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Supplementary Information

Understanding trends in conductivity in four isostructural multifunctional crystals of Se Substituted BisDithiazolyl radicals

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Section 1: Choice of active space for CASSCF calculation of reorganization energy, λ .

Reorganization energies were calculated at CASSCF and CASPT2 levels using a (7,7) for neutral monomers and, (6,7) and (8,7) active spaces for cation and anion, respectively (see main text Table 1 for results). Note that (n,m) refers to (number of electrons, number of orbitals). The choice of the seven molecular orbitals and seven electrons active space was made to consider both the symmetry and the occupation of the orbitals. The selected active space was the minimal that recovered the symmetry of the orbitals. Note that the occupation numbers of the active orbitals range from 0.05 to 1.94. See below natural orbitals with associated occupation number corresponding to (3,3), (5,5) and (7,7) active spaces for the (S,S) bisDTA material.







1.000

1.000



0.086

0.105

0.11



0.059

0.077





Figure S1.1 Representation of natural orbitals included in the active spaces of CASSCF(3,3), CASSCF(5,5) and CASSCF(7,7) calculations. Occupation number is included below each orbital.

Section 2: Crystal packing analysis and cluster model selection for evaluation of H_{DA} electronic couplings.

The four bisDTA crystals studied (namely, pure bisdithiazolyl (S,S), mixed thiaselenazolyl (S,Se) and (Se,S), and pure bisdiselenazolyl (Se,Se) according to the (E_1,E_2) element substitution, see Figure S2.1a) are isostructural and, excluding small differences in distances and tilting angles, display analogous crystal packing. All four derivatives share a tetragonal unit cell of $P\overline{4}2_1m$ symmetry. The packing of these materials consists of eclipsed π -stacks of four symmetry equivalent molecules around a C₄ axis, parallel to the *c*-crystalline direction (see Figure S2.1b).

Hereafter we describe the terminology used for all of them in order to name the selected radical···radical interactions (note the crystal data is extracted from X-Ray structure at 100 K). Taking a radical (identified as "central" in Figure S2.2) as reference, the *ab*-plane of the crystal shows five non-symmetry related π -stacks (namely, 1, 2, 3, 5 and 8 in Figure S2.2a, which are highlighted in blue). Notice that π -stacks 4, 6 and 7 are equivalent to 2, 3 and 5, respectively. Further analysis shows that the interactions between "central-2" and "central-5" radicals are equivalent. From each π -stack, the three radicals closest to the central reference radical are referred to as "#a, "#b" and "#c", where # stands for the number that identifies the stack (see Figure S2.2b).



Figure S2.1. (a) Radicals are classified according to whether E_1 and E_2 positions are S or Se atoms. In the following, radicals will be referred to as (E_1, E_2) , namely, as pure bisdithiazolyl (S,S) radical, mixed thiaselenazolyl (S,Se) and (Se,S) radicals, and pure bisdiselenazolyl (Se,Se) radical. (b) Crystal structure of pure bisdithiazolyl (S,S) material. View of *ab*-plane of the unit cell with a 4-fold pinwheel-like center.



Figure S2.2. Selection of pairs of radicals that might contribute to the overall conductivity. (a) View along the *ab*-plane (see region highlighted in blue for non-symmetry related π -stacks). (b) View along the π -stacking (*c*-axis) direction of the 3 dimers formed by the "central" reference radical and the radicals in the π -stack numbered "2".

A total of 13 dimers for each system have been selected, i.e., the pairs of radicals evaluated are central vs. 1a-c, central vs. 2a-c, central vs. 3a-c, central vs. 8a-c, and central vs. top (or bottom) radical to assess the π -stack (see Figure S2.2 for a clear view of the dimers).

Section 3: Koopman's theorem variation for open-shell materials constituted by monoradical centers

The Koopmans' theorem is a commonly used approximation to evaluate electronic couplings (H_{DA}) . In the Restricted Hartree-Fock framework and assuming that orbitals for the ion form are equivalent to those for the neutral molecule, this theorem states that the first ionization energy of a molecule is equal to the energy of the HOMO with a sign reversal. Thanks to this approach, electron H_{DA}^- (hole H_{DA}^+) electronic couplings can be estimated as half the energy difference between the LUMO+1 and LUMO (HOMO and HOMO-1) (see Figure S3.1a, where L, H, and S stand for LUMO, HOMO, and SOMO respectively).



Figure S3.1. Schematic representation of the Koopman's theorem applied to (a) a closed-shell singlet moiety and (b) open shell dimer cluster for the evaluation of electron (H_{DA}^{-}) and holes (H_{DA}^{+}) or mean (\overline{H}_{DA}) electronic couplings.

Although this theorem has been successfully applied in the study of closed-shell systems, the hypothesis assuming that HOMO/HOMO-1 and LUMO+1/LUMO orbitals govern the description

of hole and electron mobility fails when applied to open-shell materials constituted by monoradical centers using a spin unrestricted formalism. Indeed, in this type of materials, according to Koopmans' theorem, first excitation energies for positively and negatively charged systems should be evaluated using the same pair of orbitals, i.e., the singly occupied molecular orbitals of the dimer cluster (SOMO, S1 and S2 in Figure S3.1b). This obviously prevents the individual evaluation of H_{DA}^+ and H_{DA}^- for open-shell singlet moieties (e.g., two S=1/2 radicals) according to Koopmans' theorem. It is then a must to adapt Koopmans' theorem to this new scenario.

In this study, we propose (and test) a modification of this well-known theorem designed for investigating open-shell materials using Restricted Open-Shell Density Functional Theory (RODFT). Firstly, the adapted method was validated by comparing the mean value of \overline{H}_{DA} obtained with CASSCF first excitation energies and $\overline{H}_{DA,K}$ values computed using $\overline{H}_{DA,K} = (E_{S1} - E_{S2})/2$) at 2b, 2c and π dimers for all 4 materials (for further details regarding nomenclature, please refer to SI Section 2). Then, the theorem was used to scan the 10 remaining pairs that could entail charge transport within the crystal packing.

Results obtained (see Table S3.1) show agreement in the order of magnitude with CASSCF calculations (see main text Table 2), validating the used of this methodology for a first screening to identify the most relevant contacts. However, the trends of the CASSCF results are at odds with the Koopman's estimated values according to which H_{2b} and H_{2c} were predominant compared to H_{π} . Hence the need to perform higher level state-specific charge localized CASSCF calculations to evaluate electronic couplings. Overall, the analysis conducted using the adapted Koopman's theorem on all four compounds revealed that, out of the thirteen directions studied, relevant conductivity-contributing contacts occurred only along three specific directions. CASSCF calculations were then necessary to precisely determine their individual contributions and their relative importance in the material's conductivity.

Table S3.1. Computed $\overline{H}_{DA, K}$ for the 13 pairs of radicals selected thought to exhibit a non-negligible electronic coupling based upon a distance criteria. Note that the largest contributions are due to 2b, 2c and π pairs for the four bisDTA S/Se materials.

	1a	1b	1c	2 a	2b	2c	3 a	3b	Зс	8a	8b	8c	π
(S,S)	4.38	1.02	4.38	2.54	63.66	32.39	4.32	4.43	4.32	2.78	0.03	2.78	20.46
(S,Se)	4.64	1.04	4.62	10.61	87.82	90.97	4.73	7.43	4.73	3.30	0.00	3.29	15.27
(Se,S)	9.85	2.17	9.83	4.26	13.17	104.60	7.16	3.79	7.16	2.45	0.01	2.45	43.44
(Se,Se)	10.16	2.55	10.16	16.88	108.78	56.63	6.04	6.44	6.04	2.35	0.00	2.35	33.99

Section 4: Choice of active space for CASSCF calculation of electronic coupling, H_{DA}

The H_{DA} electronic coupling has been computed using the selected 13 dimers detailed in the previous Section 2 for all four bisDTA-based S/Se compounds. After the dimer selection, the two diabatic charge localized states (either D^+A / DA^+ or D^-A / DA^-) were computed via state-specific CASSCF calculations, to then obtain the adiabatic energies needed to compute H_{DA} using RASSI. The diabatic calculations at the TS geometry have been computed at CASSCF level using a (15,14) and a (13,14) active space for anion and cation calculations, respectively.

Note that, since two molecules are considered in the calculations, the natural orbitals included in the active space are twice those chosen in the λ reorganization energy evaluation (see SI Section 1). In this case, the total number of 15 / 13 electrons comes from subtracting or adding one electron for anion and cation solutions, respectively. In the following, the 14 orbitals of four calculations, both diabatic solutions of bisdithiazolyl (S,S) 2b and π dimers, are shown as an example.

(S,S) - 2b orientation: Diabatic calculation, state 1





0.120024

1.003980



0.111325

0.027936



0.073231



0.074206









Figure S4.2 Representation of the 14 natural orbitals included in the active space. Occupation number is shown below each orbital.

(S,S) - π -stacking : Diabatic calculation, state 1





Figure S4.3 Representation of the 14 natural orbitals included in the active space. Occupation number is shown below each orbital.

(S,S) - π -stacking : Diabatic calculation, state 2









Figure S4.4 Representation of the 14 natural orbitals included in the active space. Occupation number is shown below each orbital.

Section 5: Donor-Acceptor charge distribution

Inner reorganization energies (λ_{in}) account for the geometric adjustments that both donor and acceptor undergo to accommodate to their new state after the fast charge transfer process has taken place. It can be computed using a 4-point scheme as:

$$\lambda_{in} = [E_c(R^N) + E_N(R^C)] - [E_c(R^C) + E_N(R^N)]$$

where E_c denotes the energy of the charged system (anion (D^-) or cation (A^+) for electron and hole transport, respectively), E_N is the energy of the neutral system, and R^N (R^c) are the equilibrium geometries of the neutral (charged) radicals.

Mulliken charges were obtained in all four calculations when evaluating the energy of the charged system at the R^N and R^C geometries, and of the neutral system using R^C and R^N geometries, for both hole (cation) and electron (anion) transport. Analysis of the resulting charge distribution shows that in all cases, the extra charge obtained (or lost) is mainly delocalized over the external N-E₁-E₂ positions (see positions in Figure S5.1). Tables S5.1 and S5.2 display the differences between the Mulliken charges of charged and neutral monomers for each geometry (R^N and R^C), indicating that, in all four materials, approximately 80% of the charge (positive or negative) is localized over these lateral positions.



Figure S5.1. General molecular representation of bisDTA radicals studied in this work. The orange circles indicate the $N-E_2-E_1$ positions where the most significant changes in charge are located.

	(S,S)		(S	,Se)	(Se	,S)	(Se,Se)		
	R ^ℕ	R ^{C+}	R ^ℕ	R ^c	R ^ℕ	R ^c	R ^ℕ	R ^c	
Central ring + R_1 + R_2	0.2477	0.2541	0.2492	0.1637	0.1991	0.2755	0.1990	0.2029	
N+E ₁ +E ₂	0.7523	0.7459	0.7509	0.8363	0.8009	0.7245	0.8010	0.7971	

Table S5.1. Mulliken charge differences between neutral (N) and cation solutions (C) per geometry.

Table S5.2. Mulliken charge differences between neutral (N) and anion solutions (C) per geometry.

	(S,S)		(S,	Se)	(Se	e,S)	(Se,Se)		
	R ^ℕ	R ^{c-}	R ^N	R ^{c-}	R ^ℕ	R ^{c₋}	R ^ℕ	R ^{c₋}	
Central									
$ring+R_1+R_2$	-0.2382	-0.1802	-0.1893	-0.1847	-0.2317	-0.1997	-0.1924	-0.1852	
N+E ₁ +E ₂	-0.7618	-0.8198	-0.8107	-0.8153	-0.7683	-0.8003	-0.8076	-0.8148	

Section 6: Qualitative insights into reorganization energy and electronic coupling of (S,Se) and (Se,S)

In the main text we have shown that the reorganization energy of (S,Se) is larger than for (Se,S) and that the electronic coupling is smaller for (S,Se). Here we will give qualitative insights into these values.

The reorganization energy (λ) originates in changes taking place inside the charge carrier (assuming, as we have done, that the outer-sphere contribution to λ can be neglected). Contrarily, the electronic coupling arises from the interaction between any two of those charge carriers. Bearing the different origin in mind, reorganization energy and electronic coupling need not be correlated. Having said that, we will now try to give some qualitative physical explanation for the trends on reorganization energy and electronic coupling of (S,Se) and (Se,S) compounds.

We will first focus on the reorganization energy. Since conductivity is mainly driven by holes, the following discussion will exclusively focus on neutral radicals and cations. Analyses of intramolecular distances show that (S,Se) experiences larger changes upon loss of an electron than (Se,S), as seen in Figure S6.1, where negative values mean that the distance is larger in the neutral radical, while positive values translate into larger distances in the cation, and Table S6.1 for individual distances between different pairs of atoms in the neutral radical and cation. The largest changes observed for (S,Se) mean that it is more difficult for this compound to adapt structurally to a new oxidation state, which is consistent with its largest value of reorganization energy compared to (Se,S). For instance, the most modified distance in both cases (see Figure S6.1), namely C3-S17 and C4-S18 for (S,Se) and C2-Se19 and C3-Se20 for (Se,S) can be explained with the topology of the SOMO (see Figure S6.2). Indeed, these distances are associated with the pair of atoms with the largest antibonding contribution to each SOMO. Upon removing an electron from this orbital, the bond distance will necessarily decrease. For (S,Se) the change is slightly larger because the SOMO is more localized on those atoms than for (Se,S).

We can also provide chemical insight upon examination of the atoms involved in the bond undergoing the largest variation. Our results show that, not only the change in C-S bond distance is larger, but the energetic penalty associated with this change is expected to be higher because the C-S bond is stronger than C-Se. Therefore, this further is in agreement with the trend in reorganization energy.

As for the electronic coupling, we will use once again the topology of the SOMOs to explain the tendency for (S,Se) and (Se,S) (see Figure S6.2). For the π -dimers, the SOMO is less distributed for (S,Se) (note that contribution in E₁ position is larger for (S,Se) than (Se,S)). Therefore, the higher degree of localization is expected to lead to a larger overlap and, in turn, to a larger electronic coupling. The same argument can be extended to the lateral 2b orientation (see Figure S6.3 for a sketch of the main overlapped regions).



Figure S6.1. Values of the difference between relevant bond distances of the cation and neutral geometries ($d_c - d_N$ in Å) for (a) (S,Se) and (b) (Se,S). Note that negative values mean that the distance is larger in the neutral radical, while positive values translate into larger distances in the cation.

Table S6.1. Relevant distances in Å between different atom pairs of isolated (S,Se) and (Se,S) molecules, using either the optimized geometry of the cation state or neutral radical (UB3LYP/6-311+G(d,p) level). Note that $(d_c - d_N)$ stands for the difference between the distance in the cation (C) and the neutral (N) geometries. See atom numbering in Figure S6.1.

(S,Se)	cation,C	neutral,N	$d_C - d_N$	(Se <i>,</i> S)	cation,C	neutral,N	$d_C - d_N$
d(1-3)	1.459	1.447	+0.012	d(1-2)	1.393	1.390	х
d(1-14)	1.302	1.306	х	d(1-3)	1.393	1.390	х
d(1-16)	1.384	1.393	-0.009	d(2-4)	1.452	1.444	+0.008
d(2-4)	1.459	1.447	+0.012	d(2-19)	1.862	1.897	-0.035
d(2-15)	1.302	1.306	х	d(3-5)	1.452	1.444	+0.008
d(2-16)	1.383	1.392	-0.009	d(3-20)	1.862	1.897	-0.035
d(3-5)	1.395	1.392	х	d(4-14)	1.304	1.304	х
d(3-17)	1.719	1.757	-0.038	d(4-16)	1.383	1.392	-0.009
d(4-5)	1.396	1.392	х	d(5-15)	1.304	1.304	х
d(4-18)	1.719	1.757	-0.038	d(5-16)	1.383	1.392	-0.009
d(14-19)	1.790	1.823	-0.033	d(14-17)	1.634	1.666	-0.032
d(15-20)	1.791	1.823	-0.033	d(15-18)	1.634	1.666	-0.032
d(17-19)	2.266	2.291	-0.025	d(17-19)	2.275	2.304	-0.029
d(18-20)	2.266	2.291	-0.025	d(18-20)	2.275	2.304	-0.029



Figure S6.2. Representation of the SOMO for an isolated (a) (S,Se) and (b) (Se,S) radical (isovalue=0.08).



Figure S6.3. Schematic representation of the overlap between SOMOs for the lateral 2b dimer of (a) (S,Se) and (b) (Se,S). Note that it is only shown the fragments directly involved in the overlap of SOMOs. Also note that the size of the π -orbital projected onto individual atoms is proportional to its contribution to the global SOMO

Section 7: Calculation of density of charge carriers, ρ_C

The density of charge carriers (ρ_c) is here obtained by evaluating the Density of States (DOS) diagram of each bisDTA crystal. In an intrinsic pure semiconductor, the concentration of electrons (or holes) comes from the excitation of electrons from the valence to the conduction bands and, using the quadratic approach of these bands, DOS can be evaluated by means of the band gap (E_g in equation S7.1).

$$\rho_c = 2 \left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2k_B T} \quad (Eq.S7.1)$$

where m_e and m_h are the effective masses of electrons and holes, respectively, assumed to be the free electron mass, and E_g values are obtained from the DOS diagram evaluated for the electronic ground state of all four crystals at UB3LYP level reported in a previous work (Roncero-Barrero et al. *Phys. Chem. Chem. Phys.*, 2022, **24**, 12196-12207. DOI: 10.1039/d2cp00415a). Without the presence of impurities in the material, both carrier's concentrations, namely holes and electrons, are equivalent.

Let us now comment on the previous Equation S7.1. The estimated density of charge carriers ρ_c depends on E_g , which is related to the activation energy associated with the charge transfer process, E_a (see Table S7.1). As mentioned above, currently, our calculation of this activation energy is restricted to vertical gaps using the ground state data, i.e., between its valence band maximum and conduction band minimum (namely, the electronic band gap). Therefore, this rigid band model approach misses relaxation processes undergone by the conduction band upon charge transfer. As such, the calculated rigid E_g fails to fully capture the physics of the conductivity process in these molecular systems. However gross the approximation is, we will still use with caution the estimated rigid E_g values to calculate ρ_c because our main goal is to study how and why the conductivity is different for the four isostructural title compounds and the conductivity is the only available experimental evidence against which we can validate all our calculations.

Analysis of the electronic band structure of the ground states of the present bisDTA-derivatives, showed that all four title materials presented similar bands with optic band gaps around 1.15 - 1.34 eV (see Table S7.1). Given that (1) these values are between 3 and 6 times larger than the experimentally determined E_a values (ranging from 0.43 to 0.19 eV) and that (2) ρ_c depends exponentially on E_g , the resulting calculated ρ_c values are expected to be massively underestimated. This will, in turn, imply that the calculated σ conductivities are to be smaller than the experimentally measured data. Absolute values of calculated ρ_c and σ are reported in Table S6.1. It is in order to minimize the impact of this issue that we report conductivity ratios in our main text. Note that the calculation of σ conductivity as " $\mu q \rho_c$ " uses the total mobility, i.e., both contributions from electron and hole mobilities, whose absolute value is in line with other calculations and also with experimental data. This has been corroborated using our

calculated mobilities and the experimental conductivity to estimate the density of charge carriers, ρ_C^{est} , as a reality check. The absolute values of ρ_C^{est} are now sensible. As a result, the trends follow the experimental relative ordering regardless of the absolute values and, consequently, in the main text we proceed discussing relative values.

Table S7.1. Computed optic band gap (E_g in eV), density of charge carriers (ρ_c^{calc} in m⁻³), total mobility at 300 K (μ in cm²/Vs), and conductivity (σ^{calc} in S·cm⁻¹). Estimated density of charge carriers (ρ_c^{est} in m⁻³) using calculated total mobility and experimental conductivity. Reported E_a and σ^{Exp} at 300 K from Robertson et al. *J. Am. Chem. Soc.*, 2008, **130**, 8414–8425. DOI: 10.1021/ja801070d.

	E _a (eV)	E _g (eV)	$ ho_{\it C}^{\it calc}$ (m ⁻³)	μ (cm²/Vs)	σ ^{calc} (S·cm ⁻¹)	σ ^{Exp} (S·cm⁻¹)	$ ho_{\it C}^{\it est}$ (m ⁻³)
(S,S)	0.43	1.34	1.39·10 ¹⁴	0.026	5.71·10 ⁻¹³	3.20·10 ⁻⁶	7.80·10 ²⁰
(S,Se)	0.27	1.15	5.97·10 ¹⁵	0.084	7.99·10 ⁻¹¹	1.00.10 -4	7.48·10 ²¹
(Se,S)	0.31	1.26	7.13·10 ¹⁴	0.106	1.22·10 ⁻¹¹	2.20·10 ⁻⁵	1.29·10 ²¹
(Se,Se)	0.19	1.17	3.73·10 ¹⁵	0.238	1.42·10 ⁻¹⁰	3.00·10 ⁻⁴	7.87·10 ²¹

Section 8: Analysis of disproportionation energies.

We have evaluated the disproportionation energy (ΔE_{disp} , see Table S8.1) associated to the reaction:

$$R^{\bullet} + R^{\bullet} \to R^+ + R^-$$

As it can be observed, the largest energy is associated to (S,S) and the lowest to (Se,Se), which translate into a larger energy requirement to generate the charge carriers for (S,S). This tendency is in remarkable agreement with the experimental activation energies reported in main text Figure 1b and Ref. 41. This is an additional corroboration that the energies used to assess reorganization energies are well evaluated. It is worth noting that ΔE_{disp} for (S,Se) is slightly smaller than for (Se,S), which agrees with the former having a larger density of charge carriers (see main text Table 4 for ρ_c^{est}). Note that our calculated ΔE_{disp} values are very similar to previously published values for closely related molecules where Chlorine and Ethyl substituents were replaced by H atoms (Beer *et al. J. Am. Chem. Soc.* **2005**, *127*, 1859). Despite the observed agreement in trends, the estimated ΔE_{disp} values are one order of magnitude larger than the experimentally obtained activation energies. This is most likely because of the model system we have used, which exclusively considers isolated molecules, thus, neglecting the strong electrostatic interactions between cation and anion species and the polarizability of the solid-state material.

Table S8.1. Computed ionization potential (IP), electron affinity (EA) and disproportionation energy (ΔE_{disp}) for the four title compounds. Also, the experimentally obtained activation energy (E_a) is reported for comparison purposes. Note all units are eV. All energies have been calculated at UB3LYP/6-311+G(d,p) level.

/ eV	(S,S)	(S,Se)	(Se,S)	(Se,Se)
IP	6.298	6.246	6.270	6.228
EA	1.869	1.927	1.946	2.007
ΔE_{disp}	4.429	4.319	4.325	4.221
E_a (exp)	0.43	0.27	0.31	0.19

The available experimental evidence against which we can compare our calculated ΔE_{disp} comes from cyclic voltammetry (CV) data (Robertson *et al. J. Am. Chem. Soc.* **2008**, *130*, 8414). These data provide the $E^{R^+|R^+}$ and $E^{R^+|R^-}$ half-wave reduction potentials, which refer to the following reactions: $R^+ + e^- \rightarrow R^-$ and $R^+ + e^- \rightarrow R^-$, respectively. Let us here use $\Delta E_{CV} = E^{R^+|R^+} = E^{R^+|R^+}$ as a signature of the feasibility of the electrochemical charge separation process. The less negative ΔE_{CV} value for (S,Se) as compared to (Se,S), -0.744 V vs -0.839 V, is in accord with the smaller computed ΔE_{disp} of (S,Se). Therefore, the CV data hints at favoring the generation of charge carriers in (S,Se). However, the outcome from this analysis should be considered carefully since the disproportionation energies were computed in gas phase while the CV data is measured in solution. For instance, across the title compound series, the values of experimental $E^{R^+|R^+}$ do not correlate so well with our calculated ionization potentials (IP) (see Table S8.1). While $E^{R^+|R^+}$ decrease monotonously along with the increase of Se content (namely, -0.018 V for (S,S), +0.013 V for (S,Se), ±0.026 V for (Se,S) and ±0.053 V for (Se,Se)), the calculated IPs do decrease from (S,S) to (Se,Se), but do not follow the experimental monotonous tendency because IP_{SSE} < IP_{SES}.

Section 9: Effect of anisotropy on the transport properties.

Along this work, we report bulk isotropic mobilities and, thus, isotropic conductivities, for four single-component organic radical conductors since the experimental measurements were performed using powder samples. Specifically, bulk isotropic mobilities depend on the diffusion coefficient (*D*), which is calculated using the Einstein-Smoluchowski relation ($\mu = q D/k_BT$ in main text Equation 4). In turn, the *D* diffusion coefficient of a molecular conductor can be approximated as an average over all crystal directions, as if the sample was powder ($D \approx (1/2n) \sum_i r_i^2 k_{DA,i} p_i$ in main text Equation 5). For a crystal with spatial dimensionality n = 3, the calculation of *D* coefficient involves assessing which is the distance between 'D' donor and 'A' acceptor molecular centres (r_i). In particular, r_i is chosen as the shortest distance between N…E₁ atoms (see main text Table 2). The probability (p_i) for each hop "*i*" to occur is here chosen to be computed as $p_i = k_{DA,i}/\sum_i k_{DA,i}$. Within this context, Equation 5 effectively averages over all crystal directions treating the sample as if it were powder, which it is. Therefore, neither experiment nor calculations bring any information regarding the anisotropy of the conductivity.

Let us now make a remark on the effect that anisotropy would have on the transport properties. Analysis of the differences in the magnitude of the charge transfer rate constants depending on the conduction path (see Table S9.1) hint at a potential role of anisotropy if it was possible to make measurements of conductivity along either the π -stack or the 2b orientation. This conclusion is also supported by the probabilities of charge transfer through the three different conduction paths, namely, π , **2b** and **2c** channels (see Table S9.1), which in addition enable us to discriminate between the dimensionality of the four title compounds in terms of their microscopic conduction paths within the crystal. It is also worth mentioning that, although hole conduction is dominant over electron conduction in all four pyridine-bridged bisDTA-based compounds, the contribution of both mobilities will be considered to calculate anisotropic conductivities (see Table S9.2 for further details).

		(5	5,S)		(S,Se)				(Se,S)				(Se,Se)			
	$k_{\rm DA}^+$	p_i^+	$k_{\rm DA}^-$	p_i^-	$k_{\rm DA}^+$	p_i^+	$k_{\rm DA}^-$	p_i^-	$k_{\rm DA}^+$	p_i^+	$k_{\rm DA}^-$	p_i^-	$k_{\rm DA}^+$	p_i^+	$k_{\rm DA}^-$	p_i^-
π	3.24	0.92	0.22	0.52	10.65	0.75	1.10	0.37	12.23	0.95	1.68	0.47	25.4	0.81	8.11	0.57
2b	0.26	0.07	0.19	0.45	3.57	0.25	1.87	0.63	0.12	0.01	0.98	0.28	5.38	0.17	5.30	0.37
2c	0.02	0.01	0.01	0.02	0.02	0.00	0.01	0.00	0.55	0.04	0.89	0.25	0.58	0.02	0.78	0.05

Table S9.1. Hole (+) and electron (-) transfer rate constants (k_{DA}^+) in THz and corresponding probabilities.

We will first computationally perform the measurement of conductivity as if a single crystal was available and could be aligned along the π -stacking (see Table S9.2). Specifically, hole and electron mobilities would only have contribution coming from that direction $(k_{\pi}^+ \text{ and } k_{\pi}^-)$ (see Table S9.1). Our results show that in the worst-case scenario, namely for (S,S) and (Se,S) 1D conductors, the mobility is enhanced by *ca*. 8%. Instead, the enhancement achieved by (S,Se) and (Se,Se) 3D conductors is about 14% and 20%, respectively. Consequently, within this family, the distinction between the least effective and most effective conductors would become more pronounced. Note that the mobility would highly diminish if the single crystal would be oriented along the 2b direction. This brings a second possible experiment using single crystals, namely, switching the direction of the electric field, be it either along π or 2b charge channels. Our estimates show that (Se,S) would feature the largest difference in terms of conductivities between the 'on' and 'off' states. However, this difference (*ca*. one order of magnitude) is likely too small to envisage possible applications.

Table S9.2. Calculated hole (+), electron (-) and total mobilities (in cm²/Vs) for the original powder case, and for a single crystal aligned along either π or 2b directions. Note ' π /orig' refers to the ratio between both cases (is given in %). Calculated conductivity (in S/cm) with total mobility for a single crystal aligned along either π or 2b directions.

		(S,S)		(S,Se)				(Se,S)		(Se,Se)			
cm²/Vs	μ_i^+	μ_i^-	μ_i	μ_i^+	μ_i^-	μ_i	μ_i^+	μ_i^-	μ_i	μ_i^+	μ_i^-	μ_i	
original	0.024	0.002	0.026	0.071	0.012	0.084	0.096	0.010	0.106	0.184	0.054	0.238	
π	0.026	0.002	0.028	0.087	0.009	0.096	0.101	0.014	0.115	0.219	0.070	0.289	
π/orig			+8%			+14%			+8%			+21%	
2b	0.002	0.001	0.003	0.027	0.014	0.041	0.001	0.007	0.008	0.039	0.038	0.077	
S/cm													
σ_{π}	(1)	3.47·10 ⁻	6	1.15·10 ⁻⁴			2	2.38.10-	5	3.64·10 ⁻⁴			
σ_{2b}	Z	4.07·10 ⁻	7	4.89·10 ⁻⁵			1.86·10 ⁻⁶			9.69·10 ⁻⁵			
σ_{π}/σ_{2b}		9		2				13		4			