Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information for:

Visualisation of individual dopants in a conjugated polymer: sub-nanometre 3D spatial distribution and correlation with electrical properties

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Material Synthesis of p($g_4$2T-T)

A dried 500 mL round bottom flask was charged with 5,5'-dibromo-3,3'-bis(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)-2,2'-bithiophene (9.78 g, 13.28 mmol) and 2,5-bis(trimethylstannyl)thiophene (5.441 g, 13.28 mmol, 1.0 eq) and dissolved in dry, sparged (30 min with N_2) THF (250 mL). Then, tris(dibenzylideneacetone)dipalladium(0) (236 mg, 257.7 µmol, 1.94 mol-%), tri(o-tolyl)phosphine (313 mg, 1,03 mmol, 7.74 mol-%) were added under nitrogen atmosphere. After dissolving, the solution was heated to 70 °C under stirring, during which the color progressed from red to deep purple and the viscosity increased. After 96 hours reaction time, the solution was cooled to room temperature and poured into hexanes under vigorous stirring which yielded blue fibers. After filtration, the polymer was redissolved in $CHCl_3$ and vigorously stirred with a 5% m/v solution of sodium diethyldithiocarbamate trihydrate in DI water at reflux under N_2. The resulting emulsion proved impossible to break, so $CHCl_3$ was removed *in vacuo*, and the resulting aqueous suspension washed successively with isopropanol to remove water and Pd-complexing agent. Then, then the polymer was Soxhlet extracted with isopropanol, hexanes and diethyl ether until each washing yielded a clear extract. After collection with $CHCl_3$ and concentrating the polymer solution *in vacuo*, the polymer was precipitated in isopropanol, dried under vacuum to yield 8.1 grams (92.2%) of the target material as a blue fibrous and sticky material. 1H NMR (1 repeating unit, 400 MHz, Chloroform-d) δ 7.08 (s, 2H), 6.98 (s, 2H), 4.41 – 4.26 (m, 4H), 4.03 – 3.90 (m, 4H), 3.80 (m, 4H), 3.74 – 3.58 (m, 8H), 3.54 – 3.47 (m, 4H), 3.35 (s, 6H).

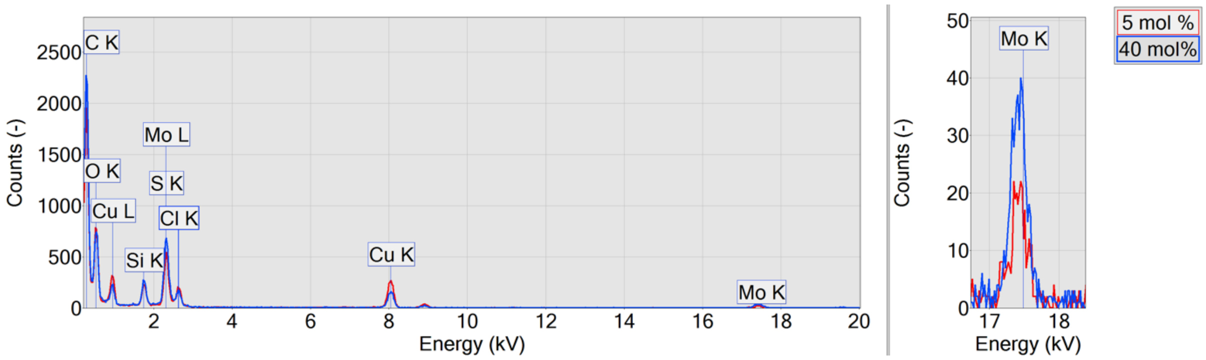

Figure S1: Energy dispersive X-ray spectroscopy (EDX) measurement of p($g_4$2T-T) doped with 5 mol% and 40 mol% Mo(tfd-$COCF_3$)$_3$, showing the presence of Mo from the dopant species.

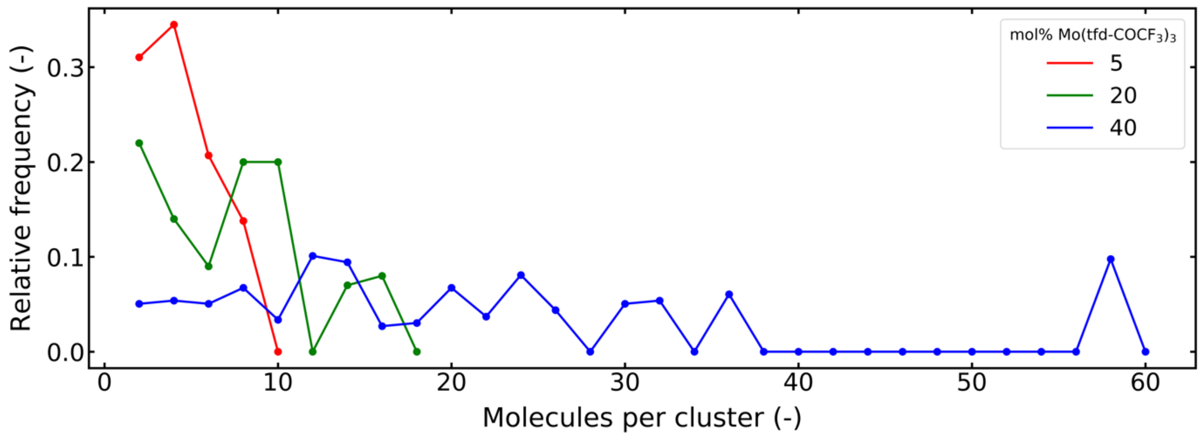

Figure S2: Distribution of the number of dopants per cluster, determined from data fit of dopant positions for 50 reconstructed clusters in each sample. Average cluster sizes of 3.4, 4.6, and 11 Mo(tfd-$COCF_3$)$_3$ species are calculated for 5 mol%, 20 mol%, and 40 mol%, respectively.

Table S1: Ionisation efficiency of Mo(tfd-COCF$_3$)$_3$ species. Values are calculated from UV-Vis-NIR absorption spectra.

Mo(tfd-COCF$_3$)$_3$ concentration (mol%)	Charge density (m^{-3})	Ionisation efficiency (%)
5	1.06×10^{26}	221 ± 25
10	1.91×10^{26}	187 ± 21
20	2.70×10^{26}	118 ± 13

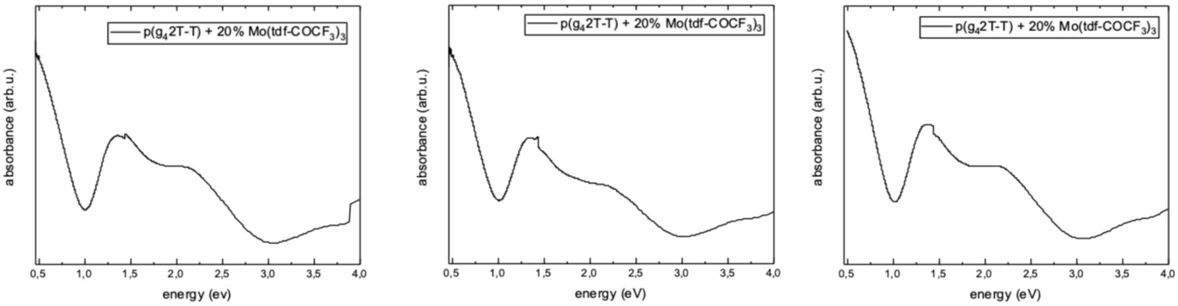

Figure S3: UV-vis-NIR absorbance spectra and electrical conductivity measurements repeated for three different samples of p(g$_4$2T-T) doped with 20 mol% Mo(tfd-COCF$_3$)$_3$ to analyse sample batch-to-batch reproducibility.