

Electronic Supplementary Information.

**Charge transfer dynamic in van der waals heterojunctions formed by
thiophene-based semiconductor polymer and exfoliated franckeite
investigated from resonantly core excited electron.**

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Fig. S2 S1s high-resolution XPS spectra of exfoliated franckeite, PFO-DBT/SiO₂ and PFO-DBT/Fr thin films.

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Table S2. Charge transfer times (τ_{CT}) in femtoseconds (fs) for PFO-DBT/Fr obtained using the sum (SGL) and product forms of Pseudo-Voigt profile functions

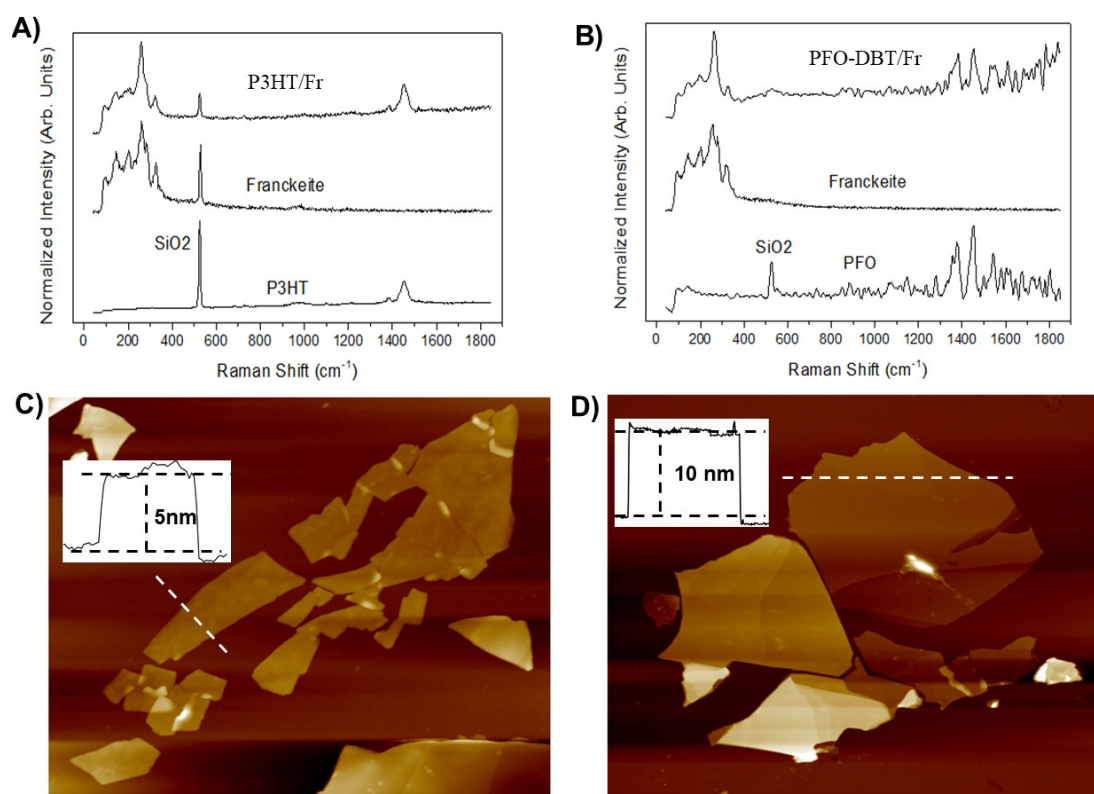


Fig. S1. A) Raman spectra of P3HT thin-film polymer, exfoliated franckeite and P3HT-DBT/Fr heterojunction. B) Raman spectra of PFO-DBT thin-film polymer, exfoliated franckeite and PFO-DBT/Fr heterojunction. C) and D) AFM topographic images of the exfoliated franckeite flakes.

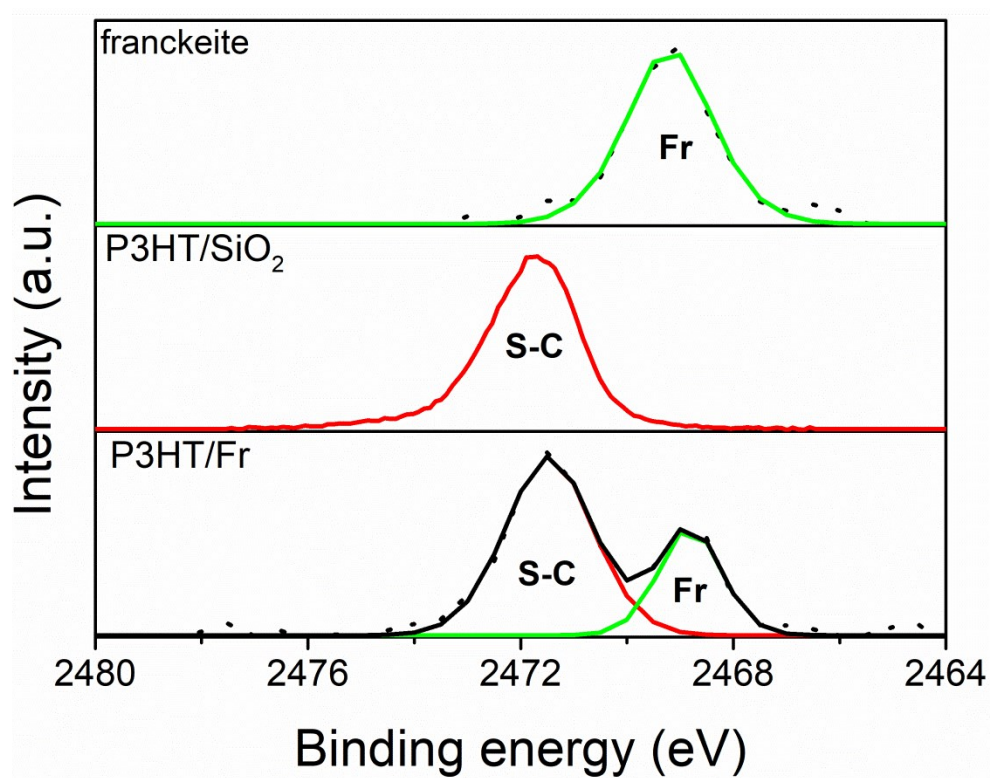


Fig.S2 S1s high-resolution XPS spectra of exfoliated franckeite, PFO-DBT/SiO₂ and PFO-DBT/Fr thin films.

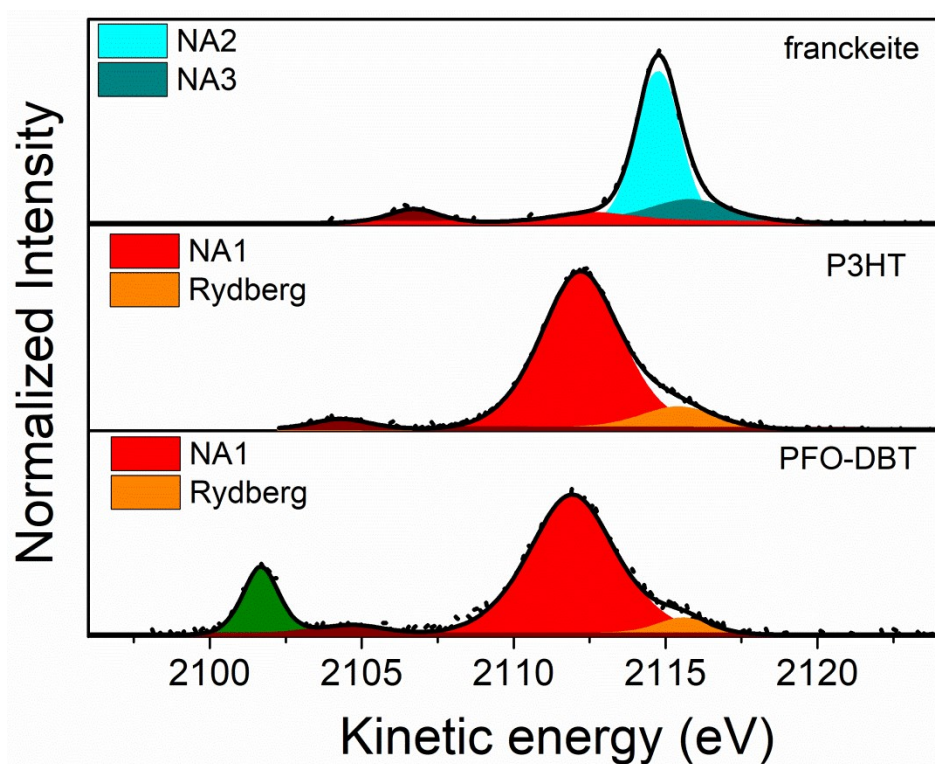


Fig. S3 Non-resonant Auger spectrum of PFO-DBT and P3HT copolymer and exfoliated franckeite measured at an X-ray energy of $h\nu=2500$ eV (above the ionization potential).

Table S1. Charge transfer times (τ_{CT}) in femtoseconds (fs) for PFO-DBT/SiO₂ obtained using the sum form (SGL) and product form Pseudo-Voigt profile functions.

Electronic Transitions	τ_{CT} (fs)	
	GL	SGL
	>12.7	>.12.7
B1 $\pi^*(S-N)$	8.33 (3)	8.80 (4)
T1 $\pi^*(S-C)$	2.69 (5)	2.63 (4)
B2 $\sigma^*(S-N)$	1.04 (4)	1.10 (6)
T2 $\sigma^*(S-C)$		

τ_{CT} standard deviation values are shown in parentheses.

Table S2. Charge transfer times (τ_{CT}) in femtoseconds (fs) for PFO-DBT/Fr obtained using the sum (SGL) and product forms of Pseudo-Voigt profile functions.

Electronic Transitions	τ_{CT} (fs)	
	GL	SGL
B1 $\pi^*(S-N)$	>0.127	>.12.7
T1 $\pi^*(S-C)$	0.158 (4)	0.180 (4)
B2 $\sigma^*(S-N)$	2.96 (4)	3.05 (4)
T2 $\sigma^*(S-C)$	1.81 (6)	2.02 (7)