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Supplementary Materials for

Self-driving laboratory for accelerated discovery of thin-film materials

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The PDF file includes:

Supplementary Materials and Methods
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Legend for movie S1

Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/6/20/eaaz8867/DC1)

Movie S1

Supplementary materials and methods

Hole mobility measurement using hole-only devices device fabrication

Hole-only devices were fabricated and used to perform hole mobility measurements of spiro-OMeTAD films using the steady-state space-charge limited current (SCLC) method[29,30] (see Fig. S5).

Indium tin oxide (ITO)-coated glass substrates (Thin Film Devices, 1.1 mm OLED/OPV grade) were cut into 1.8cm × 3.5 cm pieces. 1.5 cm of the ITO coating was removed by etching with Zn powder and 2M HCl. The etched substrates were then sonicated for 5 minutes in each of the following: detergent (Extran® 300), distilled water, acetone, isopropanol. The ultrasonically cleaned substrates were then blown dry with nitrogen and subjected to a UV-ozone treatment for 30 minutes directly before use.

A PEDOT:PSS ink was formulated by filtering an aqueous dispersion of PEDOT:PSS (Heraeus Clevios™ AI 4083) through a 40 μm PVDF filter and then combining 1 part by volume of this dispersion with 2 parts by volume of isopropanol. PEDOT:PSS films were then manually deposited on the ITO substrates by dynamic spin-coating 100 μL of the PEDOT:PSS ink at 3000 RPM for 1 minute. A Kimwipe ® soaked in water was then used to remove 1 cm of the PEDOT:PSS from each side of the device before baking the device for 1 h at 150 °C.

Spin-coating inks with FK 102 Co(III) TFSI:spiro-OMeTAD molar ratios of 0, 14, 42, 56, 84 and 98% were prepared by robotic pipetting using the *Ada* platform as described in the *Materials and Methods* section of the manuscript. Spiro-OMeTAD films of varying doping levels were then manually deposited on the glass/ITO/PEDOT:PSS devices by dynamic spin coating 50 μL of each ink at 3000 RPM for 1 minute. A Kimwipe soaked in acetone was then used to remove 1 cm of the spiro-OMeTAD film from each side of the device.

To complete the devices, 80 nm-thick gold contact layers were deposited by electron beam evaporation through a Kapton ® shadow mask. The final device area was 3.5 mm^2.

Film thicknesses for the HTM layers on the hole-only devices were measured by stylus profilometry (Bruker Dektak XT). Current-voltage curves were obtained for each device using a source-measure unit (Keithley 2400); the applied voltage ranged from 0 to 1 volts and measurements occurred in air. Following Xu et. al[30], , hole mobilities were extracted using the SCLC method by fitting the quadratic region of the current density curve to the Mott-Gurney law

$$J = \frac{9}{8}\mu\varepsilon\varepsilon_0\frac{V^2}{d^3}$$

where $\mu$is the mobility of the HTM layer, $\varepsilon$is the relative permittivity of the HTM (for which we assumed a value of 3),$\varepsilon_o$is the vacuum permittivity and $d$is the HTM thickness.

With the exception of the device with a dopant:HTM molar ratio of 84% which was removed from the dataset as reliable thickness data was not obtained, the hole mobilities reported in figure S6C are the mean values obtained from all the working devices obtained for each doping level, numbering between 3 - 7. The error bars are the standard deviations across all the measured devices.

Robotic pseudomobility measurements for comparison to hole mobility measurements

The pseudomobility values reported in figure S6C are the average of quadruplicate measurements made on HTM films with FK 102 Co(III) TFSI:spiro-OMeTAD molar ratios of 0, 14, 42, 56, 84 and 98%. These films were prepared and characterized using the *Ada* platform as described in the *Materials and Methods* section of the manuscript. The pseudomobility error-bars shown in figure S6C are the standard deviation of the quadruplicate measurement results.

Determination of the melting point of FK102 Co(III) TFSI by Differential Scanning Calorimetry

The melting of FK102 Co(III) TFSI salt (see Fig. S7) was measured by a Differential Scanning Calorimeter (Netzsch DSC 214 Polyma) using heating and cooling rates of 10 K min^{-1} and a N_2 purge. The sample was heated and cooled five times between 0 °C and 250 °C, with the final two cycles showing a stabilized melting point of 189 °C. The DSC traces from the final two heating cycles are shown in Fig. S7.

Supplementary figures

All figures containing numerical data were created in Python using the matplotlib library.

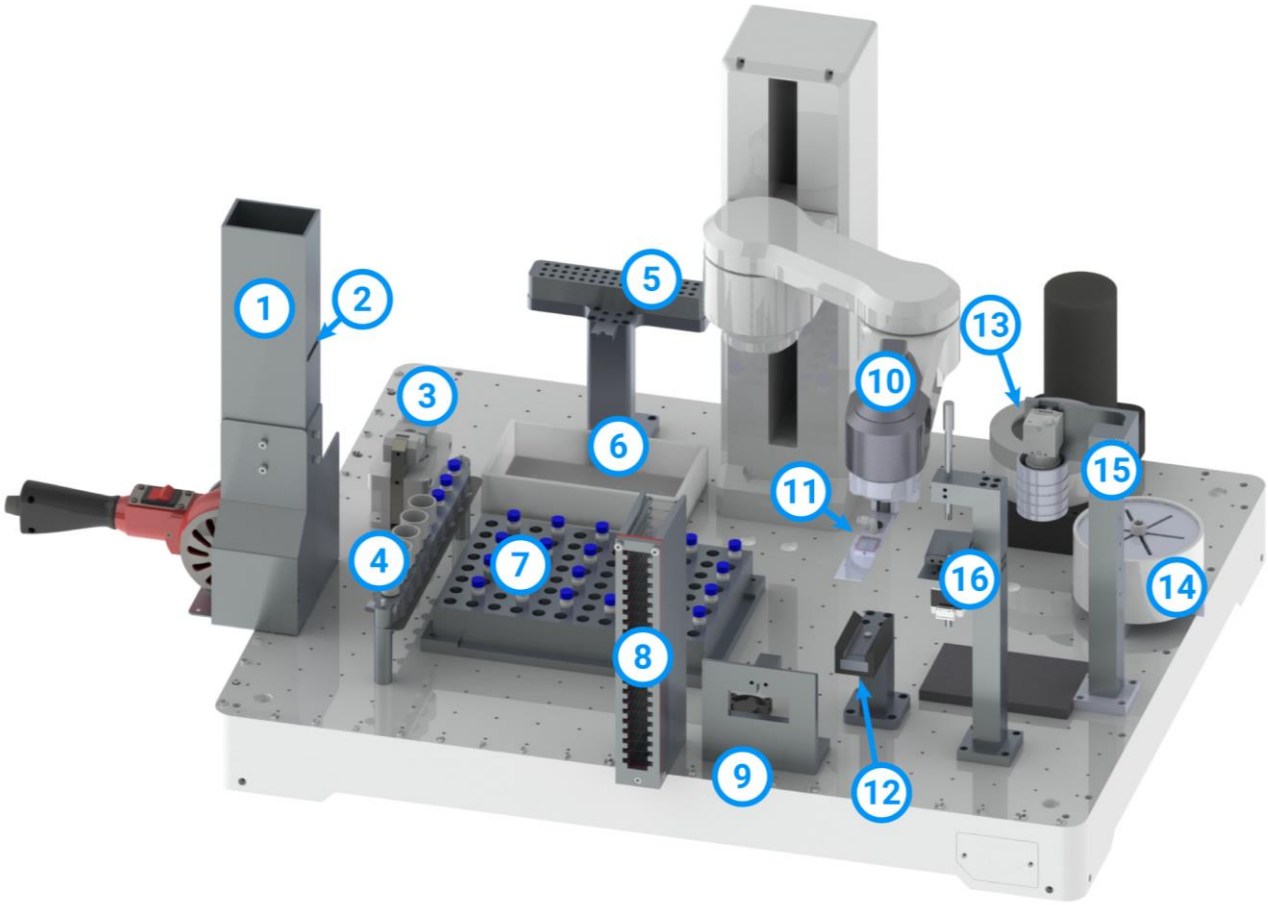

Fig. S1. *Ada* robotic platform for thin film fabrication and characterization. This platform includes: (1) an annealing furnace with (2) a slot-shaped sample port; (3) a weigh scale for feedback dispensing of solutions; (4) a rack for stock solution vials; (5) a rack for storing clean pipet tips and (6) a container for disposal of used tips; (7) a rack for clean mixing vials; (8) a rack for clean glass slides; (9) a 4-point probe for measuring film conductance; (10) a robotic arm for handling vials and slides with (11) an attachment for gripping slides and (12) a station for storing this attachment when not in use; (13) a spin coater with (14) a removable lid; (15) a camera for dark field imaging; (16) a spectrometer for transmission and reflection measurements.

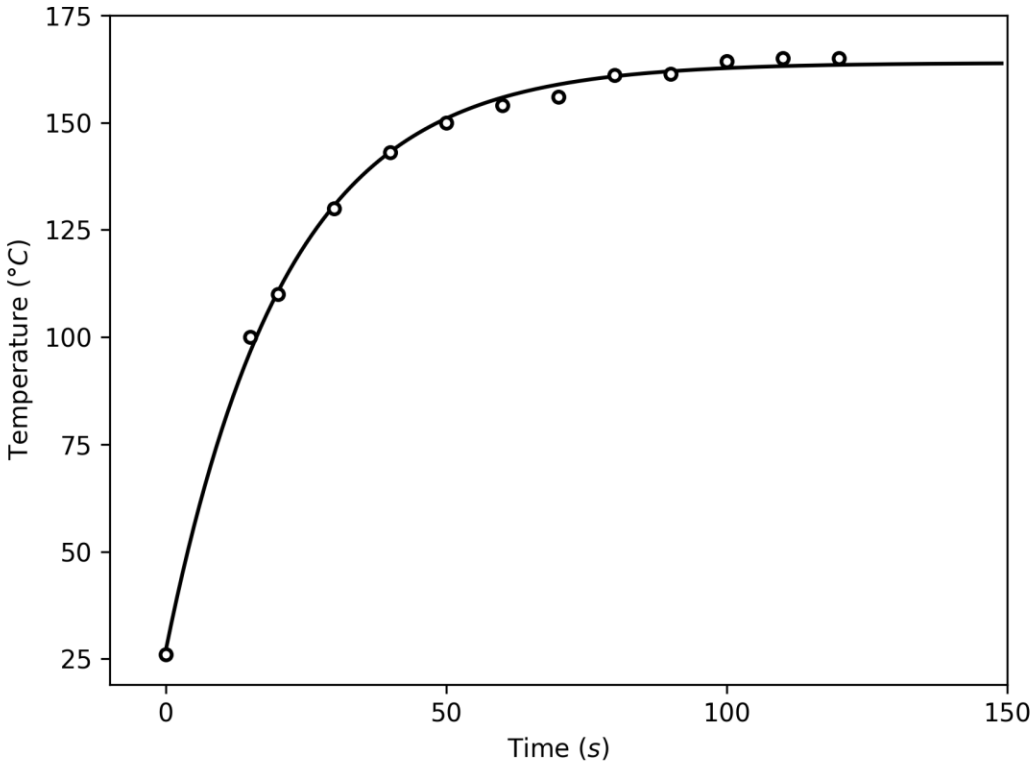

Fig. S2. Temperature profile of the heating protocol employed by *Ada's* annealing furnace. A thermocouple was contacted to a glass microscope slide and the measured temperature was collected at a series of times after the heat gun was turned on. The data was fit to an asymptotic regression model.

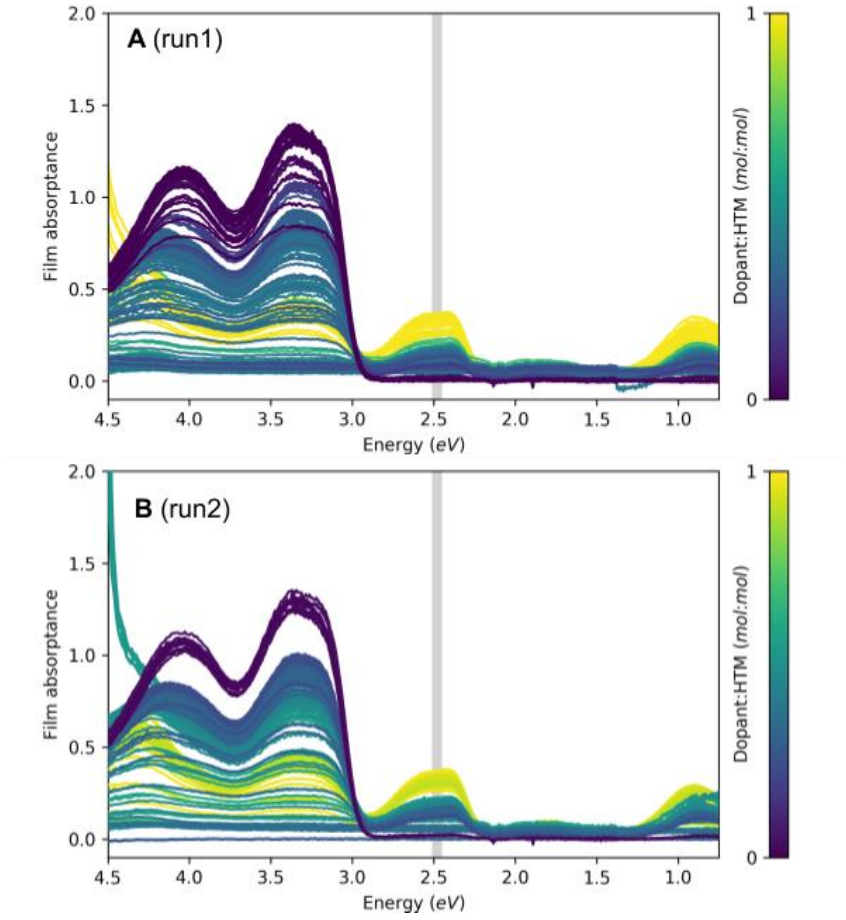

Fig. S3. UV-Vis-NIR film absorptance spectra for both optimization runs. (**A)** spectra for run 1. (**B)** spectra for run 2. The film absorption was calculated from the transmission and reflection spectra of both the glass substrate and the deposited film on the glass substrate. Absorption values for films with varying dopant:HTM ratios are shown, as indicated by the side bar. The mean absorption from 495 - 505 nm (indicated by the grey bar) was used to calculate pseudomobility.

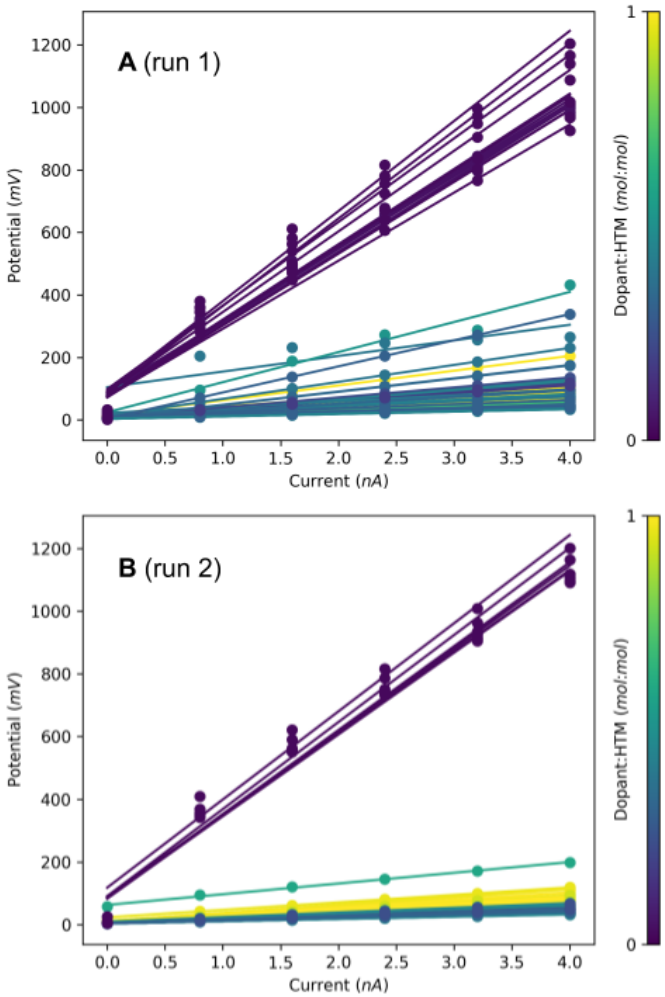

Fig. S4. Current-voltage relationships for both optimization runs. (**A)** I-V curves for run 1. (**B)** I-V curves for run 2. Potentials were recorded with a 4-point probe delivering a current between 0 and 4 nA for films with varying dopant:HTM ratios as indicated by the side bar. Conductance was calculated from the fitted slope of the current-voltage plots.

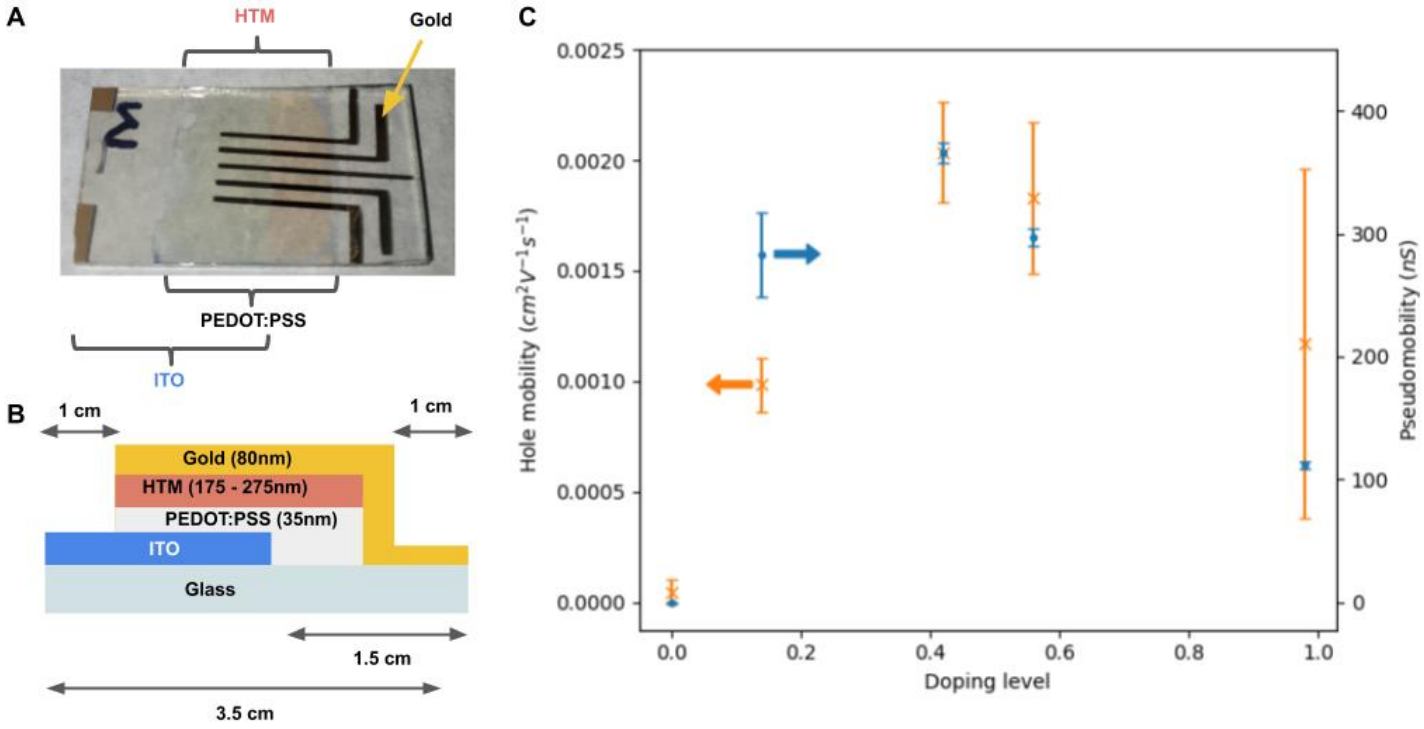

Fig. S5. Correlation between pseudomobility measured using *Ada* and hole mobility measured using hole-only thin film devices. (**A)** Photograph of an array of hole-only devices used for measuring hole mobility (**B)** Schematic of the prepared hole-only devices. (**C)** Comparison between manually-measured hole mobility data from the hole-only devices and the pseudomobility data measured using the *Ada* platform. To facilitate visual comparison, the y-axes have been scaled such that the maxima of the two data-sets are equal. Photo credit: David J. Dvorak, The University of British Columbia.

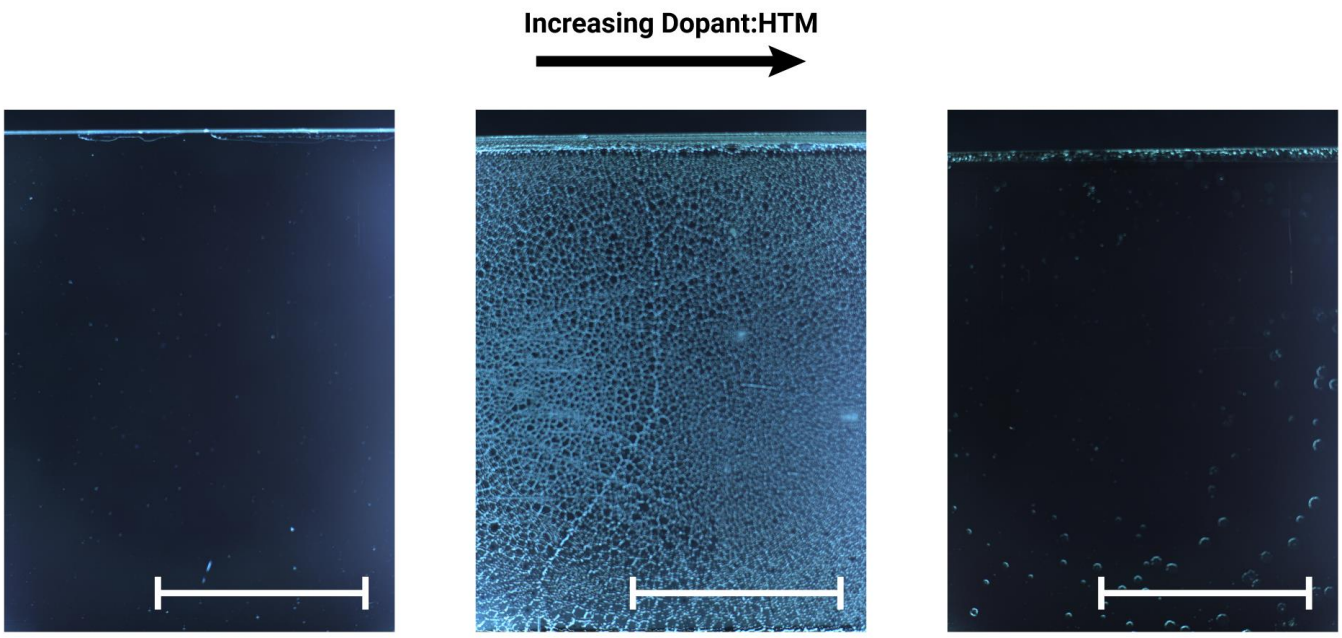

Fig. S6. Dark field images of highly annealed spiro-OMeTAD thin films with different ratios of dopant. Shown above are the images of three representative samples from run 2. When no dopant was added, no dewetting was observed. Dewetting was much more significant at an intermediate dopant:HTM ratio compared to a high dopant:HTM ratio. Scale bars are 1 cm.

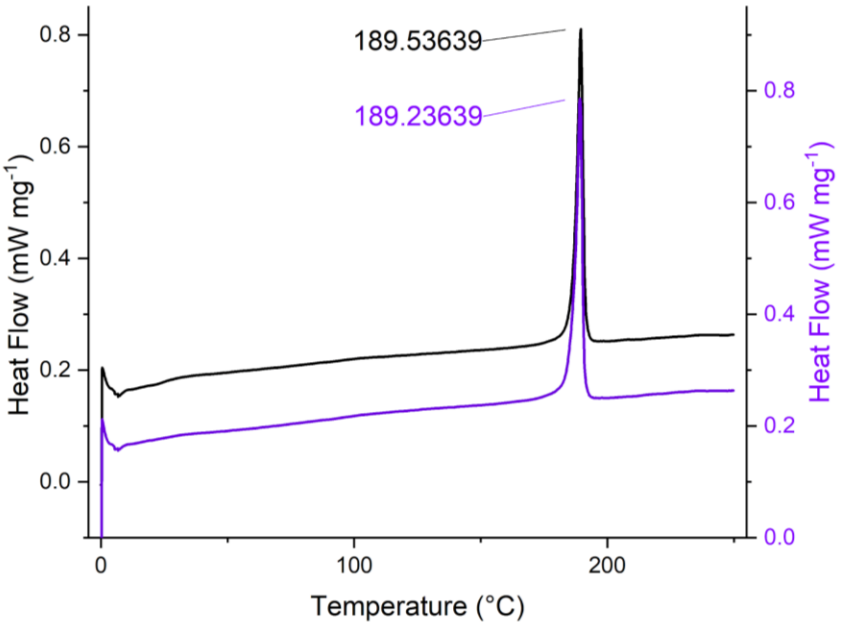

Fig. S7. Differential scanning calorimetry traces of FK102 Co(III) TFSI salt. The sharp, labelled endothermic peak in each trace indicates the temperature of the crystalline-to-liquid phase transition. Traces of the fourth and fifth heating cycles are offset vertically for clarity.

Table S1. Values of manipulated and responding variables for run 1.

Sample	Dopant:HTM (mol:mol)	Annealing time (s)	Conductance (nS)		HTM^+ Absorptance at 500 nm		Pseudomobility (nS)	
			mean	*st. dev.*	*mean*	*st. dev.*	*mean*	*st. dev.*
0	0.358	115	7.6	20.0	0.079	0.050	47	124
1	0.994	202	50.7	3.3	0.324	0.020	157	19
2	0	237	0.0	0.0	0.001	0.000	0	0
3	0.761	133	0.0	0.0	0.067	0.004	0	0
4	0.979	1	35.9	0.3	0.258	0.006	139	3
5	0.987	227	41.8	17.9	0.314	0.038	136	59
6	0.046	2	4.2	0.1	0.026	0.000	161	4
7	0.994	216	42.2	9.6	0.329	0.033	129	30
8	0	0	0.0	0.0	0.005	0.002	0	0
9	0.178	21	39.2	0.9	0.086	0.003	458	23
10	0.491	0	60.8	2.0	0.183	0.004	332	11
11	0.341	49	73.8	20.5	0.135	0.002	548	156
12	0.394	3	52.2	17.4	0.153	0.003	341	114
13	0.444	23	66.5	25.9	0.163	0.006	410	165
14	0.025	128	3.9	0.4	0.022	0.003	184	25
15	0.402	76	120.7	1.1	0.164	0.003	734	13
16	0.458	238	0.0	0.0	0.055	0.002	0	0
17	0.409	92	16.6	28.6	0.102	0.049	98	168
18	0.522	88	10.7	24.4	0.098	0.048	60	129
19	0.395	69	74.5	36.2	0.152	0.009	485	237
20	0.389	73	109.8	10.1	0.160	0.003	685	52

21	0.387	81	47.4	54.0	0.142	0.038	281	319
22	0.975	88	68.0	0.8	0.357	0.196	218	59
23*	0.376*	72*	104.0*	18.4*	0.044*	0.014*	2,600*	935*
24	0.345	73	55.9	54.8	0.153	0.008	355	347
25	0.308	82	58.1	39.3	0.139	0.006	421	281
26	0.529	172	0.0	0.0	0.073	0.010	0	0
27	0.372	70	94.9	42.9	0.163	0.003	580	261
28	0.685	75	10.4	27.6	0.129	0.064	51	134
29	0.315	63	102.4	2.5	0.141	0.004	727	13
30	0.235	167	4.5	11.8	0.090	0.030	34	90
31	0.337	72	60.8	42.0	0.138	0.021	427	262
32	0.31	81	97.7	11.1	0.141	0.008	692	74
33	0.45	58	126.6	1.5	0.180	0.003	703	10
34	0	93	0.0	0.0	0.002	0.000	0	0

*A brief spectrometer power failure resulted in calibration errors between the spectra of the glass slide and the spectra of the thin film, invalidating the calculation of thin film absorptance. This outlier was removed in all following analyses.

Table S2. Values of manipulated and responding variables for run 2.

Sample	Dopant:HTM (mol:mol)	Annealing time (s)	Conductance (nS)		HTM^+ Absorptance at 500 nm		Pseudomobility (nS)	
			mean	*st. dev.*	*mean*	*st. dev.*	*mean*	*st. dev.*
0	0.988	202	53.5	3.0	0.354	0.013	152	13
1	0.359	115	9.3	24.6	0.082	0.044	58	154
2	0.702	151	0.0	0.0	0.067	0.003	0	0
3	0.032	4	2.4	0.1	0.019	0.000	122	3
4	0.904	175	77.6	6.4	0.300	0.009	259	29
5	0.927	233	46.0	28.6	0.285	0.084	190	134
6	0.973	206	39.0	21.6	0.299	0.056	139	92
7	0	237	0.0	0.0	0.008	0.016	0	0
8	0.967	212	48.9	38.7	0.284	0.102	241	245
9	0.98	1	39.3	0.1	0.275	0.002	143	1
10	1.009	147	39.8	27.1	0.290	0.068	161	144
11	0.543	0	78.5	0.5	0.204	0.003	384	5
12	1.026	159	49.4	16.9	0.318	0.016	155	54
13	0.516	1	76.9	1.2	0.192	0.005	399	5
14	0.535	43	125.6	1.0	0.219	0.005	574	15
15	0.491	0	71.0	1.7	0.189	0.008	376	21
16	0.504	58	88.2	53.4	0.190	0.007	457	272
17	0.023	127	3.7	0.1	0.023	0.001	158	2
18	0.567	67	47.3	55.9	0.170	0.051	225	260
19	0.508	233	0.0	0.0	0.055	0.004	0	0
20	0.464	47	131.5	1.3	0.185	0.003	712	6

21	0.592	59	100.6	36.7	0.191	0.035	515	151
22	0.472	41	130.2	1.6	0.184	0.002	707	14
23	0.337	70	108.5	7.4	0.155	0.009	701	27
24	0.482	62	126.7	15.4	1.556	2.310	438	287
25	0.314	70	107.3	5.6	0.149	0.008	722	42
26	0.441	50	133.3	0.4	0.182	0.002	734	7
27	0.239	79	57.5	39.9	0.122	0.001	470	326
28	0.469	66	47.4	51.2	0.154	0.039	269	277
29*	0.292*	57*	0.0*	0.0*	0.001*	0.000*	0*	0*
30	0.313	28	92.7	1.3	0.138	0.003	671	11
31	0.329	58	109.0	2.7	0.146	0.003	745	18
32	0.367	19	87.1	0.9	0.148	0.002	587	13
33	0.247	59	88.9	0.6	0.119	0.001	748	7
34	0.314	34	90.5	3.7	0.127	0.007	717	54

*An alignment error during spin coating resulted in no precursor solution deposited onto the glass slide. This outlier was removed in all following analyses.

Table S3. Repeatability of a pseudomobility measurement made using *Ada*. The Pseudomobility values shown below were measured on 10 replicate samples with nominal doping ratio 0.247 and annealing time 59 seconds. These samples were robotically prepared and characterized by the Ada platform in a single run over the course of 3.75 hours

Replicate number	Pseudomobility (nS)
1	662.5
2	667.7
3	640.4
4	655.8
5	643.8
6	651.1
7	659.7
8	663.9
9	657.5
10	658.2
mean	656.1
standard deviation	8.687
standard deviation / mean	1.324%

Supplementary movies

Movie S1 - Robotic workflow. For high-resolution version, see: https://youtu.be/0wVLjVdrYEE

This video shows the *Ada* robotic platform performing workflow steps identical or similar to those used to perform the experiments reported in the manuscript.