Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Material for

Structural diversity in conducting bilayer salts (CNB-EDT-TTF)$_4$A

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Experimental

Synthesis and Electrochemical Crystallization

(CNB-EDT-TTF)$_4$AuI$_2$, (CNB-EDT-TTF)$_4$I$_2$Br, and (CNB-EDT-TTF)$_4$AsF$_6$ charge transfer salts were prepared as small single crystals following the previously described procedures to prepare other compounds in this family.[1] A dichloromethane solution of the donor CNB-EDT-TTF and the corresponding anion salt *n*-Bu$_4$NAuI$_2$, *n*-Bu$_4$NI$_2$Br, or *n*-Bu$_4$NAsF$_6$, respectively, was added to an H shaped two-compartment cells that were separated by frit glass with Pt electrodes and sealed under nitrogen. In a first stage, a current density of approximately 0.5 μA/cm2 was applied (during the first five days) until the first crystals become clearly visible growing on the anode. Subsequently, the current was raised to ~1 μA/cm^2 for another two weeks. The black elongated plate shaped crystals that grew on the electrode were collected and washed with dichloromethane.

X-ray crystallography

Crystals suitable for X-ray diffraction study were mounted on a loop with Fomblin protective oil. Data were performed with a Bruker APEX II CCD detector diffractometer at 150K, using graphite monochromated MoKα radiation (λ=0.71073 Å), in the φ and ω scans mode. The X-ray generator was operated at 50 kV and 30 mA, and the X-ray data collection was monitored by the APEX2 program. All data were corrected for Lorentzian polarization and absorption effects using SAINT[2] and SADABS[3] programs.

The structures were solved by direct methods using SIR97[4] and SHELXS-97[5] and refined by full matrix least-squares methods using the program SHELXL-2014[6] using the winGX[7] software package. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics and packing

diagrams were prepared using MERCURY-4.3[8]. [CCDC 2018237 and 2018237] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data for *β"*-(CNB-EDT-TTF)$_4$A

X	**AuI_2**	**AsF_6**
Empirical formula	$C_{26}H_{14}N_2O_4Au_{0.5}IS_{12}$	$C_{26}H_{14}F_3N_2S_{12}As_{0.5}$
Formula weight	964.49	833.57
Temperature (K)	150(2)	150(2)
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
a (Å)	4.8480(2)	4.8398(5)
b (Å)	5.7558(2)	5.8172(6)
c (Å)	27.2970(12)	28.1649(17)
α (°)	89.436(3)	90.457(6)
β (°)	89.331(2)	91.510(6)
γ (°)	84.313(2)	95.030(7)
V (Å^3)	757.87(5)	789.59(13)
Z, D_{Cal}(mg/m^3)	1, 2.113	1, 1.753
Absorption coeff. μ (mm^{-1})	4.316	1.393
Crystal size (mm)	0.20 × 0.03 × 0.02	0.20 × 0.04 × 0.02
θ range for data collection (°)	2.985 to 25.340	3.516 to 25.679
Index range (h, k, l)	-5/5, -6/6 , -32/32	-5/3, -7/7, -33/34
Reflections collected / unique	5909 / 2740 [Rint = 0.0338]	6264 / 2939[Rint = 0.0853]
Completeness to θ	25.24 99.2 %	25.24 98.5 %
Data / restraints / parameters	2740/ 0 / 193	2939 / 0 / 208
Goodness-of-fit on F^2	1.158	1.044
Final R indices [I>2σ(*I*)]	R1 = 0.0531, wR2 = 0.1194	R_1 = 0.0934, wR_2 = 0.2207
Largest difference peak and hole (e Å^3)	1.046 and -0.805	0.681 and -0.945
CCDC reference	2018237	2018238

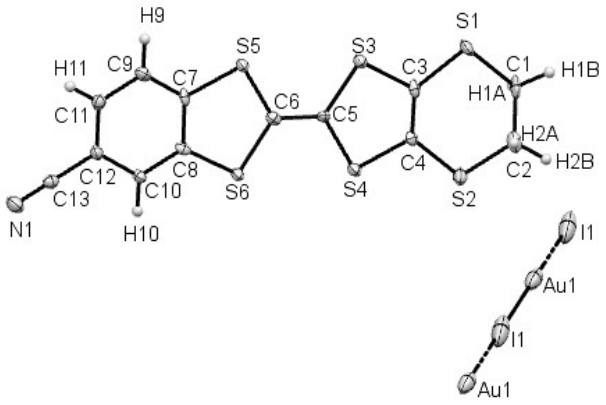


Figure S1. ORTEP diagram of compound *β"*-(CNB-EDT-TTF)$_4$AuI$_2$ drawn at the 50% probability level with the atomic numbering scheme.

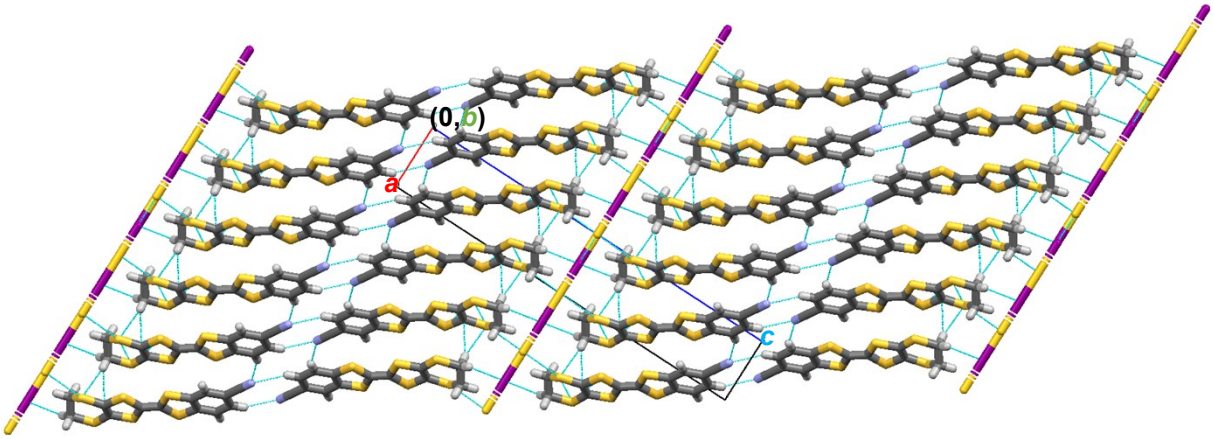


Figure S2. Crystal structure of *β"*-(CNB-EDT-TTF)$_4$AuI$_2$ view along the *b*-axis, blue lines represent short contacts.

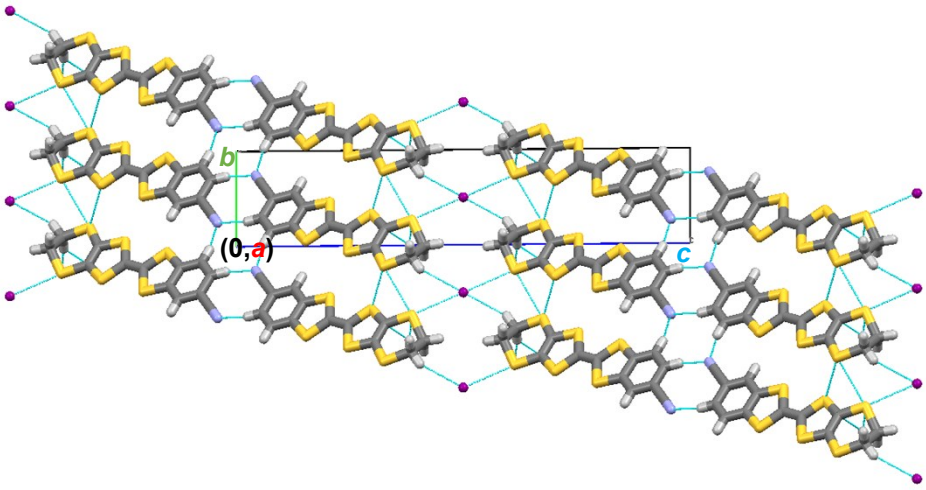


Figure S3. Crystal structure of *β"*-(CNB-EDT-TTF)$_4$AuI$_2$ view along the *a*-axis, blue lines represent short contacts.

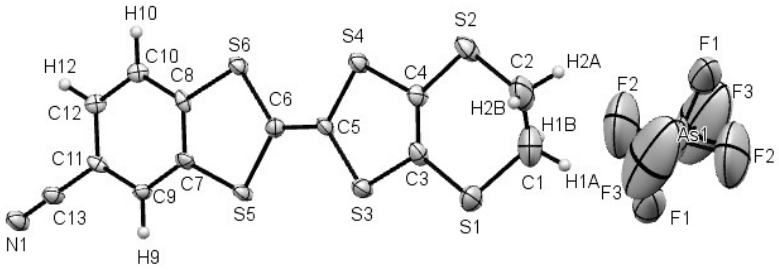


Figure S4. ORTEP diagram of compound *β"*-(CNB-EDT-TTF)$_4$AsF$_6$ drawn at the 50% probability level with the atomic numbering scheme.

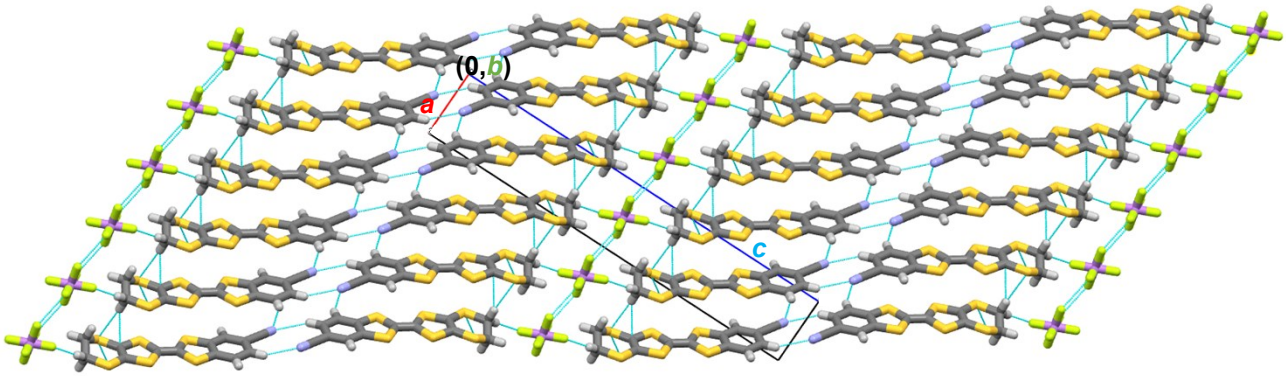


Figure S5. Crystal structure of *β"*-(CNB-EDT-TTF)$_4$ AsF$_6$ view along the *b*-axis, blue lines represent short contacts.

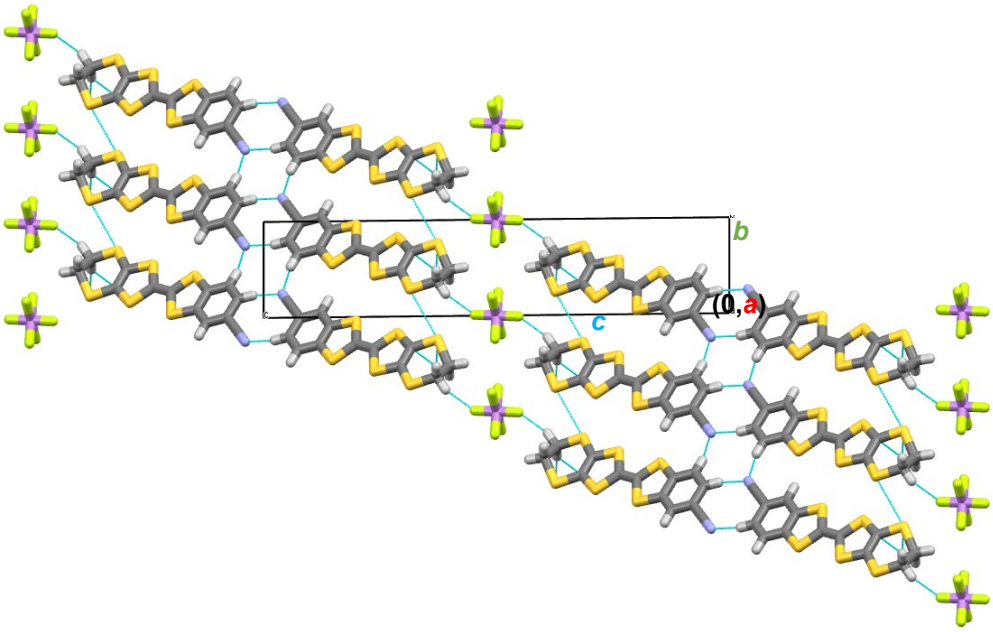


Figure S6. Crystal structure of *β"*-(CNB-EDT-TTF)$_4$ AsF$_6$ view along the *a*-axis, blue lines represent short contacts.

Computational Details

Molecular conformation calculations were performed using the GAUSSIAN 09 software package[9] without symmetry constraints. The optimized geometries were obtained with the the PBE0 functional and a standard 6-31G(d,p) basis set.[10] That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock[11] exchange with DFT[12] exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[13] Frequency calculations were performed showing no imaginary modes and confirming the stationary points as minima. The electronic energies (E_{b1}) were converted to enthalpy at 298.15 K and 1 atm (H_{b1}) by using zero point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level.

Single point energy calculations were performed on the geometries optimized at the PBE0/6-31G(d,p) level, using the M06-2X functional and a standard 6-311++G(d,p) basis set.[14] The M06-2X functional is a hybrid meta-GGA functional developed by Truhlar and Zhao,[15] and it was shown to perform very well for main group element systems, providing a good description of weak and long range interactions.[16] The enthalpy values presented (H_{b2}) were derived from the electronic energy values obtained at the M06-2X/6-311++G(d,p)//PBE0/6-31G(d,p) level (E_{b2}) according to the following expression: $H_{b2} = E_{b2} + H_{b1} - E_{b1}$.

Table S2. Atomic coordinates of the optimized geometries (PBE0/6-31G**)

CNB-EDT-TTF

S	-1.666666	0.712837	0.470703
S	-0.484384	-1.572603	1.943678
S	0.326422	0.095077	-2.061589
S	1.485298	-2.183419	-0.600524
S	2.716747	0.350689	-3.900802
S	4.065101	-2.171916	-2.083119
N	-4.193909	3.316792	5.554754
C	-0.477906	-0.591385	0.475996
C	-1.909211	0.692657	2.212973
C	-1.351614	-0.391113	2.908028
C	-2.642538	1.656589	2.890032
H	-3.071223	2.502512	2.363460
C	-1.530345	-0.510649	4.284668
H	-1.091716	-1.345007	4.822332
C	-2.824542	1.528792	4.272962
C	-2.268135	0.446162	4.966365
H	-2.412847	0.363960	6.037822
C	-3.579668	2.516189	4.979214
C	0.335719	-0.844168	-0.569107
C	1.968081	-0.386374	-2.503201
C	2.500730	-1.430581	-1.836874
C	3.303761	-1.206843	-4.646511
H	2.445477	-1.874958	-4.754113
H	3.670476	-0.949579	-5.645010
C	4.425329	-1.850836	-3.859809
H	5.314263	-1.217058	-3.884127
H	4.672798	-2.822265	-4.300704

$R^2_2(10)$ synthons

H	-10.304091	2.347376	9.821919
H	-9.769317	3.962914	10.337040
H	-7.569761	3.090020	10.999786
H	-8.836334	2.082432	11.728855
H	9.768886	-3.962577	-10.337249
H	10.303646	-2.347050	-9.822080
H	8.835955	-2.082066	-11.729060
H	7.569355	-3.089666	-11.000054
H	-2.973705	3.132715	1.886221
H	-1.416874	1.558782	0.764717
H	-1.060929	-0.702473	4.415865
H	1.060341	0.702719	-4.416247
H	2.973031	-3.132533	-1.886635
H	1.416192	-1.558607	-0.765134
S	2.782784	-0.918388	-6.196857
S	3.923191	-3.195779	-4.678706
S	5.075518	-1.333841	-8.511246
S	6.191222	-3.602686	-7.001625
S	7.643803	-0.886727	-10.055743
S	8.919075	-3.387832	-8.175947
N	-0.469408	1.309949	-1.359050
C	4.035039	-2.157655	-6.102011
C	2.340562	-1.029500	-4.496937
C	2.878406	-2.109504	-3.780706
C	1.476541	-0.140442	-3.875249
C	2.549547	-2.300806	-2.440382
C	1.146375	-0.343449	-2.528650
C	1.680873	-1.421305	-1.809786
C	0.255455	0.568038	-1.881713
C	4.971486	-2.327346	-7.057306
C	6.781556	-1.709136	-8.776295
C	7.294583	-2.748423	-8.086910
C	8.379927	-2.389438	-10.782879
C	9.441456	-3.012566	-9.901810
S	-2.783347	0.918654	6.196481
S	-3.923806	3.196007	4.678311
S	-5.076010	1.334148	8.510926
S	-6.191770	3.602957	7.001292
S	-7.644239	0.887061	10.055521
S	-8.919579	3.388132	8.175720

N	0.468769	-1.309744	1.358655
C	-4.035611	2.157912	6.101641
C	-2.341164	1.029737	4.496550
C	-2.879032	2.109723	3.780309
C	-1.477149	0.140675	3.874861
C	-2.550203	2.301002	2.439974
C	-1.147012	0.343658	2.528250
C	-1.681535	1.421496	1.809377
C	-0.256097	-0.567833	1.881314
C	-4.972029	2.327621	7.056961
C	-6.782039	1.709446	8.776025
C	-7.295091	2.748718	8.086637
C	-8.380340	2.389786	10.782652
C	-9.441900	3.012896	9.901608

$R^2_4(10)$ synthons

H	-10.859976	5.511700	10.532631
H	-12.263857	4.489488	10.903982
H	-13.376519	5.082840	8.828787
H	-12.913885	6.576749	9.674218
H	5.411100	0.696027	-12.330262
H	4.090026	-0.171475	-11.521925
H	6.203188	-1.351955	-11.092813
H	6.990689	0.155763	-10.575623
H	-6.991261	-0.154605	10.575503
H	-6.203757	1.353104	11.092716
H	-4.090627	0.172597	11.521904
H	-5.411739	-0.694887	12.330197
H	12.912591	-6.576640	-9.674931
H	13.375448	-5.082721	-8.829638
H	12.262567	-4.489391	-10.904722
H	10.858656	-5.511478	-10.533141
H	-3.329033	4.948267	1.113276
H	-4.956232	6.453685	2.228134
H	-3.630874	2.173979	4.403138
H	-1.199879	4.190110	-4.233314
H	0.401100	0.030777	-2.003293
H	-0.823499	1.760300	-0.696706
H	-0.401547	-0.029752	2.003365
H	0.823051	-1.759289	0.696784
H	1.199400	-4.189081	4.233411
H	3.630290	-2.173102	-4.403157
H	4.955633	-6.452772	-2.228072
H	3.328535	-4.947268	-1.113185
S	0.113440	2.423173	-6.211612
S	1.055905	-0.049442	-4.872906
S	2.076768	1.779973	-8.758425
S	2.998523	-0.682460	-7.439535
S	4.538339	1.958027	-10.515164
S	5.627959	-0.768823	-8.845607
N	-2.349343	4.858461	-1.009379
C	1.173729	1.014606	-6.275432
C	-0.183285	2.304767	-4.480853
C	0.262950	1.135544	-3.847047
C	-0.855592	3.278446	-3.756794
C	0.039739	0.933848	-2.486679
C	-1.084582	3.068238	-2.390697
C	-0.637728	1.900677	-1.757136
C	-1.781319	4.058728	-1.631683
C	1.974346	0.752347	-7.328300
C	3.687995	1.197420	-9.190702
C	4.116123	0.069470	-8.588052
C	5.002337	0.407334	-11.356979
C	6.043660	-0.387626	-10.598780
S	5.519533	-3.642191	-6.141289
S	6.304878	-6.188732	-4.836706
S	8.082086	-3.923938	-8.183130
S	8.830320	-6.460614	-6.891850
S	10.863532	-3.463194	-9.282852
S	11.706055	-6.310712	-7.632846
N	1.670865	-1.910014	-1.557069
C	6.668157	-4.978763	-6.069755
C	4.822649	-3.963470	-4.558417
C	5.192357	-5.169199	-3.943136
C	3.918350	-3.112225	-3.940864
C	4.658972	-5.524701	-2.705862
C	3.379919	-3.483944	-2.701405
C	3.748232	-4.685393	-2.080493
C	2.439416	-2.617051	-2.065566
C	7.712928	-5.093646	-6.914598
C	9.783560	-4.393202	-8.268604
C	10.130024	-5.553795	-7.676352
C	11.647771	-4.894881	-10.095256
C	12.529636	-5.690864	-9.157084
S	-5.520256	3.642947	6.141221
S	-6.305617	6.189505	4.836682
S	-8.082999	3.924475	8.182857
S	-8.831260	6.461163	6.891618
S	-10.864540	3.463480	9.282234
S	-11.707070	6.311024	7.632271
N	-1.671332	1.911018	1.557130
C	-6.668934	4.979472	6.069658
C	-4.823291	3.964308	4.558400
C	-5.193005	5.170046	3.943141
C	-3.918934	3.113112	3.940866
C	-4.659564	5.525608	2.705908
C	-3.380452	3.484889	2.701445
C	-3.748768	4.686349	2.080556
C	-2.439901	2.618039	2.065619
C	-7.713785	5.094263	6.914414
C	-9.784515	4.393619	8.268163
C	-10.130991	5.554218	7.675928
C	-11.648989	4.895066	10.094614
C	-12.530796	5.691031	9.156373
S	-0.113910	-2.422117	6.211697
S	-1.056332	0.050503	4.872971
S	-2.077295	-1.778883	8.758476
S	-2.998975	0.683560	7.439554
S	-4.538930	-1.956902	10.515133
S	-5.628459	0.769956	8.845530
N	2.348883	-4.857446	1.009479
C	-1.174185	-1.013538	6.275499
C	0.182833	-2.303723	4.480939
C	-0.263387	-1.134499	3.847124
C	0.855130	-3.277413	3.756887
C	-0.040176	-0.932816	2.486755
C	1.084123	-3.067217	2.390788
C	0.637284	-1.899655	1.757217
C	1.780835	-4.057728	1.631778
C	-1.974818	-0.751264	7.328351
C	-3.688530	-1.196309	9.190700
C	-4.116624	-0.068355	8.588033
C	-5.002939	-0.406201	11.356928
C	-6.044226	0.388771	10.598691

The total electronic energies of the β''- and κ- phases were calculated using Density Functional Theory [17] as implemented in the VASP code [18,19,20,21]. We used the PBE [22] and SCAN [23,24] exchange and correlation functionals. Both functionals were used with and without the inclusion of dispersion forces through the Tkatchenko-Scheffler [25] method with iterative Hirshfeld partitioning [26,27]. For the β''-phase, as the number of electrons per unit cell is odd, both spin-polarized and spin-unpolarized optimizations were performed. Electron-nuclei interactions were modelled using the projector augmented wave (PAW) method [28,29]. Given the size of the unit cells, only the Γ point was used for the Brillouin zone (BZ) sampling, and the partial occupancies of each orbital were set using a gaussian smearing of 0.03 eV. Kinetic energy cutoff was set at 400 eV. Convergence was reached when total electronic changed between iterations by less than 10^{-7} eV. The structural optimization process ended when atomic forces became smaller than 0.005 eV/Å.

Table S3: Total energies, in meV/atom, of the κ phase (222 atoms per unit cell) with respect to the spin-unpolarized β''-phase (111 atoms per unit cell).

	Without dispersion forces	**With dispersion forces**
PBE	47.676	52.034
SCAN	55.779	65.552

Table S4: Total energy, in meV/atom, of the spin-polarized β''-phase with respect to the spin-unpolarized calculation.

	SCAN with dispersion forces
Spin unpolarized	0
Spin polarized	0.744

Table S5: Impact of the inclusion of dispersion effects – total energies, in meV/atom, of the dispersion corrected calculations with respect to the same calculation without any dispersion correction.

	β''-phase	**κ-phase**
PBE	-95.461	-91.103
SCAN	-109.148	-99.375

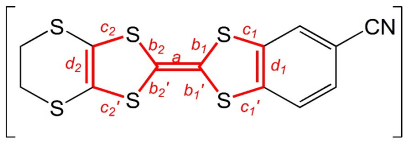
Table S6: Experimental and calculated Lattice parameters (in Å and degrees) of the β"-phase using different functionals. The inclusion of dispersion forces is indicated with "+VdW".

	PBE	PBE+VdW	SCAN	SCAN+VdW spin-unpolarized	SCAN+VdW spin-polarized	**Experimental**
a (Å)	4.7722	4.7750	4.7772	4.7371	4.7301	**5.7669**
b (Å)	9.9658	9.8397	9.8107	9.6577	9.6531	**9.7113**
c (Å)	31.0031	28.8154	28.7172	28.1653	28.1849	**27.7724**
α (º)	85.082	86.712	84.767	85.756	85.648	**86.793**
β (º)	95.925	93.856	93.395	93.287	93.349	**89.079**
γ (º)	81.442	80.901	80.830	80.702	80.582	**84.558**

Table S7: Experimental and calculated Lattice parameters (in Å and degrees) of the κ-phase using different functionals. The inclusion of dispersion forces is indicated with "+VdW".

	PBE	PBE+VdW	SCAN	SCAN+VdW	**Experimental**
a (Å)	28.0853	27.8071	27.6087	27.3702	**27.9810**
b (Å)	8.3129	8.0135	7.9443	7.7862	**8.1197**
c (Å)	13.6140	13.3005	13.3048	13.0584	**13.6070**
α (º)	90.000	90.000	90.000	90.000	**90.000**
β (º)	96.450	97.818	98.123	98.938	**96.908**
γ (º)	90.000	90.000	90.000	90.000	**90.000**

Table S8. Bond lengths (Å) of the (CNB-EDT-TTF) donor in *β”*-(CNB-EDT-TTF)$_4$I$_3$ and *k”*-(CNB-EDT-TTF)$_4$I$_3$ compounds, experimental and optimized values.

		a (Å)	b1 (Å)	b1’ (Å)	b2 (Å)	b2’ (Å)	c1 (Å)	c1’ (Å)	c2 (Å)	c2’ (Å)	d1 (Å)	d2 (Å)	δ=(b+c)-(a+d)
β”$_{To}$-[CNB-EDT-TTF]$_4$I$_3$ (Experimental	I	1.37(1)	1.749(9)	1.749(9)	1.751(9)	1.735(9)	1.742(9)	1.741(9)	1.746(9)	1.766(9)	1.41(1)	1.36(1)	0.740
	II	1.35(1)	1.757(9)	1.756(9)	1.748(9)	1.75(1)	1.742(9)	1.76(1)	1.76(1)	1.767(9)	1.41(1)	1.35(1)	0.780
β”$_{To}$-[CNB-EDT-TTF]$_4$I$_3$ (spin.unpolarized)	I	1.3736	1.7294	1.7388	1.7225	1.7329	1.7475	1.7013	1.7374	1.7572	1.3895	1.3642	0.7163
	II	1.3737	1.7299	1.7398	1.7238	1.7328	1.7328	1.7008	1.7384	1.7573	1.3891	1.3649	0.7132
	III	1.3737	1.7299	1.7398	1.7238	1.7328	1.7469	1.7008	1.7384	1.7573	1.3891	1.3649	0.716725
	IV	1.3736	1.7294	1.7388	1.7225	1.7329	1.7475	1.7013	1.7374	1.7966	1.3895	1.3642	0.72615
β”$_{To}$- [CNB-EDT-TTF]$_4$I$_3$ (spin-polarized)	I	1.3737	1.7291	1.7386	1.7222	1.7328	1.7472	1.7011	1.7374	1.757	1.3893	1.3644	0.7158
	II	1.3739	1.7297	1.7395	1.7235	1.7326	1.7468	1.7005	1.7384	1.757	1.3889	1.365	0.71615
	III	1.3739	1.7297	1.7395	1.7235	1.7326	1.7468	1.7005	1.7384	1.757	1.3889	1.365	0.71615
	IV	1.3737	1.7291	1.7386	1.7222	1.7328	1.7472	1.7011	1.7374	1.757	1.3893	1.3644	0.7158
κ-[CNB-EDT-TTF]$_4$I$_3$ (Experimental)	I	1.31(3)	1.77(2)	1.76(2)	1.75(2)	1.77(2)	1.73(2)	1.76(2)	1.74(3)	1.78(2)	1.40(3)	1.33(3)	0.84
	II	1.34(3)	1.74(2)	1.73(2)	1.76(2)	1.76(2)	1.76(2)	1.79(2)	1.75(2)	1.77(2)	1.38(2)	1.28(3)	0.845
κ-[CNB-EDT-TTF]$_4$I$_3$ (optimized)	I	1.3582	1.7435	1.7354	1.7321	1.7329	1.7384	1.7247	1.7391	1.7405	1.3989	1.3559	0.73605
	II	1.3582	1.7435	1.7354	1.7321	1.7329	1.7383	1.7247	1.7391	1.7405	1.3989	1.3559	0.736025
	III	1.3577	1.734	1.7372	1.7293	1.7255	1.728	1.7262	1.732	1.7356	1.4004	1.3582	0.72495
	IV	1.3577	1.734	1.7372	1.7293	1.7255	1.728	1.7262	1.732	1.7356	1.4004	1.3582	0.72495
	V	1.3582	1.7435	1.7354	1.7321	1.7329	1.7384	1.7247	1.7391	1.7405	1.3989	1.3559	0.73605
	VI	1.3582	1.7435	1.7354	1.7321	1.7329	1.7384	1.7247	1.7391	1.7405	1.3989	1.3559	0.73605
	VII	1.3577	1.734	1.7372	1.7293	1.7255	1.728	1.7262	1.732	1.7356	1.4004	1.3582	0.72495
	VIII	1.3577	1.734	1.7372	1.7293	1.7255	1.728	1.7262	1.732	1.7356	1.4004	1.3582	0.72495

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