Effect of Conjugated Structures of Bipyridinium Cations on Ion Assembly and Charge-Transfer of Their Tetrathiafulvalene- Dicarboxylate Salts

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Figure:

Table:

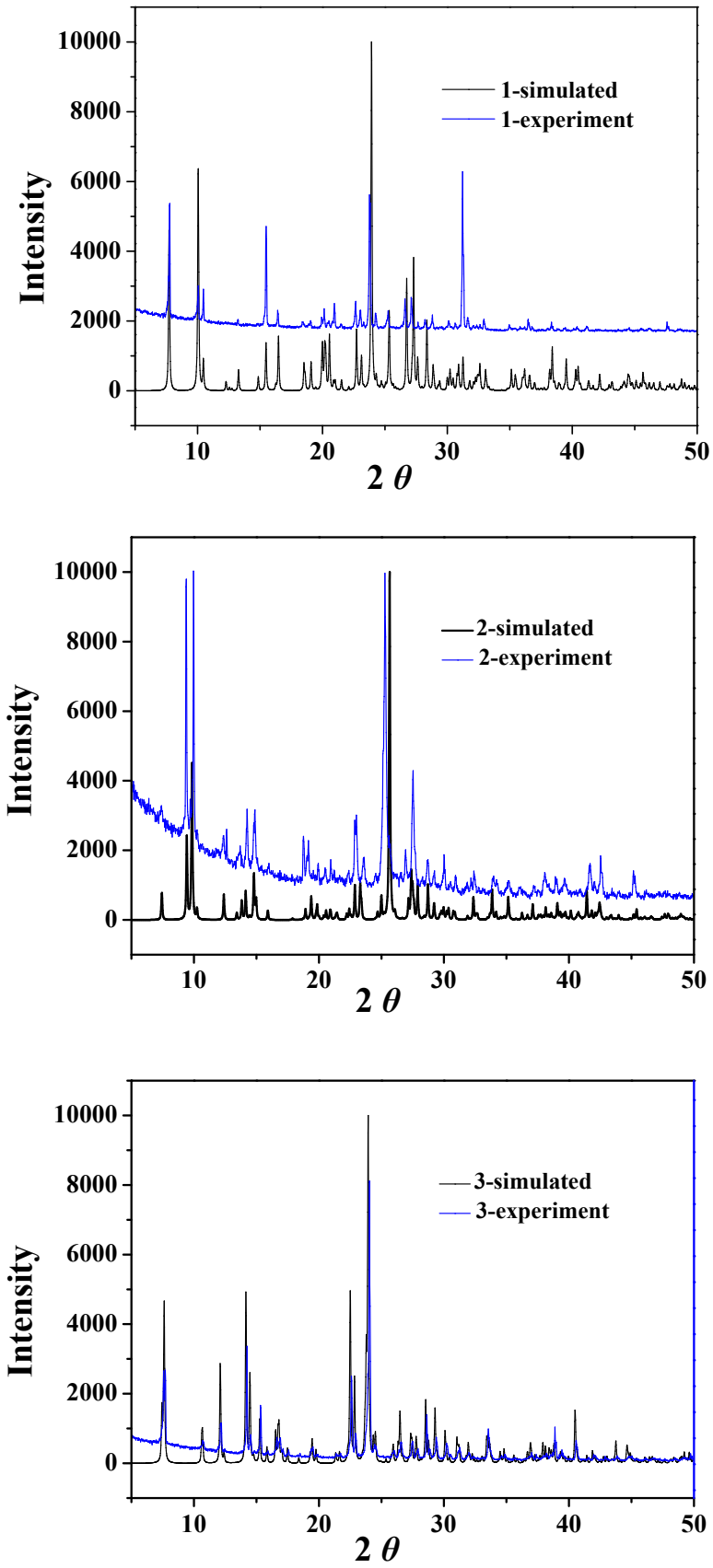


Figure S1. The experimental powder XRD patterns and the simulated patterns from the crystal data of compounds **1**–**3**.

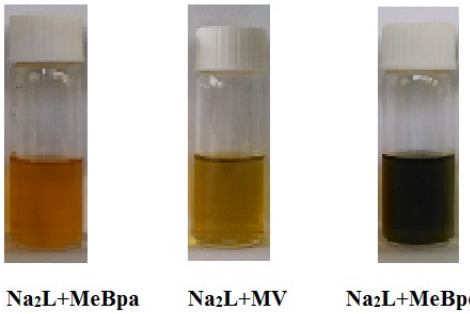
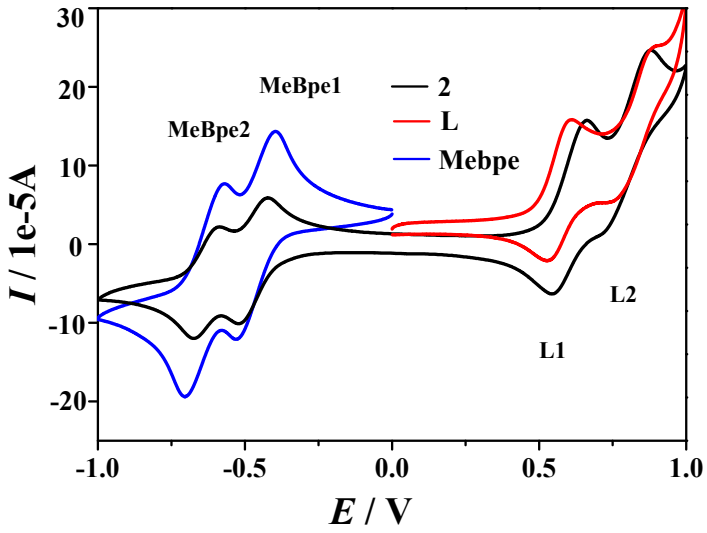
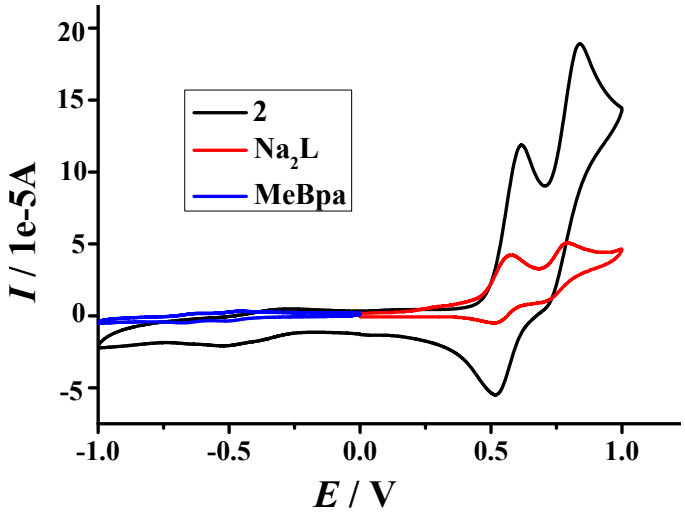


Fig. S2 Photos of the colors of the mixed methanol solutions of Na_2L with MeBpa, MV, or MeBpe (2.5×10^{-3} mol·L^{-1}).



(a)



(b)

Fig. S3 Cyclic voltammogram of **2**(a) and **3** (b) along with the starting compounds Na_2L, MeBpe and MeBpa in DMF (1.0×10^{-3} mol·L^{-1}) (0.1 mol·L^{-1} Bu_4NClO_4, 100 mV s^{-1}).

Table S1. Crystal Data and Structural Refinement Parameters for **1**–**3**.

	1	**2**	**3**
formula	$C_{16}H_{14}NO_4S_6$	$C_{18}H_{21}NO_6S_6$	$C_{17}H_{16}NO_4S_6$
fw	476.64	539.72	490.67
cryst size (mm^3)	0.20 × 0.20 × 0.40	0.25 × 0.40 × 0.80	0.20 × 0.30 × 0.60
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.837(3)	9.5145(19)	7.5801(15)
b (Å)	9.956(2)	9.960(2)	11.601(2)
c (Å)	12.431(4)	13.139(3)	12.317(3)
α (deg)	67.08(2)	107.14(3)	89.25(3)
β (deg)	85.63(3)	106.56(3)	74.54(3)
γ (deg)	73.08(2)	94.37(3)	88.44(3)
V ($Å^3$)	962.9(5)	1122.8(4)	1043.5(4)
Z	2	2	2
ρ_{calcd} ($g\ cm^{-3}$)	1.644	1.596	1.562
F(000)	490	560	506
μ (mm^{-1})	0.734	0.646	0.680
T (K)	293(2)	293(2)	293(2)
reflns collected	9011	10281	9979
unique reflns	4290	4971	4685
observed reflns	3032	3637	3461
no. params	253	290	260
GOF on F^2	1.029	1.049	1.041
R_1 [I>2σ(I)]	0.0436	0.0510	0.0388
$_wR_2$ [I>2σ(I)]	0.1033	0.1439	0.0926

Table S2. The energy of the frontier orbitals of MV, MeBpa, and MeBpe (eV).

orbital	MV^{2+}	$MeBpe^{2+}$	$MeBpa^{2+}$
LUMO+2	–8.62683	–7.93484	-7.84749
LUMO+1	–8.96615	–8.33131	-8.56805
LUMO	–10.5545	–9.87147	-8.87254
HOMO	–15.4626	–13.8179	-14.7233
HOMO-1	–15.5331	–14.8307	-14.7396
HOMO-2	–15.664	–14.8356	-14.821

Table S3. The energy of the frontier orbitals of **1**–**3** (eV).

orbital	**1**	**2**	**3**
LUMO+2	–2.821	–2.264	–2.321
LUMO+1	–3.130	–2.668	–3.014
LUMO	–4.753	–4.170	–3.354
HOMO	–5.271	–5.226	–5.210
HOMO-1	–5.380	–5.206	–5.213
HOMO-2	–6.862	–6.718	–6.687

Table S4. Important electrochemical data of the starting materials MV, MeBpe, L and crystals **1** and **2** (V).

	MV(1)	**MV(1) in 1**	**L(1)**	**L(1) in 1**
E_{cp}	–0.449	–0.443	0.528	0.540
E_{ap}	–0.344	–0.357	0.610	0.649
$E_{1/2}$	–0.395	–0.400	0.569	0.595
	MeBpe	**MeBpe in 2**	**L(1)**	**L(1) in 2**
E_{cp}	–0.529	–0.523	0.528	0.543
E_{ap}	–0.395	–0.424	0.610	0.662
$E_{1/2}$	–0.462	–0.474	0.569	0.603