An ionic charge-transfer dyad prepared cost-effectively from tetrathiafulvalene carboxylate anion and TMPyP cation

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Table S1. Crystal Data and Structural Refinement Parameters for **1** and **2**

	1	**2**
formula	$C_{84}H_{72}N_8O_{19}S_{24}$	$C_{64}H_{52}N_8O_{21}S_8$
fw	2267.07	1525.61
cryst size (mm^3)	0.25 × 0.26 × 0.75	0.05 × 0.12 × 0.20
cryst syst	monoclinic	monoclinic
space group	$P\,2_1/m$	$C\,2/c$
a (Å)	10.8302(4)	23.6681(8)
b (Å)	33.4895(16)	22.0587(6)
c (Å)	13.8319(6)	13.2272(4)
α (deg)	90.00	90.00
β (deg)	99.191(4)	111.589(3)
γ (deg)	90.00	90.00
V ($Å^3$)	4952.4(4)	6421.3(4)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.492	1.578
F(000)	2300	3152
μ (mm^{-1})	5.376	0.365
T (K)	293(2)	293(2)
reflns collected	20829	19610
unique reflns	9892	5651
observed reflns	6181	4629
no. params	638	486
GOF on F^2	1.182	1.034
R_1 [I>2σ(I)]	0.0837	0.0401
$_wR_2$ [I>2σ(I)]	0.1767	0.1063

Table S2. The energy of the frontier orbitals and the energy gaps of **2.**

orbital	energy (eV)	energy gap
LUMO+1	–3.132	$E_{LUMO+1} - E_{HOMO}$ = 1.164 eV (1065.2 nm)
LUMO	–3.259	$E_{LUMO+1} - E_{HOMO-1}$ = 1.171 eV (1058.8 nm)
HOMO	–4.296	$E_{LUMO} - E_{HOMO}$ = 1.001 eV (1238.6 nm)
HOMO-1	–4.303	$E_{LUMO} - E_{HOMO-1}$ = 1.044 eV (1187.6 nm)

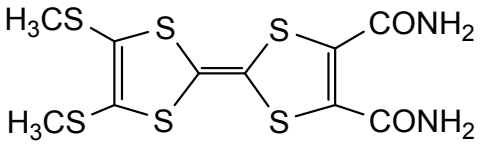


Chart S1 Structure of $TTF(CONH_2)_2$.

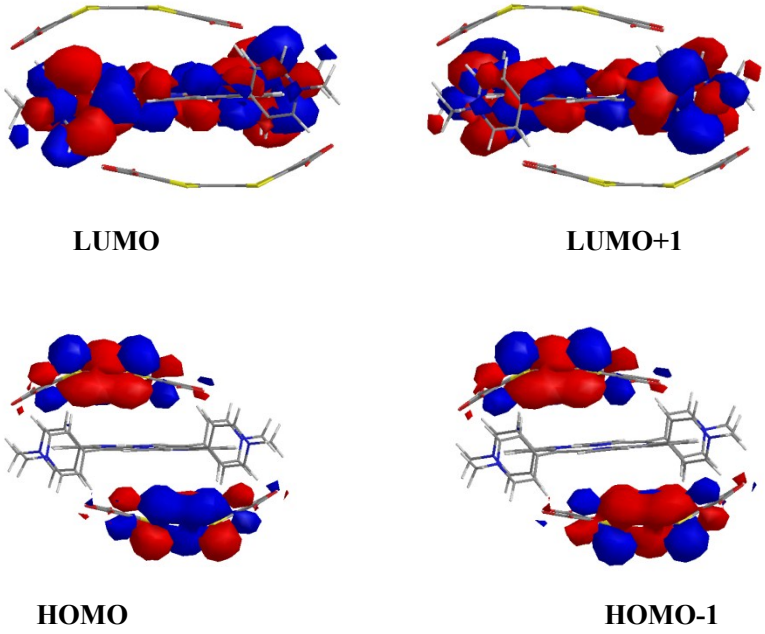


Fig. S1 Frontier molecular orbitals of **2** calculated using DFT B3LYP/6-311G** method.

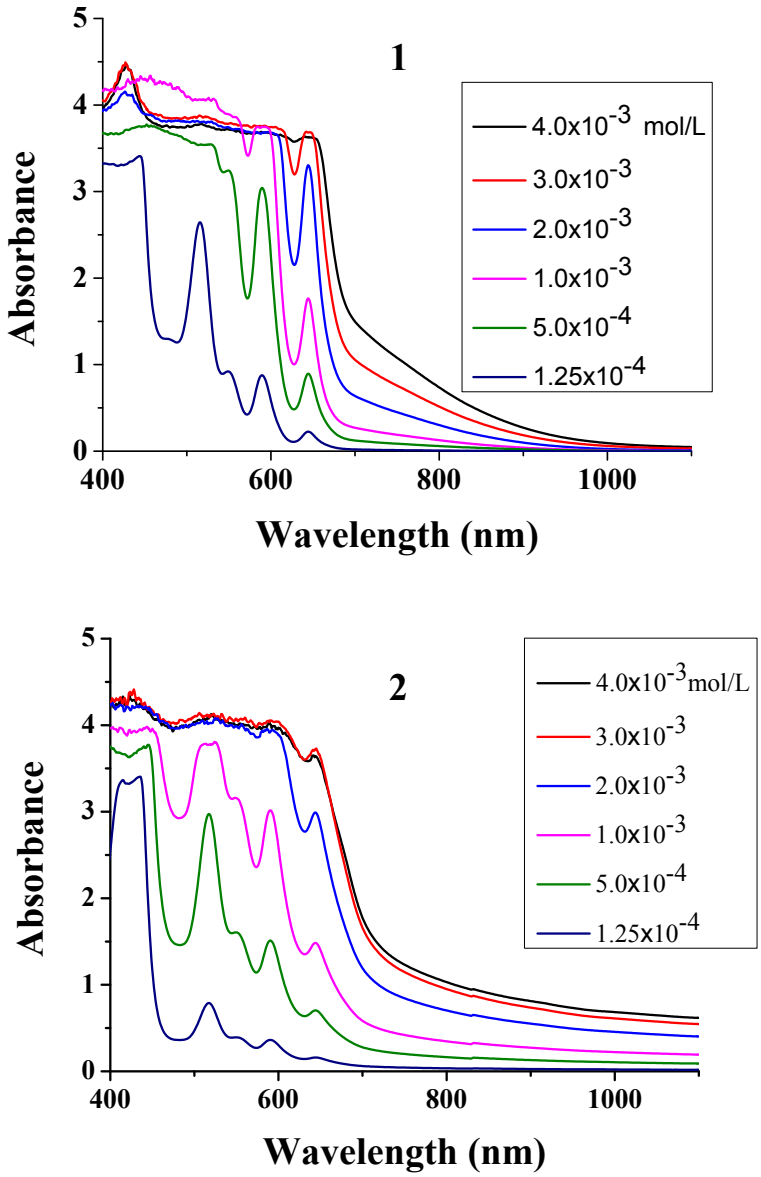


Fig. S2 UV-vis absorption of crystals **1** and **2** in DMF in different concentrations.

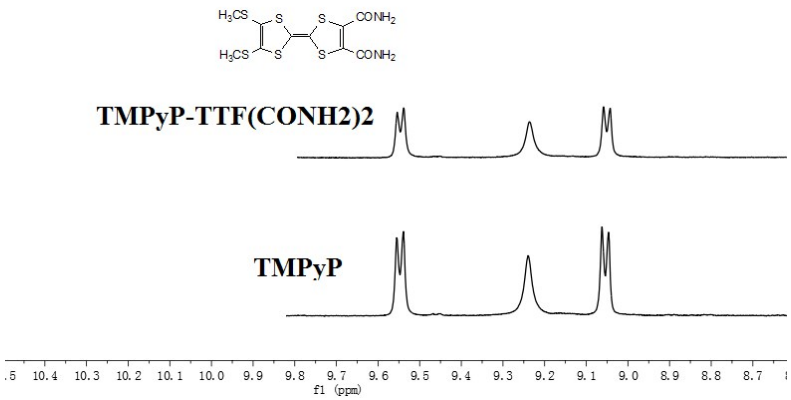


Fig. S3 Partial ^{1}H NMR spectra of TMPyP and the mixture of TMPyP and 4eq. $TTF(CONH_2)_2$ in *d*6-DMSO (the concentration of TMPyP is 4×10^{-3} mol·L^{-1}).

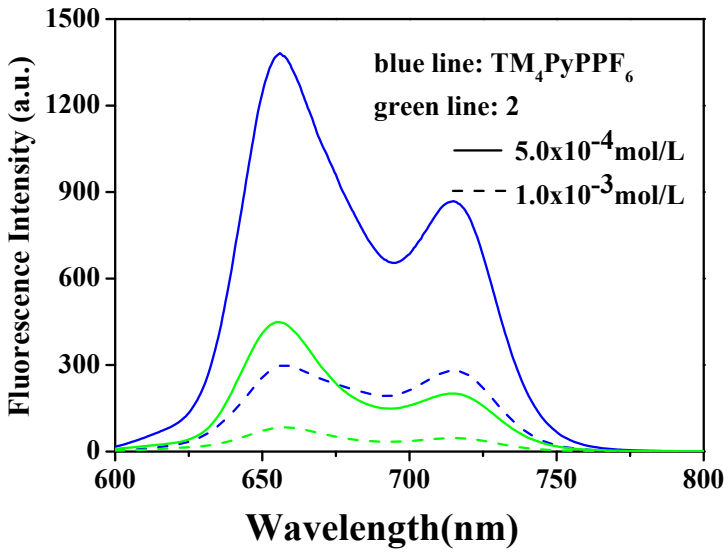


Fig. S4 Comparison of the fluorescence spectra of **2** (λex = 488 nm) with that of **TMPyP** (λex = 470 nm), recorded at 1.0×10^{-3} and 5.0×10^{-4} mol·L^{-1} concentrations in DMF at room temperature.

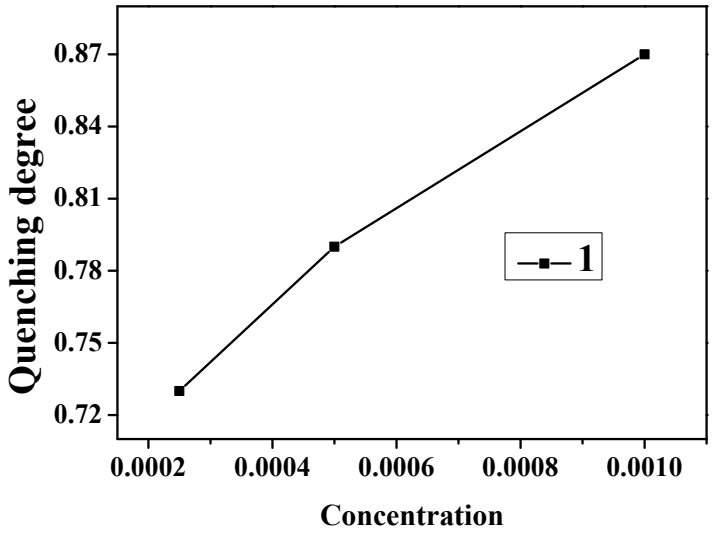


Fig. S5 The relationship between the quenching degree of the fluorescence spectra at the peak of 652 nm and the concentration of **1** [Y-axis (quenching degree) = (fluorescence intensity of TMPyP – fluorescence intensity of **1**)/ fluorescence intensity of TMPyP].

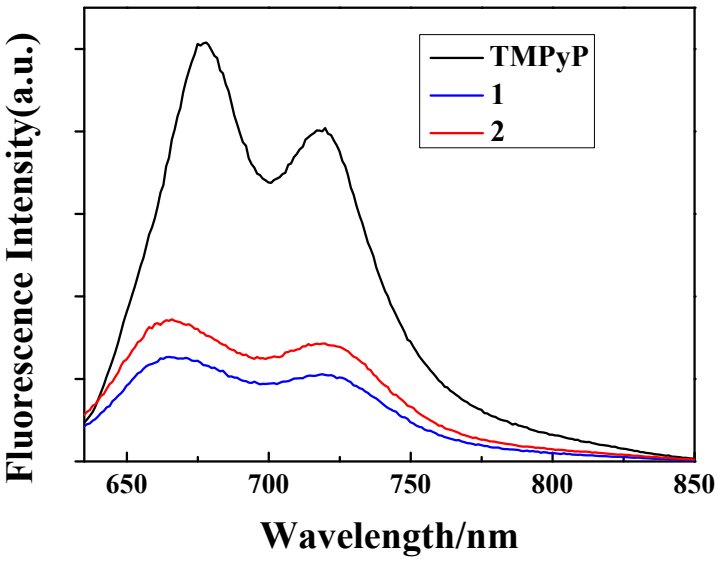


Fig. S6 Fluorescence spectra of TMPyP, **1**, and **2** in solid state at room temperature.

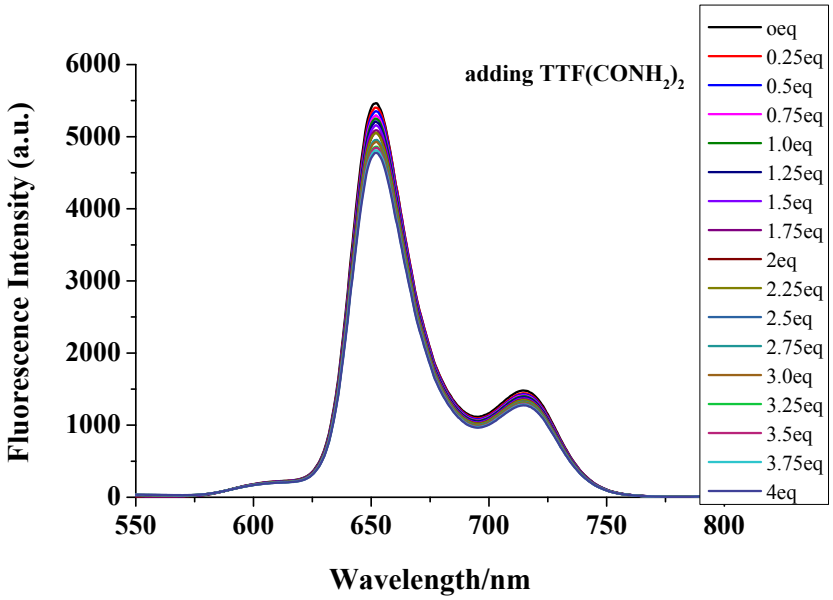
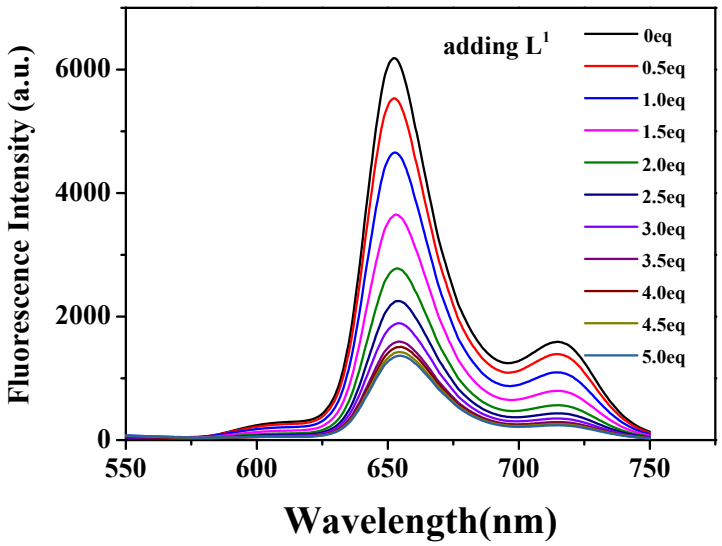


Fig. S7 Changes of fluorescence spectra of TMPyP in DMF at room temperature, upon quantitative titration of $TTF(CONH_2)_2$.



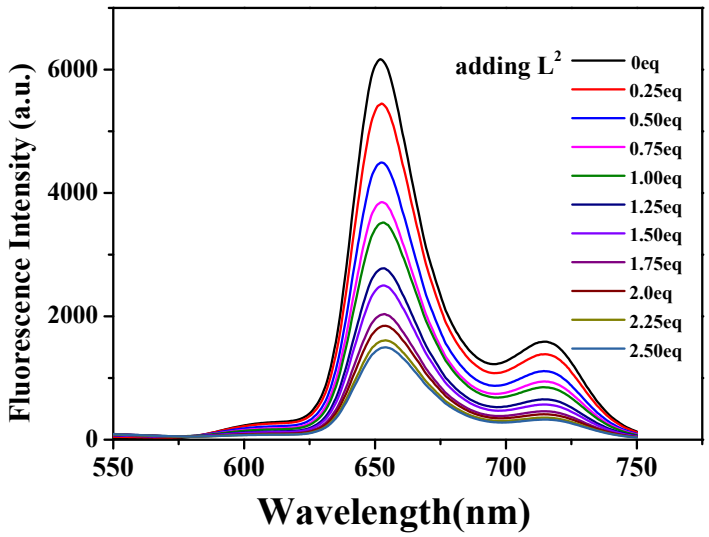


Fig. S8 Changes of fluorescence spectra of TMPyP (2.0×10^{-5} mol·L^{-1}) in DMF at room temperature, upon quantitative titration of L^1 and L^2.