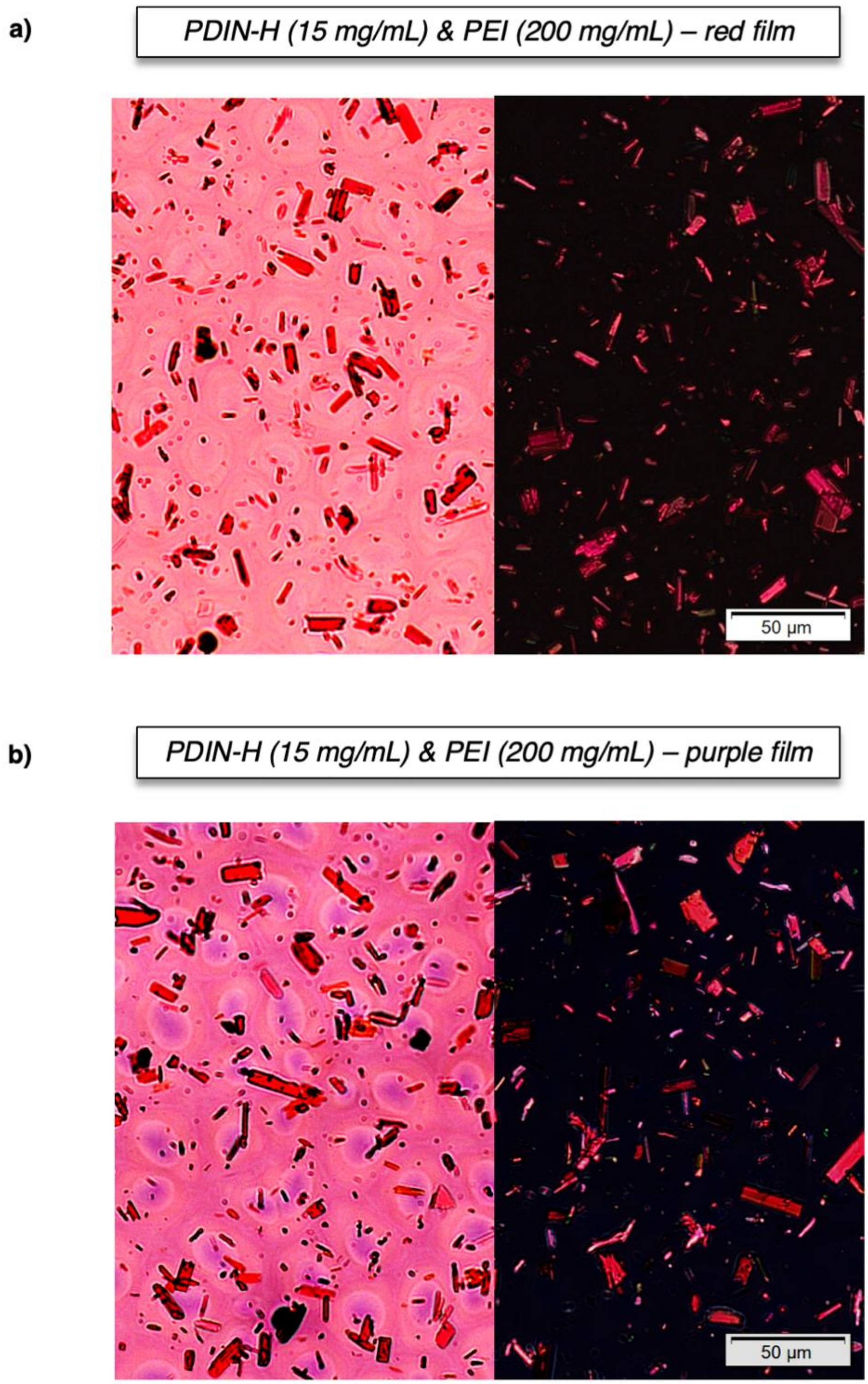

Figure S15. Optical (left) and polarized optical (right) microscopy images of **TTI-15** films a) cooled to 0°C (red film), and b) warmed to 20°C for 90 minutes (purple film).

Chromaticity Diagrams & Data for TTI-5, TTI-10, and TTI-15 films

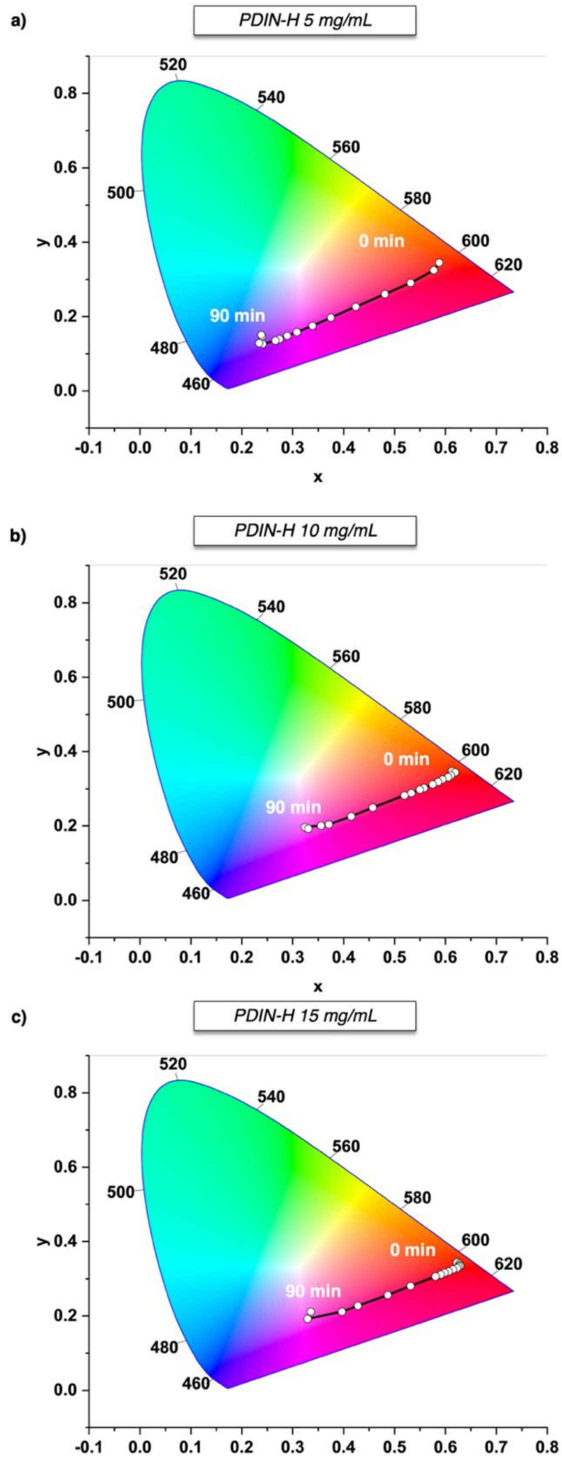

Figure S16. Chromaticity diagram of thermochromic films when warmed from 0 °C to 20 °C made using inks of PEI (200 mg/mL) and a) PDIN-H at 5 mg/mL (TTI-5), or b) PDIN-H at 10 mg/mL (TTI-10), or c) PDIN-H at 15 mg/mL (TTI-15), that were not sonicated.

Table S5. Chromaticity data for **TTI-5** films warmed from 0°C to 20°C

Time (min)	R	G	B	x	y	Y
0	247.183164	66.7072021	42.0872926	0.58839081	0.34446194	0.23844
1	218.085502	46.2849736	54.872549	0.57793411	0.32397216	0.17131
2	185.814385	32.7132353	72.6662896	0.53199941	0.28978471	0.11818
3	162.528092	27.8083522	83.7286011	0.48162647	0.25980112	0.09092
4	143.197398	23.2669683	94.0928544	0.4242396	0.22561904	0.07262
5	129.993024	20.9574849	103.759144	0.37549925	0.19644055	0.06148
6	118.236897	17.9585219	109.886972	0.33937343	0.17427372	0.05357
7	111.388669	18.8277715	117.088895	0.30846002	0.1574898	0.05097
8	106.410539	19.1292421	122.620381	0.28943123	0.14744892	0.04936
9	100.99293	18.4489065	124.529412	0.27454113	0.13858163	0.04598
10	98.1888198	19.6863688	127.709747	0.26626094	0.13444714	0.04595
15	90.1895739	26.4995287	136.284314	0.24118496	0.12528048	0.0469
20	88.5970965	33.2729072	140.458333	0.23458347	0.12751898	0.05056
25	93.3588801	48.3119344	144.960124	0.24031183	0.14628564	0.06455
30	94.6663839	53.943816	148.282334	0.23859388	0.15004248	0.07064
60	104.662236	77.1179299	156.210407	0.24865819	0.18440735	0.10651
90	109.648379	85.8049585	151.401301	0.26144468	0.20691084	0.11982

Table S6. Chromaticity data for **TTI-10** films warmed from 0°C to 20°C

Time (min)	R	G	B	x	y	Y
0	236.574755	52.5886124	9.12452866	0.61344049	0.34738372	0.20315
1	225.929864	42.6220777	6.93080694	0.61969206	0.34331981	0.17682
2	213.978601	36.9073341	26.349736	0.61137431	0.33502066	0.15487
3	201.054299	32.5907805	31.2122926	0.60601775	0.33048864	0.13554
4	190.585407	30.4885935	38.293175	0.59498691	0.32428568	0.12019
5	177.797323	26.1935332	41.096908	0.58646687	0.31797592	0.10249
6	169.22483	24.5255468	45.9073341	0.57569761	0.31127583	0.09281
7	162.651018	23.9131787	51.1154789	0.55873308	0.30174273	0.08536
8	155.006599	22.0725867	52.8578431	0.55035861	0.29730658	0.07793
9	148.700509	21.6151961	56.2160633	0.53347348	0.28783959	0.0712
10	146.593609	22.9315611	60.9034691	0.52006743	0.28146572	0.07013
15	125.549114	21.1782617	70.6710973	0.45777074	0.2486265	0.0534
20	109.756976	19.0756976	73.7832768	0.41524106	0.22518368	0.04199
25	101.166949	21.6620475	81.203997	0.37125873	0.20325373	0.03898
30	102.210219	26.4020551	87.7697021	0.35605419	0.20001882	0.04252
60	103.707862	49.3461538	100.882164	0.32424636	0.21639262	0.06001
90	106.954374	57.5781486	99.1921192	0.33108247	0.23623775	0.06892

Table S7. Chromaticity data for **TTI-15** films warmed from 0°C to 20°C

Time (min)	R	G	B	x	y	Y
0	238.963612	42.7059766	1.92892157	0.62348654	0.34269479	0.19841
1	226.878017	32.1688348	1.67043741	0.62812685	0.33896002	0.17209
2	213.512726	25.4110106	7.2897813	0.62827343	0.33551562	0.14862
3	199.346814	19.3585973	7.9841629	0.62972066	0.33370332	0.12627
4	188.778092	16.7919495	13.9826546	0.6266412	0.33107544	0.11095
5	175.257259	12.8869721	17.6515837	0.62333415	0.32777758	0.0942
6	170.035256	13.078997	23.9677602	0.61562591	0.32459148	0.08899
7	162.242459	11.9572964	28.2848793	0.60731231	0.31924564	0.08007
8	155.1875	11.1848605	31.8854638	0.59928359	0.3154374	0.07309
9	147.888857	9.54392911	33.8881033	0.5919458	0.31062124	0.0651
10	144.620758	10.1170814	37.9499434	0.58100287	0.30552989	0.06282
15	123.703431	9.38980015	47.7944005	0.53179891	0.27940642	0.04613
20	107.457768	8.8905543	52.7848793	0.48726252	0.25532527	0.03548
25	98.2149321	11.1863688	62.7020173	0.42848002	0.22643253	0.03185
30	93.4833145	12.3355958	67.6750566	0.39729009	0.21033418	0.02996
60	86.2971342	26.049491	82.6615762	0.32972724	0.19144896	0.03327
90	88.4472097	34.3063725	81.5355392	0.33613352	0.21073284	0.03813

5. Thermochromic Kinetics

Temperature-dependent kinetics were monitored by collecting time-resolved UV-visible spectra after mixing PDIN-H with PEI and warming to 20 °C, which in our case was the room temperature. The evolution of the PDIN-H → $PDIN^-$ conversion was tracked at 602 nm (growth of $PDIN^-$ band). The 407 nm isosbestic point was used to correct the spectra at 602 nm ($A_{602,corr}$) as artefacts arise from small changes in optical path/film positioning. The presence of persistent isosbestic behaviour over the kinetic window supports a clean conversion of PDIN-H to $PDIN^-$. With PEI present in large excess (i.e., the concentration of amine sites responsible for acid-base reactivity is effectively constant over the fitting window), the conversion of PDIN-H → $PDIN^-$ was treated as a pseudo-first order reaction. Because the 602 nm signal approaches a plateau at long times, the kinetics are treated as a first-order approach to equilibrium. As per the Beer-Lambert law, $A_{602,\text{corr}}(t)$ is proportional to the extent of conversion, therefore, the integrated pseudo-first-order form can be written in terms of absorbance as:

$$A(t) = A_\infty - (A_\infty - A_0)\ ^{-k't}$$

where A(t) is $A_{602,corr}$ at time t, A_0 is the corrected absorbance at the start of the fitted window ($t = t_0$), A_∞ is the average plateau value (estimated using the late-time data), and k' is the apparent pseudo-first-order rate constant. To extract k', the standard linearized form was used:

$$\ln\left[\frac{A_\infty - A(t)}{A_\infty - A_0}\right] = -k't$$

where plots of ln $[(A_\infty - A_t)/(A_\infty - A_0)]$ vs. time are shown in Figures S13-S16, and k' was obtained as the negative slope of each. While linearization is convenient for visual assessment of first-order behaviour and straightforward k' extraction, it is noted that linear vs nonlinear least-squares treatments can differ in how experimental error is weighted across the time trace.[7] Certainly, future work will include more rigorous kinetic studies.

Additional considerations for kinetic modelling: At low temperature (0°C) PDIN-H exhibits aggregation, and upon warming/mixing an initial period is required for (1) thermal equilibration and (2) physical mixing/intercalation prior to chemical conversion. Because of this, early time points can deviate from single-exponential behaviour and were excluded from fits, thus t_0 was defined as the first time point after this transient period. This avoids conflicting thermal equilibration and mixing time with the apparent chemical conversion rate.

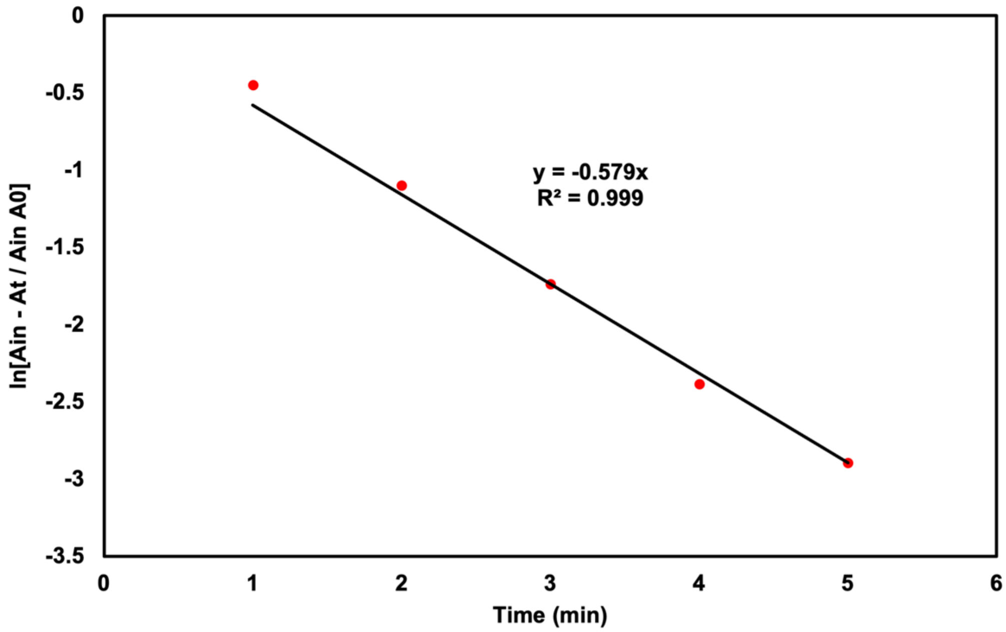

Figure S17. Pseudo-first order reaction rate plot for **TTI-5S**, where spectral data was collected every minute, and where A_0 is equal to the absorbance at 602 nm (corrected by isosbestic point at 407 nm) at t = 1 min.

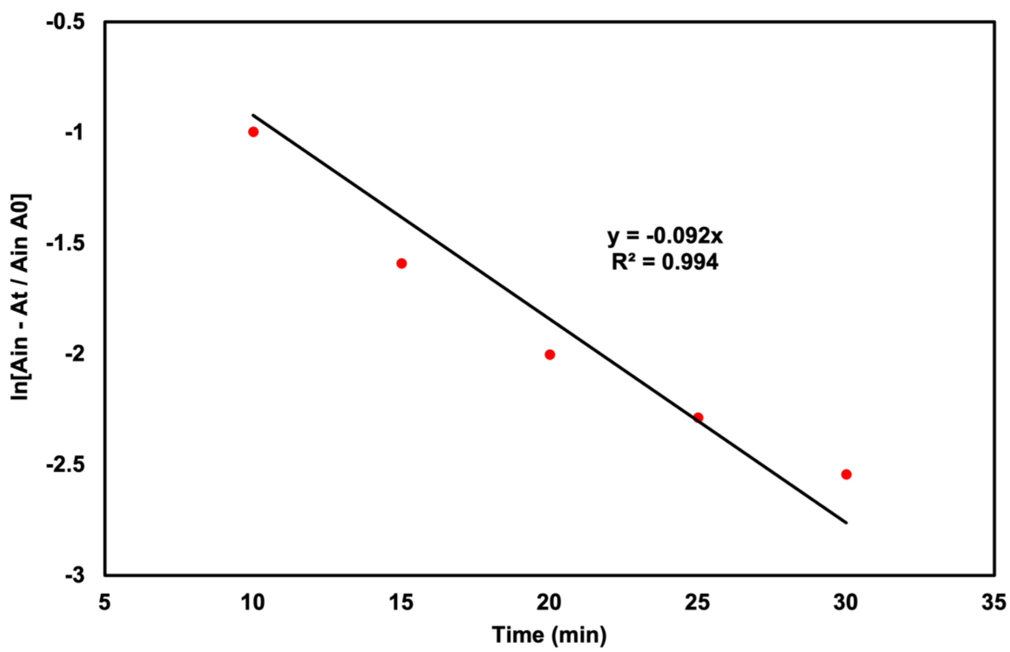

Figure S18. Pseudo-first order reaction rate plot for **TTI-5**, where spectral data was collected every five minutes, and where A_0 is equal to the absorbance at 602 nm (corrected by isosbestic point at 407 nm) at t = 5 min.

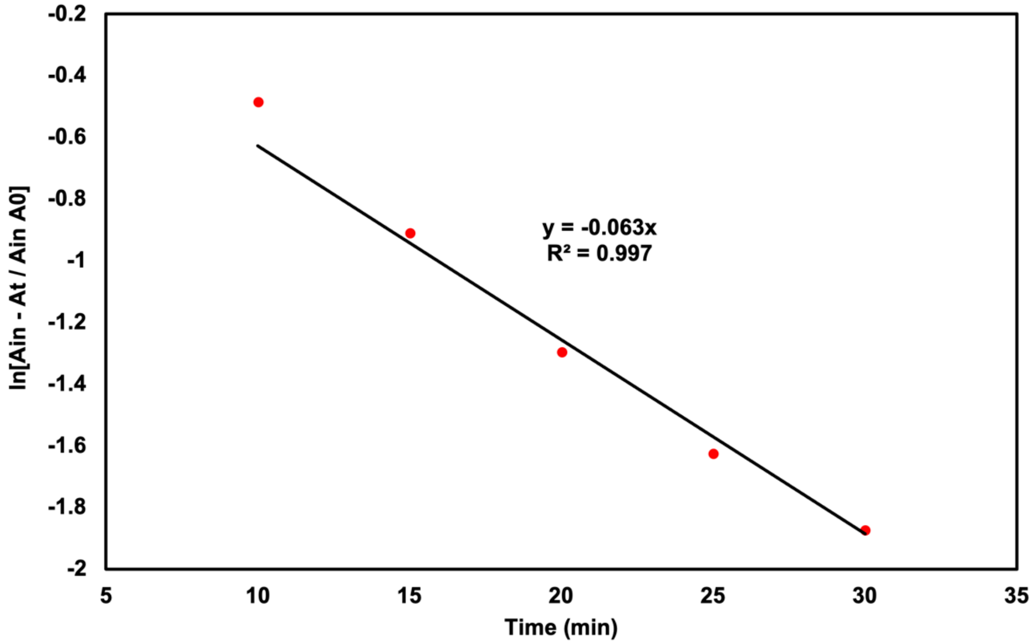

Figure S19. Pseudo-first order reaction rate plot for **TTI-10**, where spectral data was collected every five minutes, and where A_0 is equal to the absorbance at 602 nm (corrected by isosbestic point at 407 nm) at t = 5 min.

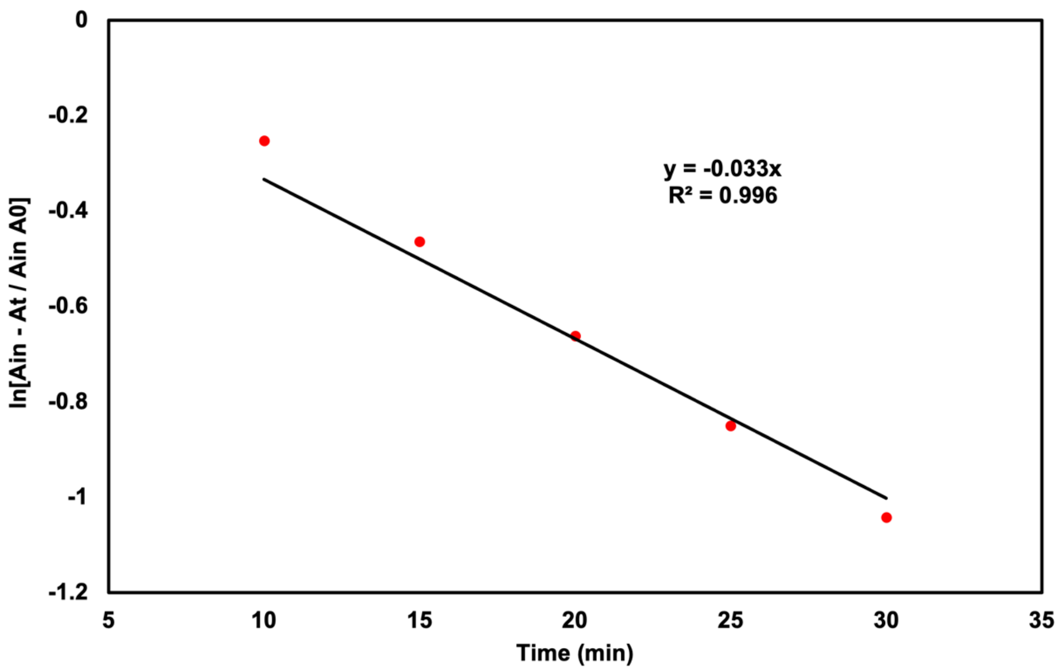

Figure S20. Pseudo-first order reaction rate plot for **TTI-15**, where spectral data was collected every five minutes, and where A_0 is equal to the absorbance at 602 nm (corrected by isosbestic point at 407 nm) at t = 5 min.

6. References

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