Supporting Information

to the article

π-Bonded molecular wires: self-assembly of mixed-valence cation-radical stacks within the nanochannels formed by inert tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anions.

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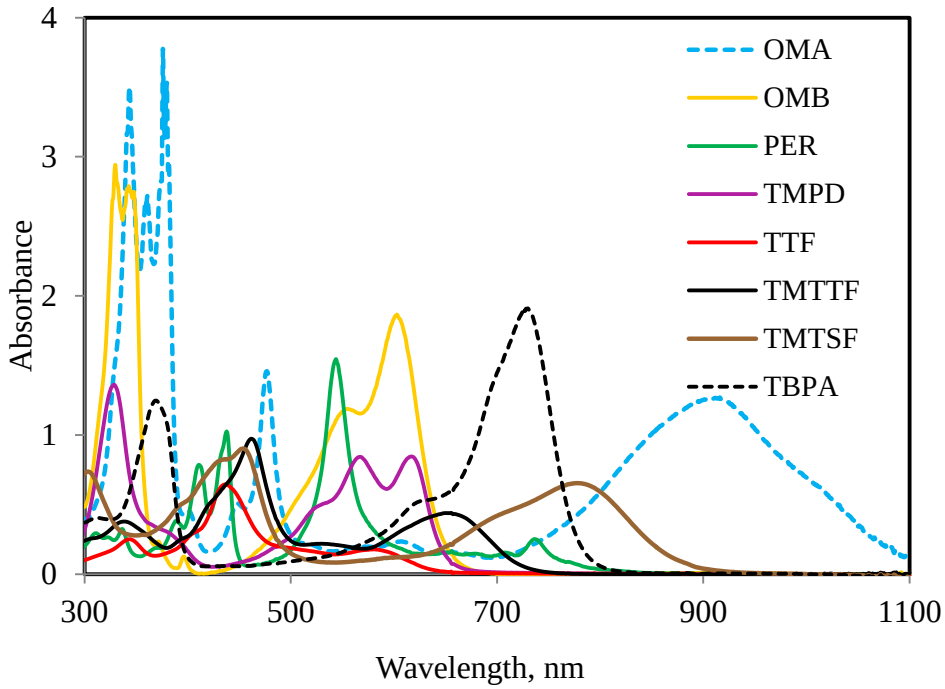


Figure S1. Spectra of the solutions of the cation-radicals of donors from Schemes 1 and 2 (as indicated) obtained by dissolution of their salts with the $TFPB^-$ anion in dichloromethane.

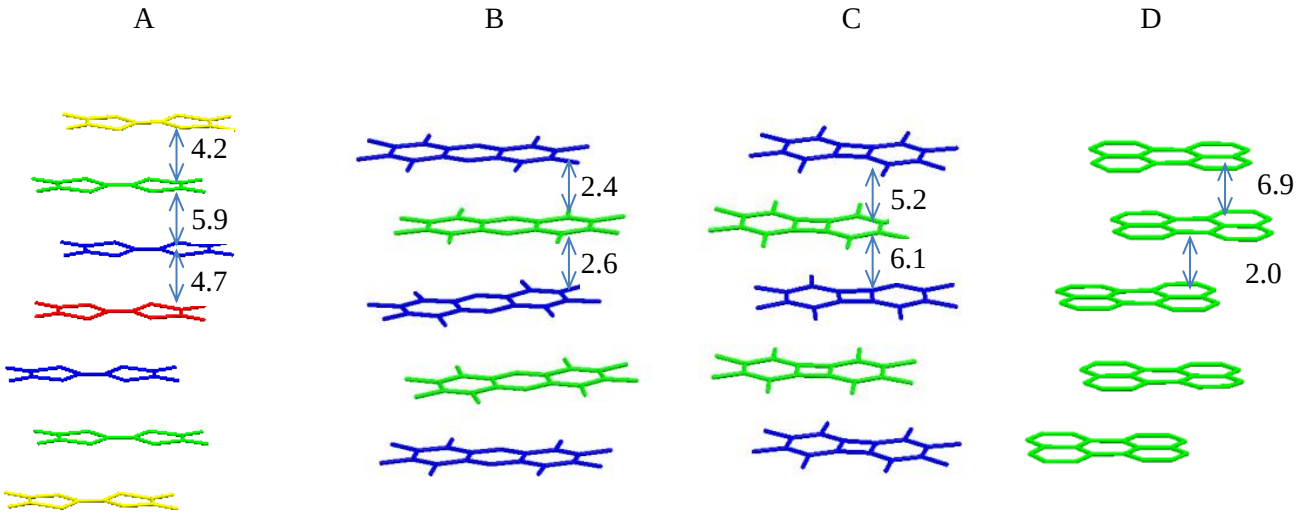


Figure S2. π-Stacking of crystallographically independent TMTSF (A), OMA (B), OMB (C) and PER (D) moieties (drawn in different colors) with the numbers representing H_{DA} values (in kcal/mol, see Table 5) for the corresponding pairs.

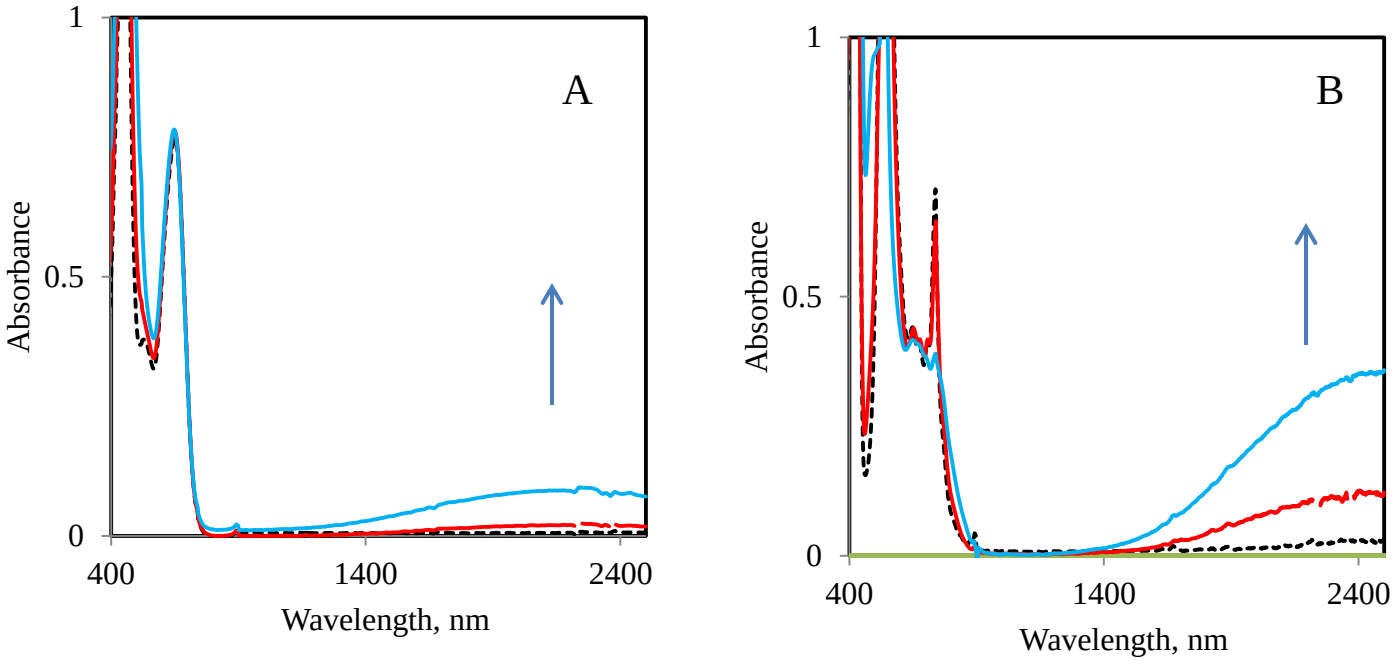


Figure S3. UV-VIS-NIR spectra of TMTTF (A) and PER (B) cation-radicals showing appearance of the absorption bands in the NIR range diagnostic of formation of dimeric $(D)_2^{+\bullet}$ associates upon addition of neutral molecules (red and blue spectra) to the solutions of the pure cation-radicals (black dashed spectra)

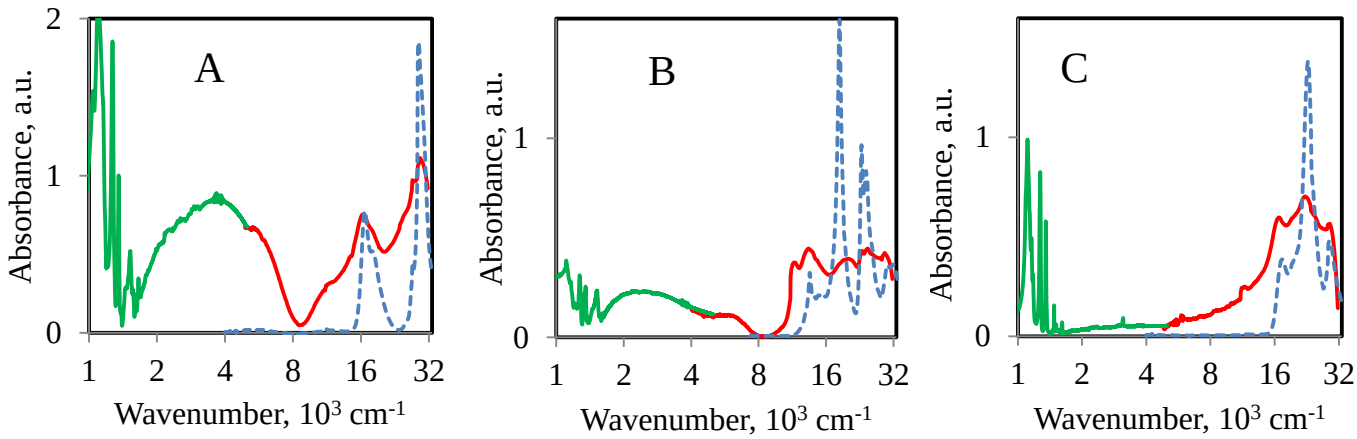


Figure S4. Absorption spectra of the cation-radical salts of OMB (A), PER (B), TTF (C) measured as neat crystalline compounds in the IR range (green lines) and as a mull in nujol oil in the UV-VIS-NIR range (red lines). Blue dashed lines represent spectra of the corresponding cation radicals in solution.

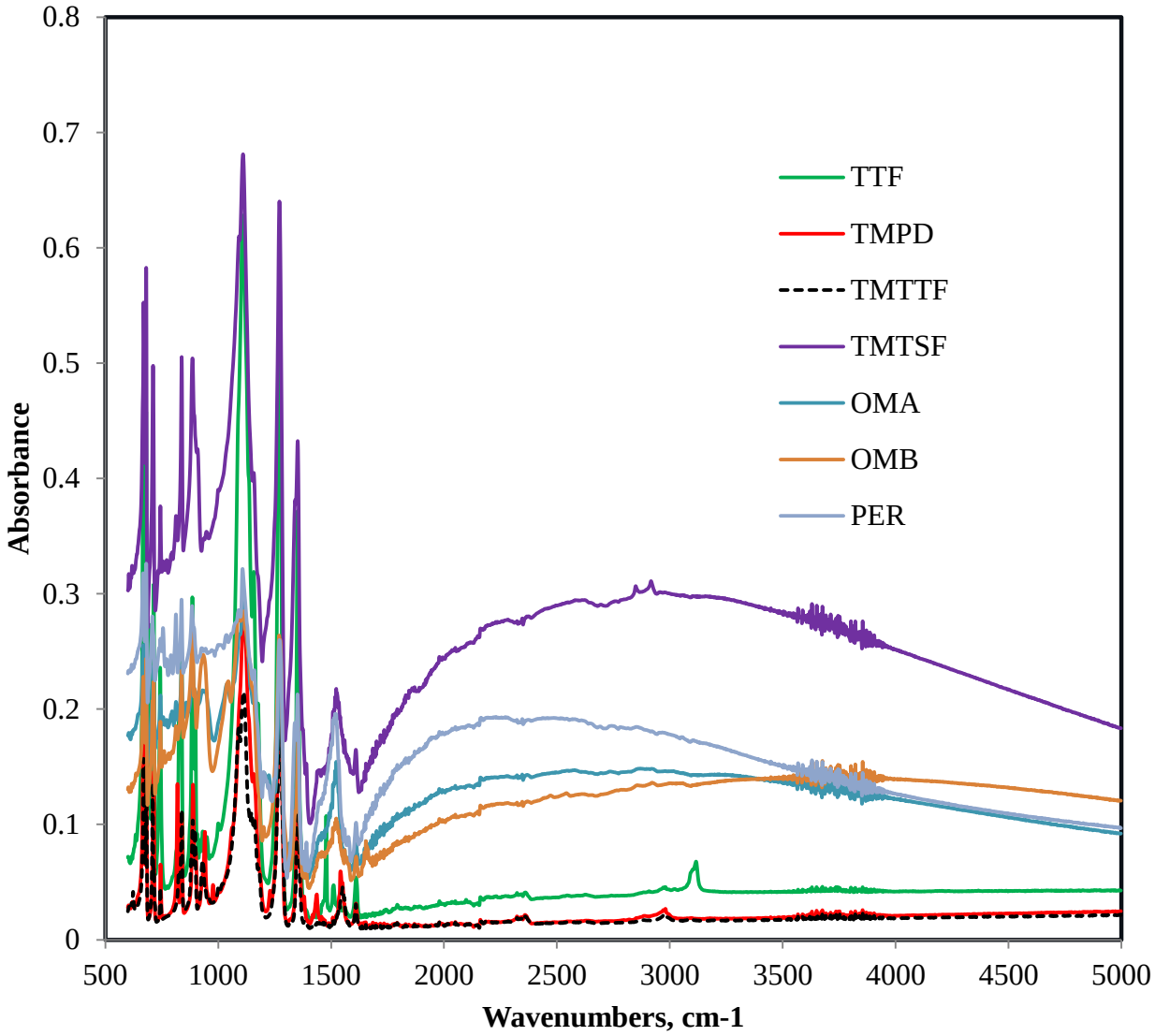
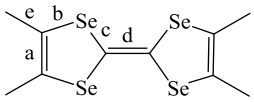


Figure S5. FT-IR spectra of the cation-radical salts (as indicated) with TFPB anions.

Table S1. Bond lengths (in Å) in the crystallographically independent TMTSF molecules A-D and neutral and cation-radical TMTSF moieties.



Bond	Individual bonds lengths			
	Molecule A (Red in Figure S2)			
a	1.341(5)	1.341(5)		
b	1.887(3)	1.896(4)	1.887(3)	1.896(4)
c	1.867(3)	1.866(4)	1.867	1.866
d	1.371(4)			
e	1.505(5)	1.508(4)	1.505(5)	1.508(4)
	Molecule B (Green in Figure S2)			
a	1.336(5)	1.338(5)		
b	1.897(3)	1.898(3)	1.894(3)	1.896(3)
c	1.880(4)	1.872(3)	1.879(3)	1.869(4)
d	1.363(4)			
e	1.504(5)	1.496(4)	1.509(4)	1.512(5)
	Molecule C (Yellow in Figure S2)			
a	1.338(5)	1.338(5)		
b	1.887(3)	1.890(3)	1.887(3)	1.890(3)
c	1.863(4)	1.863(4)	1.863(4)	1.863(4)
d	1.375(4)			
e	1.504(5)	1.499(4)	1.504(5)	1.499(4)
	Molecule D (Blue in Figure S2)			
a	1.335(5)	1.343(6)		
b	1.894(3)	1.898(3)	1.891(3)	1.889(4)
c	1.872(4)	1.881(3)	1.869(3)	1.876(4)
d	1.361(4)			
e	1.505(5)	1.501(4)	1.508(5)	1.509(5)

Table S1. TMTSF bond lengths (continued).

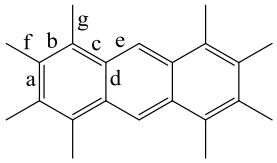
	Neutral TMTSF (ref. code TMBDSE)			
a	1.3150(2)	1.3150(2)		
b	1.9024(3)	1.9097(5)	1.9024(3)	1.9097(5)
c	1.8880(5)	1.8969(3)	1.8880(5)	1.8969(3)
d	1.3524(4)			
e	1.4998(4)	1.4980(2)	1.4998(4)	1.4980(2)
	$TMTSF^{+\bullet}$ (ref. code CAQJAF)			
a	1.337(40)	1.373(40)		
b	1.859(30)	1.876(30)	1.906(30)	1.959(30)
c	1.827(30)	1.860(30)	1.857(30)	1.832(30)
d	1.429(50)			
e	1.480(50)	1.492(40)	1.467(50)	1.475(40)
	$TMTSF^{+\bullet}$ (ref. code DOXQAI)			
a	1.324(10)	1.342(10)		
b	1.903(9)	1.873(10)	1.877(9)	1.901(9)
c	1.855(9)	1.843(8)	1.860(8)	1.875(9)
d	1.381(10)			
e	1.490(10)	1.495(10)	1.503(10)	1.503(10)

Table S2. Evaluation of charges on the TMTSF moieties in the $(TMTSF)_3(TFPB)_2$ salt.

Molecule	q^i (e) based on individual bonds[a]							q (e)
	a	*a*	*c*	*c*	*c*	*c*	*d*	
A	0.90	0.90	0.61	0.64	0.61	0.64	0.36	0.67(0.19)
B	0.72	0.79	0.30	0.49	0.33	0.57	0.21	0.49(0.22)
C	0.79	0.79	0.71	0.71	0.71	0.71	0.43	0.69(0.12)
D	0.69	0.97	0.49	0.28	0.57	0.40	0.17	0.51(0.27)

a) Calculated as $q^i = (l^i - l_N^i)/(l_{CR}^i - l_N^i)$, where l^i is an individual bond length in the TMTSF moieties A-D in $(TMTSF)_3(TFPB)_2$ and l_N^i and l_{CR}^i are average lengths of the corresponding bonds in the neutral and cationic TMTSF. b) In parenthesis – standard deviations calculated based on the variations of individual q_i values.

Table S3. Bond lengths (in Å) in the OMA molecules in $(OMA)_2TFPB$ salt .



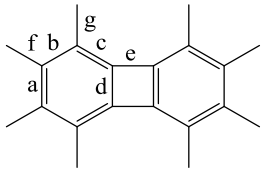
Bond	Individual bond lengths			
	Molecule A (Blue in Figure S2)			
a	1.420(6)		1.405(7)	
b	1.405(7)	1.414(5)	1.396(7)	1.391(7)
c	1.416(6)	1.432(5)	1.420(7)	1.428(6)
d	1.437(6)		1.447(6)	
e	1.396(7)	1.400(5)	1.386(7)	1.400(5)
f	1.514(6)	1.522(7)	1.500(7)	1.486(6)
g	1.506(6)	1.509(6)	1.510(6)	1.491(6)
	Molecule B (Green in Figure S2)			
a	1.440(8)		1.429(8)	
b	1.371(7)	1.360(7)	1.369(7)	1.388(7)
c	1.444(7)	1.446(6)	1.444(7)	1.435(7)
d	1.430(6)		1.418(6)	
e	1.409(7)	1.388(7)	1.389(7)	1.412(7)
f	1.518(7)	1.521(7)	1.512(7)	1.523(7)
g	1.522(7)	1.517(7)	1.505(7)	1.489(7)

Table S4. Evaluation of the charge on the OMA moieties in the $(OMA)_2TFPB$ salt.

Bond	q^i (e) based on individual bonds[a]				q(e)
		Molecule A (Blue in Figure S2)			
a	0.82		1.16		
b	1.21	1.46	0.96	0.82	
c	1.78	0.89	1.56	1.11	
e	0.11	0.32	-0.43	0.32	0.86(0.61)
		Molecule B (Green in Figure S2)			
a	0.36		0.61		
b	0.25	-0.06	0.20	0.73	
c	0.22	0.11	0.22	0.72	
e	0.81	-0.32	-0.27	0.97	0.33(0.40)

a) Calculated as described in footnote a in Table S2 using bond length values (in Å) 1.456 (a) , 1.362 (b) , 1.448 (c) and 1.394 (e) for neutral OMA (obtain from B3LYP/6-311G* calculations) and 1.412 (a) , 1.3975 (b), 1.430 (c) and 1.4125 (e) (from: R.Sebastiano, J.D.Korp, J.K.Kochi Chem.Commun. (1991), 1481 (CSD Ref. code SONXUO)).

Table S5. Bond lengths (in Å) in the OMB molecules in $(OMB)_2TFPB$ salt.



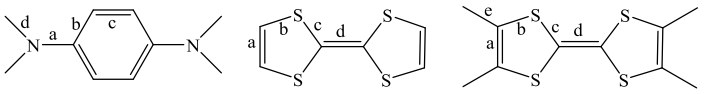
Bond	Individual bond lengths			
	Molecule A (Blue in Figure S2)			
a	1.412(7)	1.406(7)		
b	1.415(7)	1.417(7)	1.412(7)	1.418(7)
c	1.380(7)	1.371(7)	1.374(7)	1.395(7)
d	1.428(7)	1.431(6)		
e	1.475(7)	1.498(7)		
f	1.528(7)	1.494(7)	1.519(7)	1.513(7)
g	1.507(7)	1.509(7)	1.505(7)	1.503(7)
	Molecule B (Blue in Figure S2)			
a	1.386(9)	1.415(9)		
b	1.430(0)	1.390(8)	1.437(8)	1.411(8)
c	1.388(8)	1.365(8)	1.374(8)	1.406(8)
d	1.402(8)	1.418(8)		
e	1.502(7)	1.488(7)		
f	1.512(8)	1.522(8)	1.499(7)	1.540(7)
g	1.476(9)	1.510(9)	1.481(9)	1.492(9)

Table S6. Evaluation of the charge on the OMB moieties in the $(OMB)_2TFPB$ salt.

charge	q^i (e) based on individual bonds[a]				q(e)
	Molecule A (Blue in Figure S2)				
a	-0.11	0.55			
b	0.29	2.65	-0.12	1.41	0.71(0.94)
c	1.15	0.00	0.45	2.05	
d	-0.53	0.00			
e	0.45	0.77			
	Molecule B (Blue in Figure S2)				
a	0.48	0.34			
b	1.18	1.06	1.35	1.00	0.77(0.41)
c	0.75	0.30	0.45	1.50	
d	0.33	0.43			
e	1.07	0.55			

a) Calculated as described in footnote a in Table S2 using bond length values (in Å) 1.391(a), 1.435 (b), 1.365 (c), 1.418 (d) and 1.522 (e) for neutral OMB (from J.B. Jones, D.S. Brown, K.A. Hales, A.G. Massey, Acta Crystallogr.,Sect.C:Cryst.Struct.Commun. (1988), 44, 1757, Ref. code GIFPAM), and 1.435 (a), 1.418(b), 1.385 (c), 1.448(d) and 1.478 (e) (from J.K. Kochi, R. Rathore, P. Le Magueres, J. Org. Chem. (2000), 65, 6826 Ref. code QETFIE).

Table S7. Bond lengths (in Å) in the TMPD, TTF and TMTTF molecules in their (D)TFPB salts.



Bond	Individual bond lengths			
		TMPD		
a	1.343(7)	1.341(8)		
b	1.415(7)	1.424(7)	1.425(8)	1.411(8)
c	1.349(8)	1.354(8)		
d	1.444(7)	1.475(8)	1.455(10)	1.471(9)
e				
		TTF		
a	1.323(6)	1.325(6)		
b	1.724(4)	1.711(4)	1.709(4)	1.718(4)
c	1.718(3)	1.719(3)	1.715(3)	1.716(3)
d	1.390(4)			
		TMTTF (A)		
a	1.346(2)	1.346(2)		
b	1.733(2)	1.734(2)	1.733(2)	1.734(2)
c	1.716(2)	1.717(2)	1.716	1.717(2)
d	1.385			
e	1.495(3)	1.494(2)	1.495(3)	1.494(2)
		TMTTF (B)		
a	1.345(3)	1.345(3)		
b	1.731(2)	1.739(3)	1.731(2)	1.739(3)
c	1.711(2)	1.710(2)	1.711(2)	1.710(2)
d	1.381(3)			
e	1.498(3)	1.500(4)	1.498(3)	1.500(4)

Table S8. Details of reorganization-energy calculations.

		-E, Eh	$\lambda_{i,}$ kcal/mol
PER	N/ N*[a]	769.5822008/ 769.5795135	3.4
	CR/CR*[b]	769.3383368/ 769.3356424	
TMTSF	N/ N*[a]	9994.53694008/9994.5324491	5.1
	CR/CR*[b]	9994.3140256/9994.3104174	

a) Optimized energy of neutral donor / single-point calculated energy of neutral donor with optimized geometry of cation-radical; b) Optimized energy of cation radical / single-point calculated energy of cation radical with optimized geometry of neutral donor.

Table S9. HOMO and HOMO-1 energies for the dimeric pairs extracted from the π-bonded mixed-valence stacks and corresponding H_{ab} values.

	E(HOMO-1), Eh	E(HOMO), Eh	H_{ab}, kcal/mol	H_{DA} , eV
OMB (A)	-0.17582	-0.15936	5.16	0.45
OMB (B)	-0.17695	-0.15742	6.13	0.53
OMA (A)	-0.17485	-0.16727	2.38	0.21
OMA (B)	-0.17557	-0.16717	2.64	0.23
PER (A)	-0.19047	-0.16853	6.88	0.60
PER (B)	-0.1816	-0.17526	1.99	0.17
TMTSF (A)	-0.16287	-0.14404	5.91	0.51
TMTSF (B)	-0.16272	-0.14198	6.51	0.56
TMTSF (C)	-0.16306	-0.14153	6.76	0.59