Supplementary Material

1 SUPPLEMENTARY EQUATIONS AND PARAMETERS

1.1 Electronic coupling of electrode and organic material

The electronic coupling used in the expression for the injection rates J_{Xi} is given by:

$$J_{Xi} = j_0^{\text{electrode}} \cdot \exp\left(-2\frac{r_i}{\delta_0^{\text{electrode}}}\right), \tag{S1}$$

where $j_0^{\text{electrode}} = 0.001\,\text{eV}$, $\delta_0^{\text{electrode}} = 0.3\,\text{nm}$ and r_i the distance between the electrode and site i.

1.2 Electronic coupling for charge transfer from site to site

The electronic coupling J_{ij} is given by (similar to eq. S1):

$$J_{ij} = j_0 \cdot \exp\left(-2\frac{r_i j}{\delta_0}\right), \tag{S2}$$

where $j_0 = 0.001\,\text{eV}$ and $\delta_0 = 0.1\,\text{nm}$. The reorganization energy for all charge transfer processes is $\lambda = 0.2\,\text{eV}$.

1.3 Dexter couplings

As discussed in the main manuscript, we treat Dexter transfer similar to charge transfer by using Marcus theory. The couplings for Dexter processes are given by:

$$J_{ij}^{\text{Dexter}} = j_0^{\text{Dexter}} \cdot \exp\left(-2\frac{r_{ij}}{\delta_0}\right), \tag{S3}$$

where the maximum dexter coupling j_0^{Dexter} is $0.0001\,\text{eV}$. The decay length is the same as for regular charge transfer $\delta_0 = 0.1\,\text{nm}$.

1.4 Transition dipole moments

The norm of the transition dipole moments used in the Foerster coupling (9) in the main manuscript can be computed with:

$$|\vec{\mu}_i| = \sqrt{\frac{k}{\frac{4}{3}\tau_{\text{rad}}\alpha^3 (E_i^X)^3}}, \tag{S4}$$

where $k = 2.418\,884\,326\,509 \times 10^{-17}\,\text{s}$, τ_{rad} is the radiative life which is the inverse radiative decay rate given in table S3, $\alpha = 1/137$ is the fine-structure constant and E_i^X is the excitation energy of site i, which is defined in equation (6) in the main paper.

To obtain the vectorial transition-dipole moment, we generate a randomly orientated unit-vector $\vec{n}_i$ for each

site. The vectorial transition-dipole moment is then given by:

$$\vec{\mu}_i = |\vec{\mu}_i|\vec{n}_i \ . \tag{S5}$$

The orientation factor κ in the Foerster-coupling is given by:

$$\kappa = \vec{n}_i \cdot \vec{n}_j - 3\left(\frac{\vec{r}_{ij}}{r_{ij}} \cdot \vec{n}_i\right)\left(\frac{\vec{r}_{ij}}{r_{ij}} \cdot \vec{n}_j\right) \ , \tag{S6}$$

where $\vec{r}_{ij}$ is the displacement vector between site i and j and r_{ij} is its length.

2 SUPPLEMENTARY TABLE: SIMULATION PARAMETERS

In this section, we provide all simulation parameters, relevant for this work.

2.1 General simulation parameters

General parameters concerning the device setup.

Parameter	Value
Device cross-section	20×20 nm^2
Periodic boundary conditions $[x$ (transport axis), $y,\ z]$	[No, Yes, Yes]
Dielectric constant in all organic layers ϵ_r	4.0
Lattice constant a (cubic lattice)	1 nm
Temperature T	300 K
Number of kMC steps	50000000

Table S1. General Simulation parameters

2.2 Charge injection and transfer parameters

Parameters relevant for charge injection and charge transport. The numbers displayed in figure 1 of the main paper show the absolute values of mean HOMO and LUMO energy in each layer.

Parameter	Value
Anode Fermi-level	$-5.4\,\mathrm{eV}$
Cathode Fermi-level	$-2.4\,\mathrm{eV}$
Energetic disorder σ for all organic materials (HOMO and LUMO)	0.1 eV
Mean HOMO in HTL and ETL	$-5.8\,\mathrm{eV}$
Mean LUMO in HTL and ETL	$-2.0\,\mathrm{eV}$
Mean HOMO in EML (host)	$-5.8\,\mathrm{eV}$
Mean LUMO in EML (host)	$-2.0\,\mathrm{eV}$
Mean HOMO in EML (guest)	$-5.5\,\mathrm{eV}$
Mean LUMO in EML (guest)	$-2.3\,\mathrm{eV}$
Mean HOMO in HIL	$-5.6\,\mathrm{eV}$
Mean LUMO in HIL	$-2.0\,\mathrm{eV}$
Mean HOMO in EIL	$-5.8\,\mathrm{eV}$
Mean LUMO in EIL	$-2.2\,\mathrm{eV}$
Mean HOMO in HBL	$-6.3\,\mathrm{eV}$
Mean LUMO in HBL	$-2.0\,\mathrm{eV}$
Mean HOMO in EBL	$-5.8\,\mathrm{eV}$
Mean LUMO in EBL	$-1.5\,\mathrm{eV}$
Parameters for transfer integrals	see equations S1 and S2
Max coupling electrode-organic $j_0^{\mathrm{electrode}}$	$0.001\,\mathrm{eV}$
Decay length for coupling electrode-organic $\delta_0^{\mathrm{electrode}}$	$0.3\,\mathrm{nm}$
Max coupling organic-organic j_0	$0.001\,\mathrm{eV}$
Decay length for coupling organic-organic δ_0	$0.1\,\mathrm{nm}$
Reorganization energy λ used in Marcus rates for charge transfer	$0.2\,\mathrm{eV}$

Table S2. Simulation parameters for charge injection and charge transport.

2.3 Excitonic parameters

Table S3 shows all excitonic rates and parameters.

	non-emitters	emitters
ISC-rate	$1 \times 10^3\,\mathrm{s}^{-1}$	$1 \times 10^{14}\,\mathrm{s}^{-1}$
RISC-rate	$1 \times 10^2\,\mathrm{s}^{-1}$	$1 \times 10^6\,\mathrm{s}^{-1}$
thermal decay rate	$1 \times 10^5\,\mathrm{s}^{-1}$	$1 \times 10^5\,\mathrm{s}^{-1}$
Exciton reorganization energy	$0.3\,\mathrm{eV}$	$0.3\,\mathrm{eV}$
Excitonic binding energy	$0.8\,\mathrm{eV}$	$0.8\,\mathrm{eV}$
Singlet-Triplet gap	$0.3\,\mathrm{eV}$	$0.3\,\mathrm{eV}$
Radiative decay rate S1	$1 \times 10^8\,\mathrm{s}^{-1}$	$1 \times 10^8\,\mathrm{s}^{-1}$
Radiative decay rate T1	$1 \times 10^1\,\mathrm{s}^{-1}$	$1 \times 10^6\,\mathrm{s}^{-1}$
Max TTA rate	$1 \times 10^6\,\mathrm{s}^{-1}$	$1 \times 10^{11}\,\mathrm{s}^{-1}$
Max TPQ rate	$1 \times 10^6\,\mathrm{s}^{-1}$	$1 \times 10^{11}\,\mathrm{s}^{-1}$
Parameters for Dexter transfer integrals	see equation S3	
Max Dexter coupling j_0^{Dexter}	$0.0001\,\mathrm{eV}$	$0.0001\,\mathrm{eV}$
Decay length for Dexter coupling δ_0	$0.1\,\mathrm{nm}$	$0.1\,\mathrm{nm}$

Table S3. Additional parameters for the excitonics.

3 SUPPLEMENTARY FIGURES

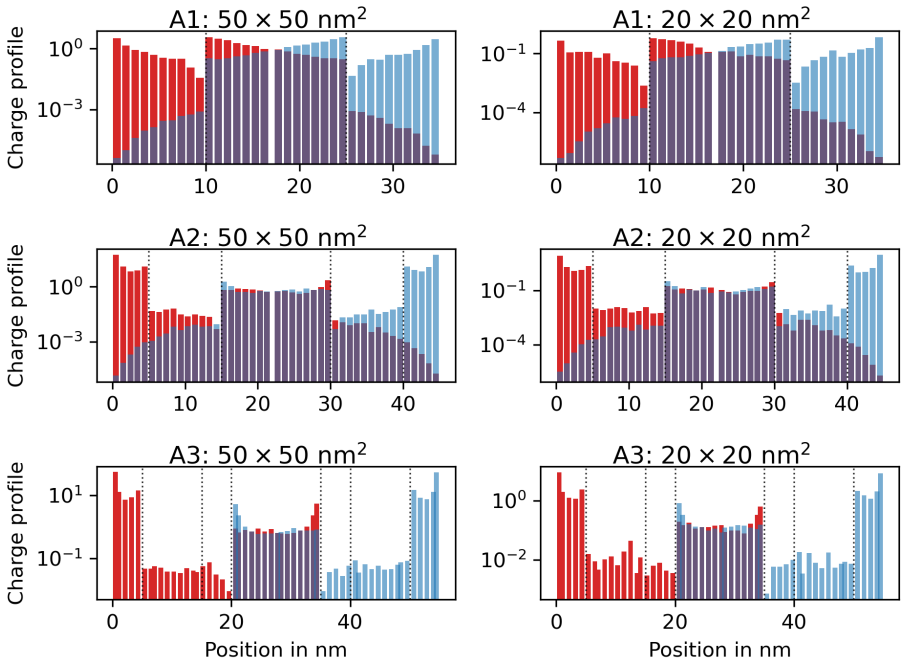

Figure S1. Charge carrier profiles of all three device architectures with different cross-section. The layer thicknesses are identical to the layer thicknesses in figure 3 of the main paper. The results indicate that a cross section of 20×20 nm^2 is sufficient to qualitatively capture the charge carrier distributions.