Supporting Information for:

Effects of alkyl chain length on film morphologies and photocurrent responses of tetrathiafulvalene-bipyridinium charge transfer salts, a study in terms of structures

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

Table S2. Important C···C, C···O or C–H···O interactions in **1–3.**

Fig. S1 (a) The seven membered planar ring structure with conjugated two carboxylate groups and the C2S4 moiety of the TTF anion. (b) Short C···C contacts (< 3.40 Å) between the HL^- and C_4V^{2+} ions.

Fig. S2 Boat-like conformation of the HL anion in compound **2** (C_8V).

Fig. S3 (a) Ball-stick structure of compound **3,** hydrogen atoms being omitted for the sake of clarity. (b) The anion arrangement showing the TTF stacking distances. (c) Molecular packing structure showing the short C-H···O contacts (red dotted line).

Fig. S4 Solid state absorption spectra of the raw materials C_4V, C_8V, $C_{12}V$, $C_{16}V$ and Na_2L derived from the diffuse reflectance spectra.

Fig. S5 (a)-(c) UV-vis spectra on titration of Na_2L (1×10^{-2} M in MeOH) with C_8V, $C_{12}V$ and $C_{16}V$, respectively; insert: a photo showing the color of Na_2L(left), C*n*V(right) and the color of Na_2L after adding C*n*V (middle) (n = 8, 12 and 16).

Fig. S6 (a) ^{1}H NMR spectrum of compound **2** and C_8V (DMSO-d_6, 1×10^{-2} M), showing the range from 3 to 10 ppm. (b) ^{1}H NMR shifts for compounds **1-3**.

Fig. S7 (a) Photocurrent responses of **1–4** and (b) photocurrent responses of the film electrodes prepared from C*n*VBr_2 and Na_2L by solution coating method.

Fig. S8 (a) Charge transfer band photocurrent responses of **1–4** and (b) the film **Fm1-Fm4** electrodes prepared from C*n*VBr_2 and Na_2L by solution coating method.

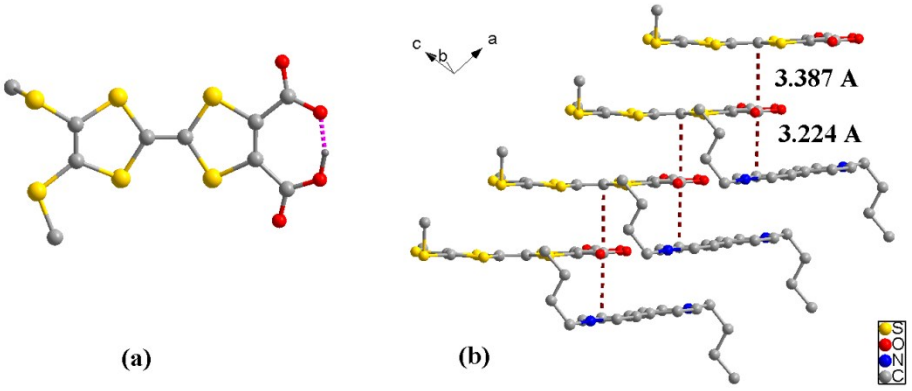
Table S1. Crystal Data and Structural Refinement Parameters for **1**–**3.**

	1	**2**	**3**
formula	$C_{19}H_{22}NO_5S_6$	$C_{46}H_{56}N_2O_8S_{12}$	$C_{54}H_{72}N_2O_8S_{12}$
fw	536.77	1149.64	1261.94
cryst size (mm^3)	0.05×0.20×0.20	0.20×0.20×0.30	0.20×0.20×0.40
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	5.3407(4)	9.7149(6)	9.6659(6)
b (Å)	10.8805(9)	13.5293(6)	13.4126(7)
c (Å)	20.8512(12)	21.8111(9)	25.3171(17)
α (deg)	93.153(6)	78.118(4)	76.598(5)
β (deg)	94.366(6)	83.149(4)	79.897(5)
γ (deg)	99.411(7)	86.593(4)	86.413(5)
V ($Å^3$)	1189.07(15)	2783.5(2)	3142.5(3)
Z	2	2	2
ρ_{calcd} (g cm^{-3})	1.496	1.372	1.331
F(000)	556	1204	1328
μ (mm^{-1})	0.606	0.521	0.468
T (K)	293(2)	293(2)	293(2)
reflns collected	8192	25623	30599
unique reflns	4200	9785	11047
observed reflns	2979	5440	7374
no. params	283	597	6752
GOF on F^2	1.047	1.014	1.153
R_1 [I>2σ(I)]	0.0792	0.0976	0.0904
$_wR_2$ [I>2σ(I)]	0.01747	0.1636	0.1706

Table S2. Important C···C, C···O or C–H···O interactions in **1**–**3** (Å).

		1	
C10···C12	3.224	C3···C10#	3.387
S5···S5 #	3.453	S6···S6 #	3.579
O1···H–O5 #	3.011	O5–H···O2	2.892
C11–H···O4#	3.167	C14–H···O5#	3.140
C15–H···O1#	3.145		
		2	
C9···C25#	3.327	C34···O8#	3.068
C26···O5 #	3.157	C24–H···O8	3.194
C22–H···O8	3.212		
		3	
C9···C40#	3.386	C37···C37	3.389
C2···S9	3.497	C42···O4#	3.215
C21···O5 #	3.036		

#: different symmetry.



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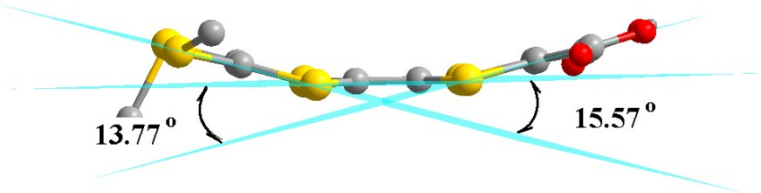

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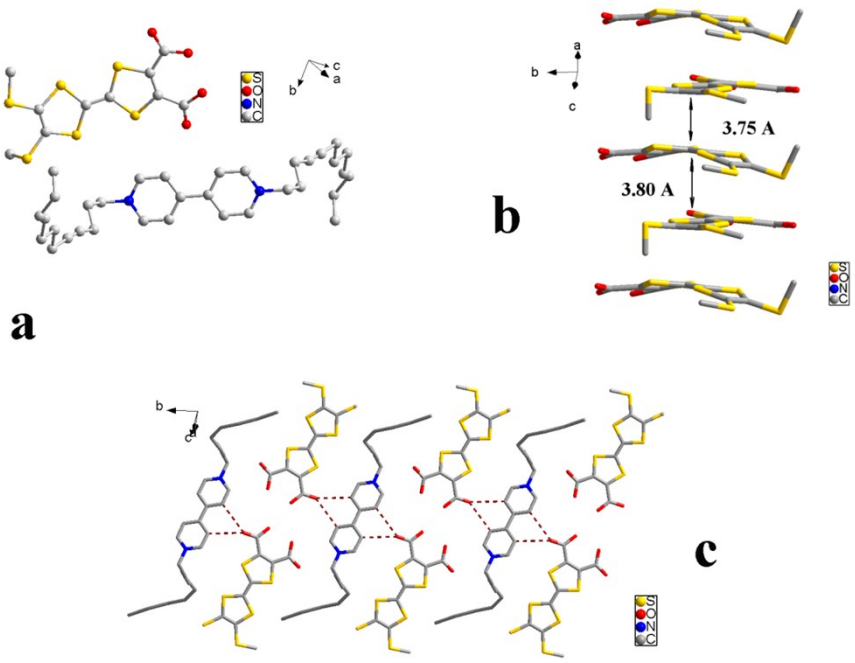

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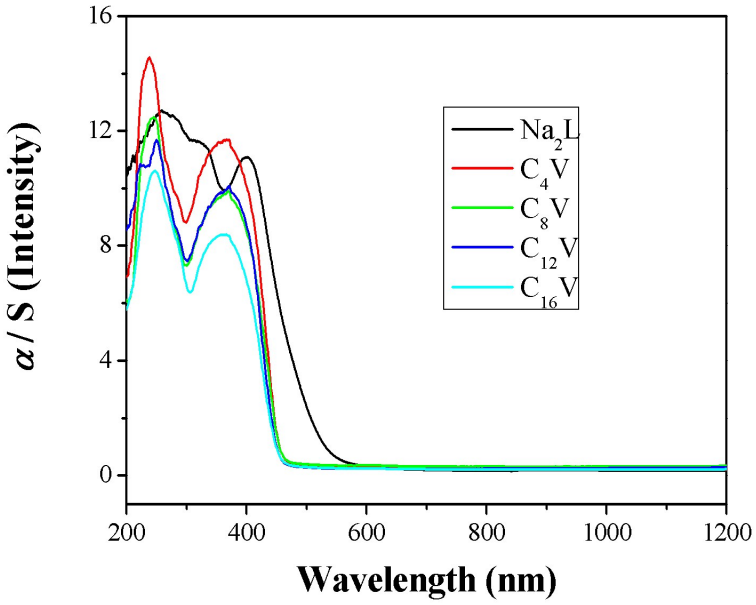

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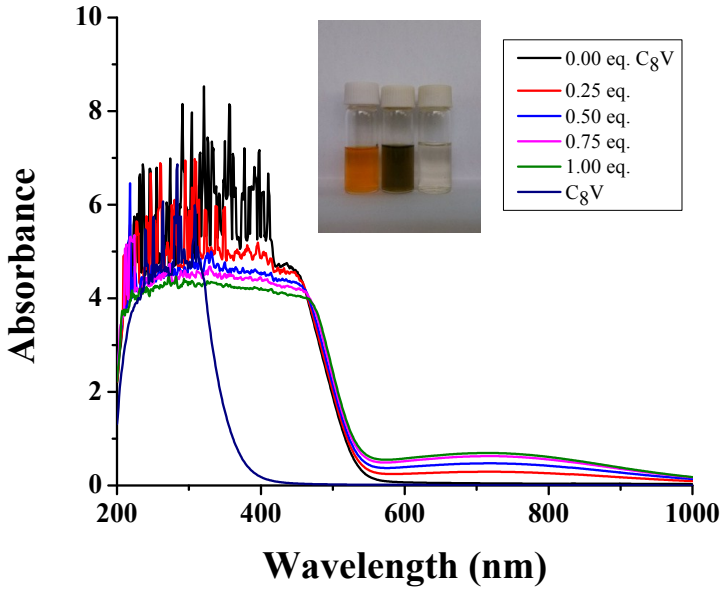
Absorbance
Wavelength (nm)
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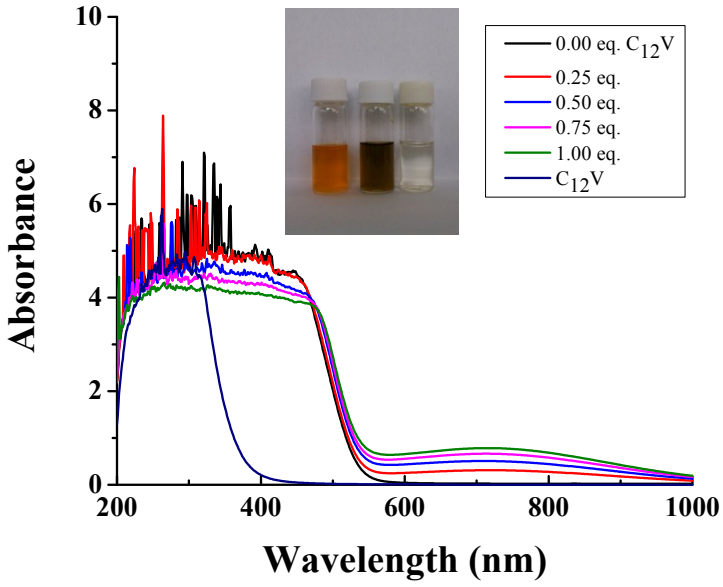
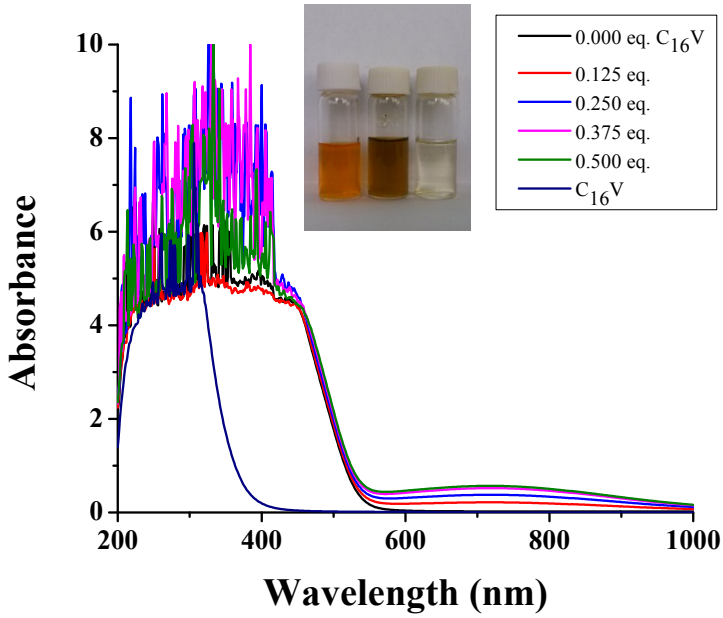
0.25 eq.
0.50 eq.
0.75 eq.
1.00 eq.
C8V


Absorbance
Wavelength (nm)
0.00 eq. C12V
0.25 eq.
0.50 eq.
0.75 eq.
1.00 eq.
C12V



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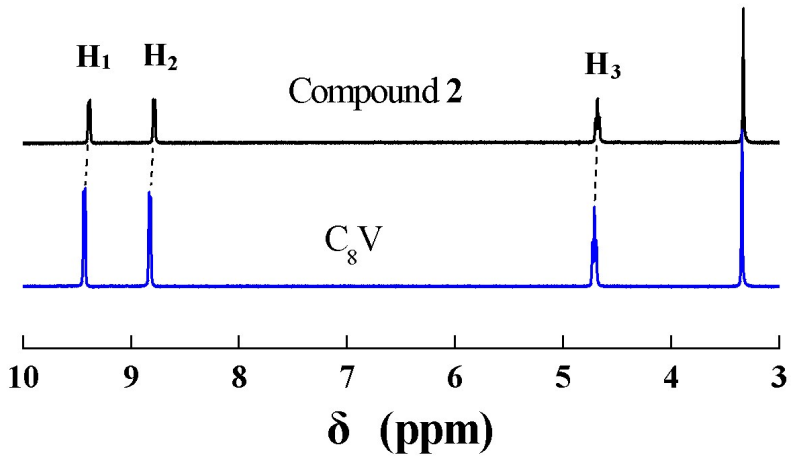
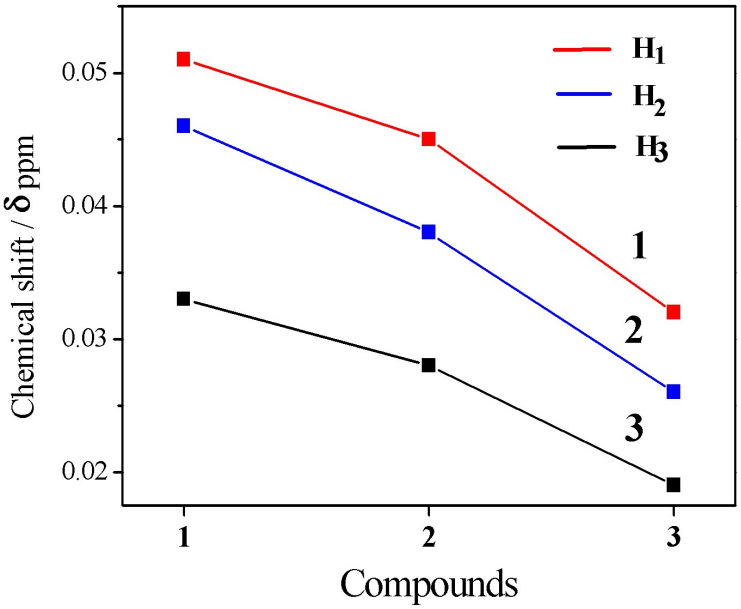


(a)



(b)

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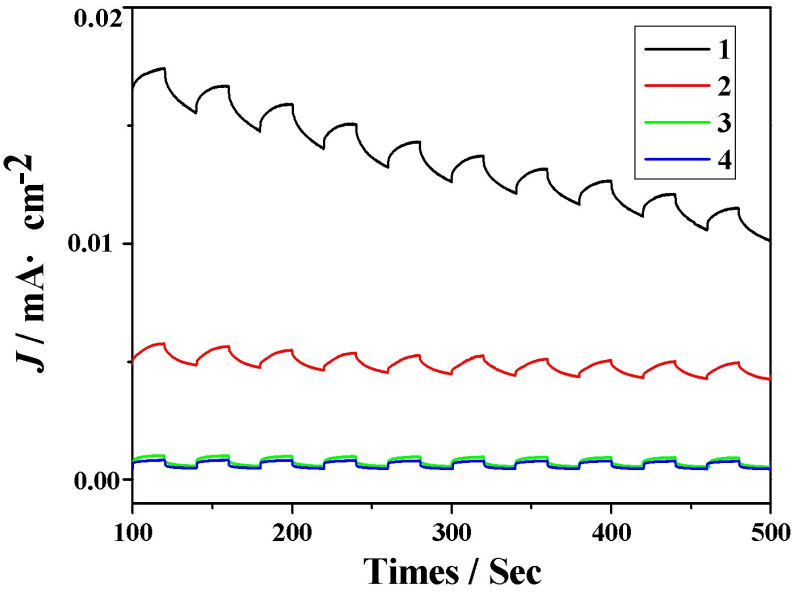
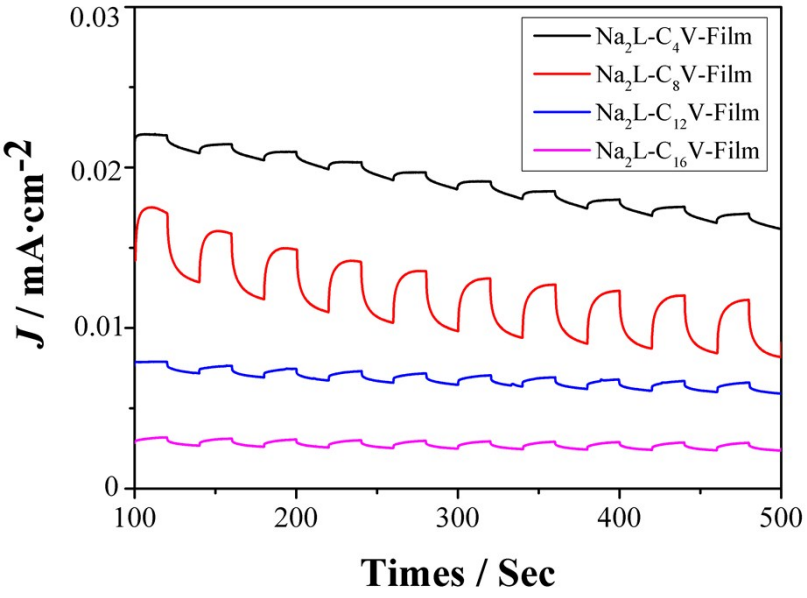


(a)



(b)

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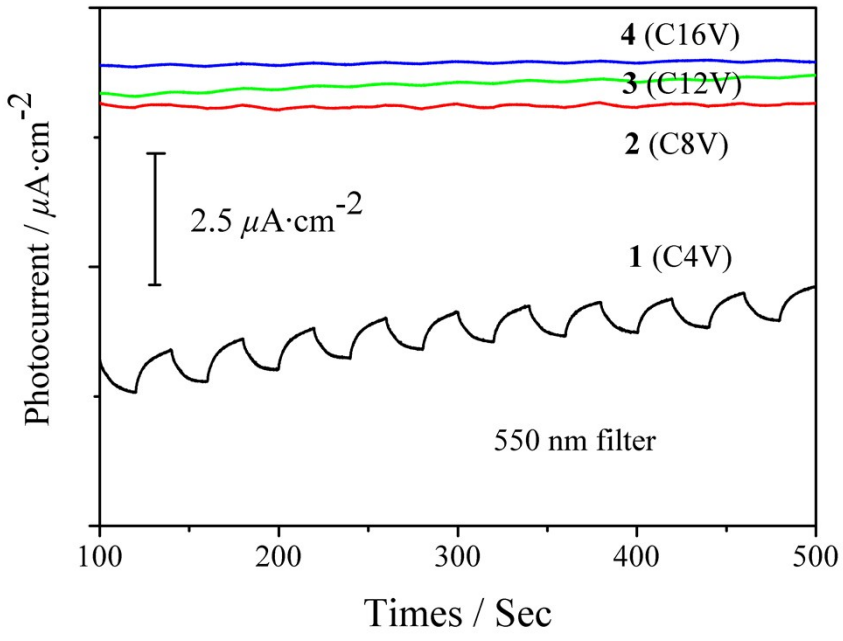
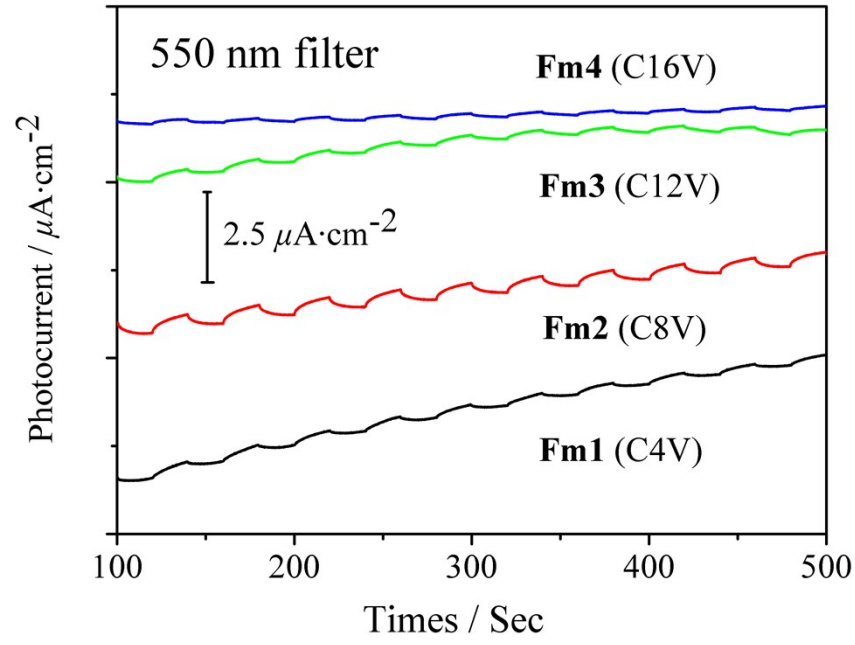


(a)



(b)

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