Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effect of intramolecular charge transfer on nonlinear optical properties of chalcone derivatives: a visual description of the charge transfer process

Supporting Information

Jidong Jia,[a] *Xingzhi Wu,*[b] *Xueru Zhang,**[a] *Yuxiao Wang,*[a] *Junyi Yang,*[c] *Yu Fang* [b] *and Yinglin Song**[a]

[a] Department of Physics, Harbin Institute of Technology, Harbin150001, China

[b] Jiangsu Key Laboratory of Micro and Nano Heat Fluid Flow Technology and Energy Application, School of Physical Science and Technology, Suzhou University of Science and Technology, Suzhou, 215009, China

[c] Department of Physics, Soochow University, Suzhou 215123, China

*E-mail: ylsong@hit.edu.cn;

*E-mail: xrzhang@hit.edu.cn.

Table of contents

1 Spectroscopic Characterization:

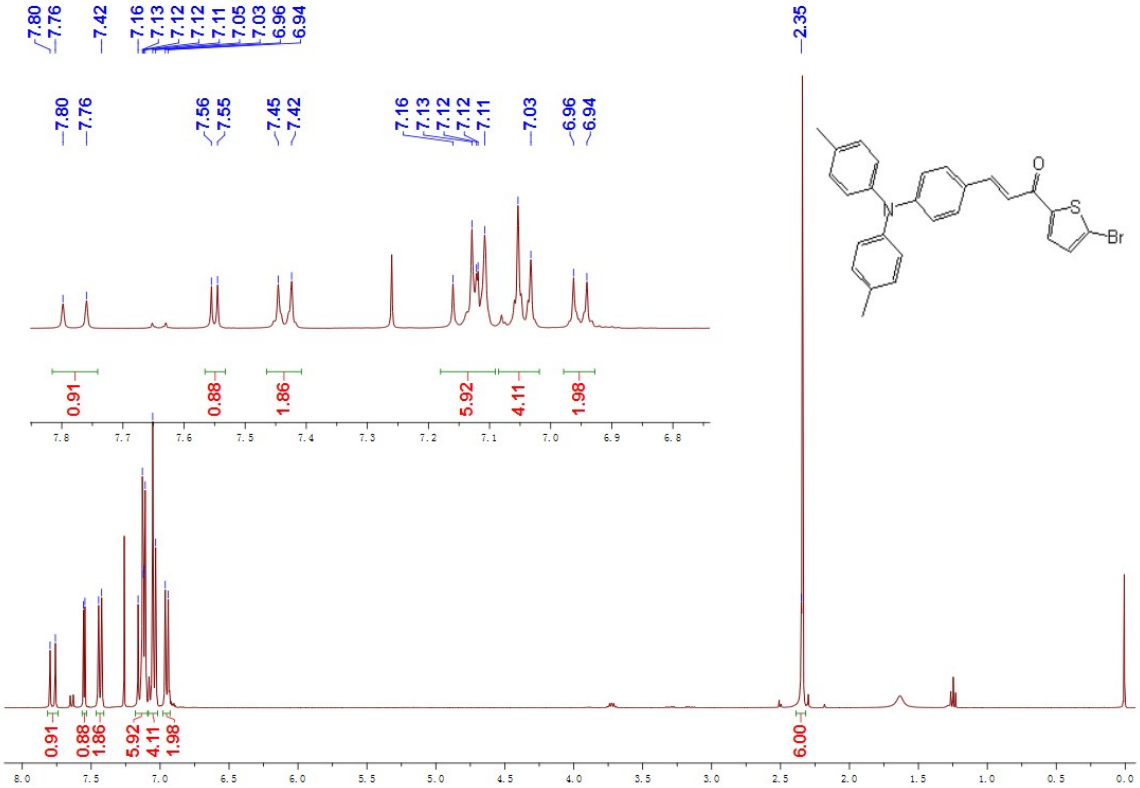

Figure S1. ^{1}H NMR spectrum of compound **3**

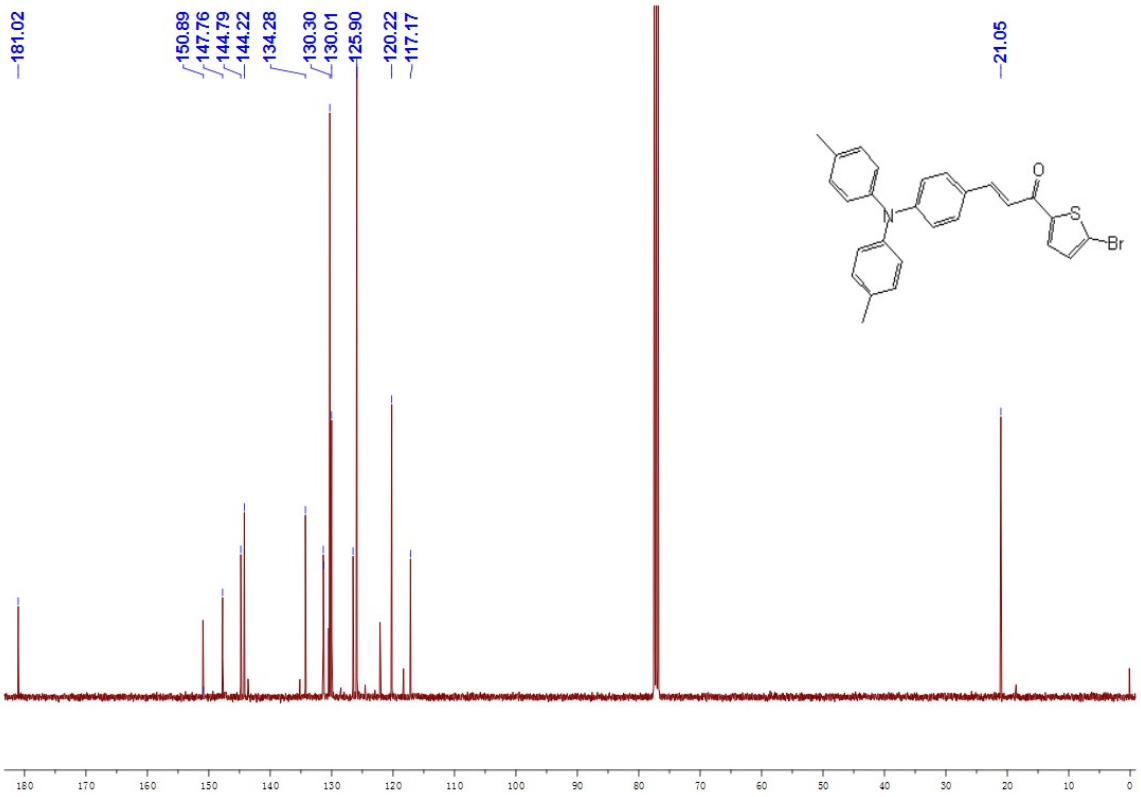

Figure S2. ^{13}C NMR spectrum of compound **3**

2 Transient Absorption Spectrum

TAS of compounds **1** and **2** in solvents of varying polarities (DMSO, DMF and THF) are shown in **Figure S3** and **S4**. The spectrum ranges from the visible to the near-infrared (from 475 to 1050 nm). The strong ESA signals of compounds **1** and **2** are concentrated at 700 nm and no obvious ESA is observed in the near-infrared region. TAS of compounds **1** and **2** in THF show typical LES feature. However, it can be found that TAS of compounds **1** and **2** in DMF and DMSO show obvious long-lived ICT processes with the increase of the solvent polarity and CTS appears centered at 565 nm within a few picoseconds. The CTS of compound **2** is more obvious compared with compound **1**, indicating that compound **2** has stronger ICT performance. We further carried out

numerical fitting of TAS data through the global fitting analysis. All parameters are shown in **Table S1**.

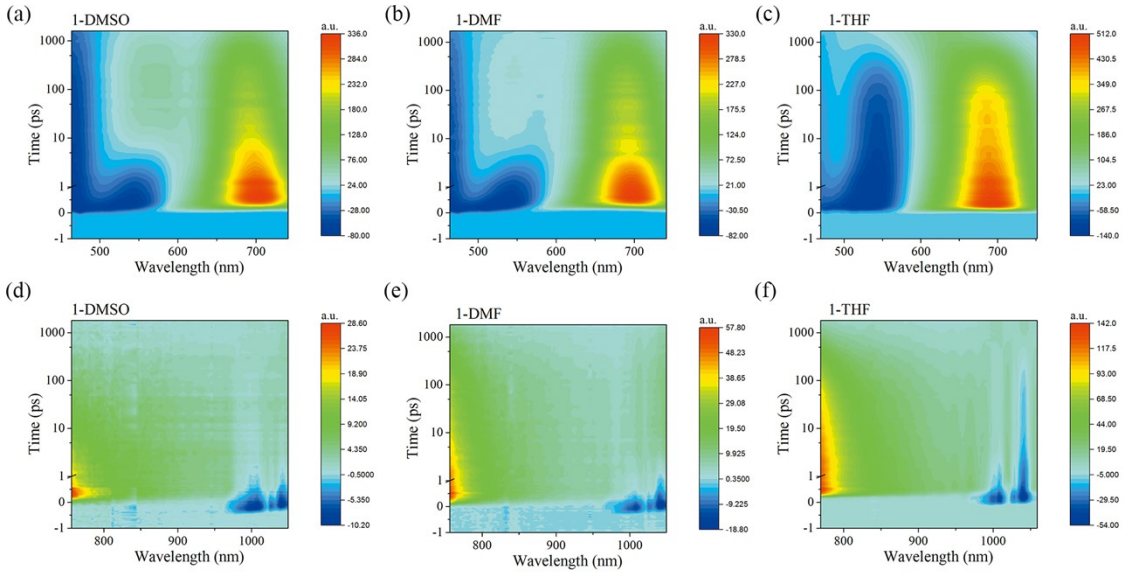

Figure S3. TAS of compound **1** in DMSO, DMF and THF

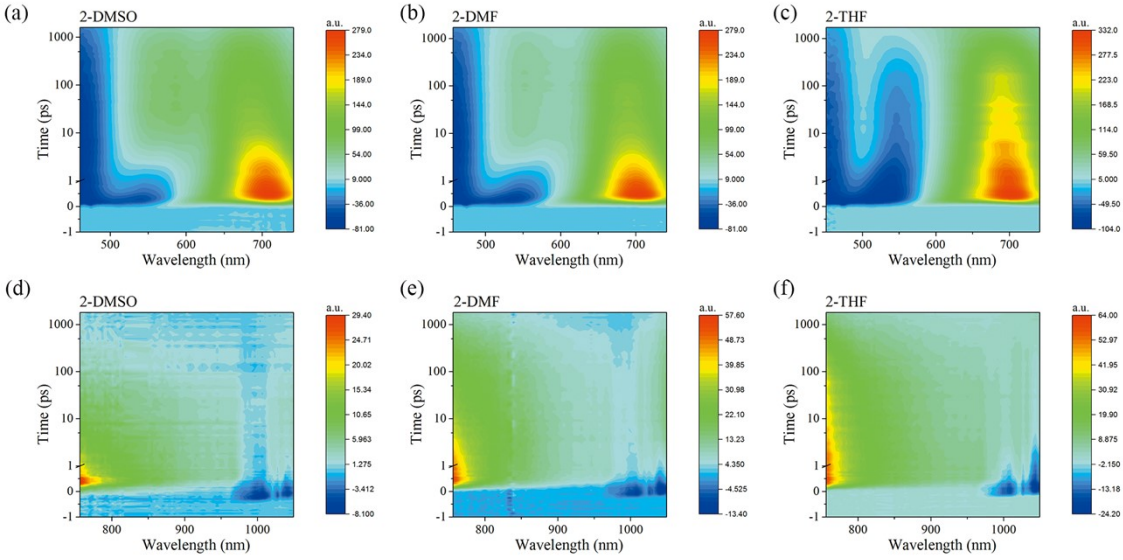

Figure S4. TAS of compound **2** in DMSO, DMF and THF

Sample	Solvent	τ_1 (ps)	τ_2 (ps)			τ_3 (ps)
			τ_a	τ_b	τ_c	
1	DMSO	<0.25	0.506	5.02	116.0	1890
	DMF	<0.25	1.117	2.87	333.5	3085
	THF	<0.25	2.163	472	-	17690
2	DMSO	<0.25	1.176	6.47	178.8	2427
	DMF	<0.25	0.958	4.90	219.6	2793
	THF	<0.25	2.421	560	-	6775

Table S1. Fitting parameters of TAS of compounds **1** and **2** in DMSO, DMF and THF

extracted from the global fitting analysis.

In order to confirm the ESA band at 565 nm in the TA results of compounds **1** and **2** in DMSO (**Figure 2** in the manuscript) is CTS, we analyzed the key kinetics at about 565 and 700 nm (Shown in **Figure S5**). It can be found that the kinetics of compound **1** at 565 and ~700 nm (**Figure S5** (a) and (b)) are extremely similar with compound 2. Therefore, we choose the kinetics of compound **1** (Figure S6 (a)) as an example for detailed discussion. The kinetics of compound **1** at 565 and 699 nm can be divided into three related processes. In the first process, the kinetics at 699 nm shows the rapid attenuation of ESA signal. At the same time, the kinetics at 565 nm shows the rapid enhancement of ESA signal. It is worth noting that the initial negative TA signal of kinetic at 565 is caused by SE effect. Therefore, the first process can be assigned to the ICT. In the second process, it can be found that the decay (kinetics at 699 nm) and increase (kinetic at 565 nm) of ESA signal tends to be slow. This is because the number of excitons between CTS and LES tends to balance. For kinetics at 565 nm, this process can be ascribed to the solvation and stability of CTS. For kinetics at 699 nm, this process can be ascribed to the number of excitons in LES tends to stabilize. In the third process, the kinetics at 565 and 699 nm both show a slow decay of the ESA signal, which is caused by the gradual relaxation of the excitons from excited state to the ground state. Based on the analysis of the key kinetics, we confirmed that the ESA bands of compounds **1** and **2** at 565 nm are CTS.

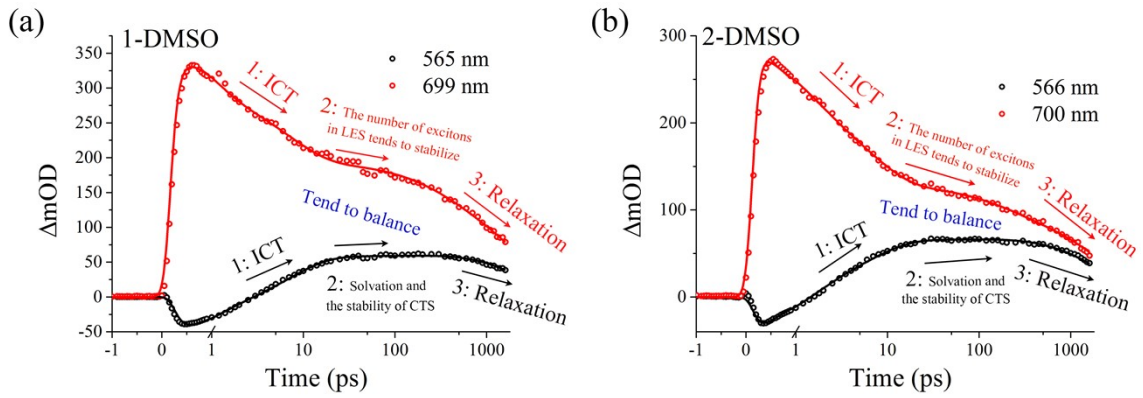

Figure S5. Transient absorption data (dots) and global analysis fits (solid lines) of compounds **1** (a) and **2** (b) at about 565 and 700 nm.

TAS of compound **3** in toluene was further conducted to determine the polarity-dependent ICT process (Shown in **Figure S6**). Strong and long-lived ESA centered at 580 nm on the LES is the main feature of compound **3** in toluene in the visible region. In the near-infrared region, compound **3** in toluene also shows strong and long-lived ESA signal with typical CTS characteristics. The CTS of compound **3** in THF is much weaker than that of compound **3** in DMSO, DMF and THF due to the decrease of ICT induced by solvent polarity.

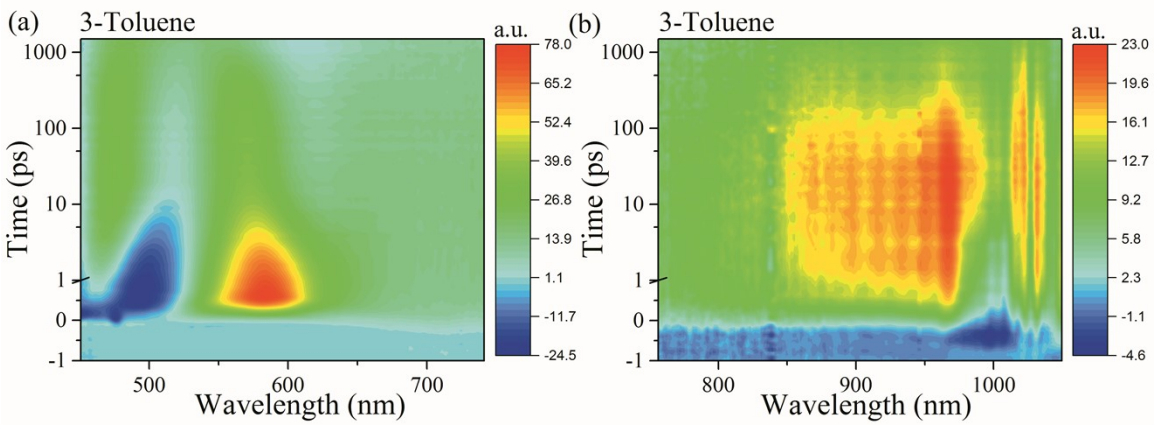

Figure S6. TAS of compound **3** in toluene

In addition, we have also analyzed the key kinetics of compound **3** (at about 520 and 580 nm, shown in **Figure S7**) in DMSO, DMF and THF to confirm the ESA band

(centered at 520 nm) and SE band (centered at 620 nm, **Figure 3** in the manuscript) are CTS. The kinetics of compound **3** at about 520 and 580 nm can also be divided into three related processes. The dynamic process of compound **3** in DMSO (**Figure S7** (a)) and DMF (**Figure S7** (b)) are very similar. Here we take **Figure S7** (a) as an example. In the first process, the dynamics at 580 nm shows that the ESA signal rapidly decays until it was a negative TA signal, which could be attributed to ICT and SE effects. At the same time, the kinetics at 523 nm shows rapid enhancement of the ESA signal. In the second process, the kinetics at 523 nm shows that the ESA signal slowly increases and tends to gradually stabilize which can be ascribed to solvation and the stability of CTS. With the decay of SE effect, the TA signal of kinetics at 580 nm gradually changes from negative signal to positive signal. The ESA signal becomes stabilized which can be ascribed to the number of excitons in LES trends to stability. In the second process, the slightly different time for the kinetics to reach equilibrium at 523 and 580 nm is due to the SE effect. In the third process, the kinetics at 523 and 580 nm both show a slow decay of the ESA signal, which is caused by the gradual relaxation of the excitons from excited state to the ground state. The kinetics of compound 3 in THF at 520 and 581 nm are significantly different from those of compound 3 in DMSO and DMF, especially the second and third processes. We infer that this is caused by the difference in the lifetime of the fluorescence emission in different CTSs. This inference can also be confirmed from the longer-lived SE band of compound 3 in THF (centered at 620 nm) than those of compound 3 in DMSO and DMF (Figure 3 in the manuscript). In the third process, the ESA signal of the kinetics of compound 3 at 520 nm shows a typical attenuation which is

caused by the relaxation of the excitons from the excited state to the ground state. The negative TA of the kinetics of compound 3 at 581 nm gradually tends to zero which can be ascribed to the attenuation of SE effect. Based on the analysis of the key kinetics, we confirmed that the ESA bands of compounds 3 at 520 nm are CTS. The discussion for the SE band has been performed in the manuscript.

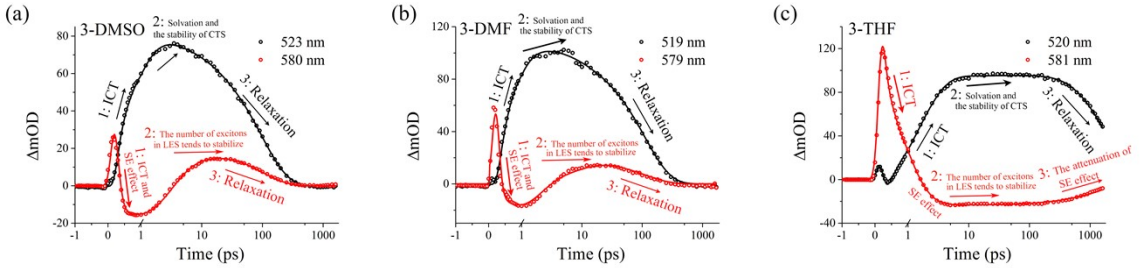

Figure S7. Transient absorption data (dots) and global analysis fits (solid lines) of compounds **3** in DMSO (a), DMF (b) and **THF** (c) at about 523 and 579 nm.

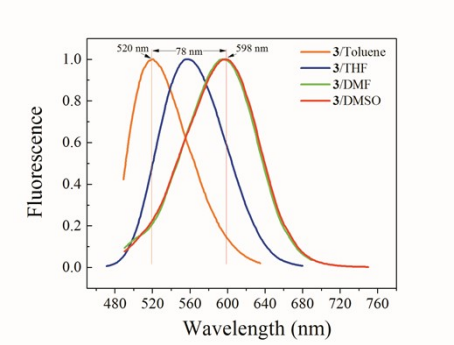

Figure S8. Normalized fluorescence emission spectra of compound **3** in different solvents (Toluene, THF, DMF and DMSO)

The optical density of compound **1**, **2** and **3** in DMSO, DMF and THF at 500, 532 and 650 nm are calculated according to the expression $OD = \lg(\frac{1}{T})$, where T denotes the linear transmittance. All parameters are shown in Table S2.

	Solvent	Wavelength (nm)	Transmittance	Optical Density
1	DMSO	500	0.54	0.268
		532	0.85	0.071
		650	0.99	0.004
	DMF	500	0.54	0.268
		532	0.94	0.027
		650	0.97	0.013
	THF	500	0.83	0.081
		532	0.91	0.041
		650	0.99	0.004
2	DMSO	500	0.12	0.921
		532	0.51	0.292
		650	0.97	0.013
	DMF	500	0.26	0.585
		532	0.77	0.114
		650	0.99	0.004
	THF	500	0.32	0.495
		532	0.86	0.066
		650	0.99	0.004
3	DMSO	500	0.36	0.444
		532	0.77	0.114
		650	0.97	0.013
	DMF	500	0.52	0.284
		532	0.89	0.051
		650	0.90	0.046
	THF	500	0.68	0.168
		532	0.94	0.027
		650	0.99	0.004

Table S2. Optical density of compounds **1**, **2** and **3** in DMSO, DMF and THF at a concentration of 5.9×10^{-4} mol L^{-1} at 500, 532, and 650 nm

3 Electron-Hole Distribution Ratios of Different Fragments in compounds **1** and **2**

We roughly divided compounds **1**, **2** and **3** into three fragments according to their typical Donator-π-Acceptor structure. Fragment 1, 2 and 3 represent the acceptor, π-bridge and the donator, respectively. Fragment 2 and 3 in compounds **1** and **2** separately denote acrolein and terthiophene. The rest includes the only remaining thiophene in compound **1** and 2-bromothiophene in compound **2**, both representing fragment 1. Fragment 1, 2 and 3 in compound **3** denote 2-bromothiophene, acrolein and 4,4'-dimethyltriphenylamine, respectively. **Table S3** shows the electron distribution ratio of different fragments in compounds **1**, **2** and **3**. Most of the electron distribution of compound **1** is concentrated in fragment 3 (terthiophene). However, it can be found that the electron distribution ratio of fragment 1 (thiophene) and fragment 2 (acrolein) in compound **1** gradually increases with the increase of solvent polarity which indicates the enhancement of ICT. Most of the electron distribution of compound **2** is concentrated in fragment 1 (2-bromothiophene) and fragment 2 (acrolein) which is different from that of compound **1**. This is because 2-bromothiophene in compound **2** has a stronger electron-withdrawing ability than thiophene in compound **1**. Compare with the electron distribution of compound **2** in THF, the electron distribution of compound **2** in DMF show stronger ICT characteristics with the increase of electron distribution ration of fragment 1 and 2. However, the electron distribution of compound **2** in DMSO unexpectedly changed. Does the decrease in the electron distribution ratio of

Fragment 1 and Fragment 2 in compound **2**/DMSO indicate a decrease in ICT? We do not think so. Imagine that a large number of fast-moving electrons gather in a small space. With the enhancement of ICT, the number of electrons is increasing. Eventually, the collision between electrons will cause the overflow of electrons, so that the electron distribution ratio of Fragment 1 and Fragment 2 in compound **2**/DMSO is slightly reduced. The electron distribution ratio in compound **3** shows completely different situations with the increase of solvent polarity. It can be found that the electron distribution ratio of Fragment 2 in compound **3** gradually increases with the increase of solvent polarity, which is completely opposite to the situation of Fragment 1 and 3. This indicates that more and more electrons leave the 4,4'-dimethyltriphenylamine and 2-bromothiophene and realize the population on the acrolein with the increase of solvent polarity, which can be attributed to the effect of the significantly distorted molecular structure.

		Electron distribution ratio		
	Solvent	Fragment 1	Fragment 2	Fragment 3
1	DMSO	12.71%	25.88%	61.29%
	DMF	12.55%	25.77%	61.56%
	THF	12.23%	25.64%	61.97%
2	DMSO	33.33%	40.00%	26.54%
	DMF	33.42%	40.05%	26.40%
	THF	33.38%	40.04%	26.45%
3	DMSO	37.32%	37.51%	25.17%
	DMF	37.34%	37.42%	25.24%

THF	38.49%	37.20%	24.31%

Table S3. The electron distribution ratio of different fragments in compounds **1**, **2** and **3**. The electron in hole-electron analysis denotes where electrons increase. All parameters are extracted from hole-electron analysis.