Supporting Information

Stimuli-responsive luminescent bithiophene-dicarbaldehyde molecular rotors by hydrogen bonding

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1. Experimental Section

1.1 Materials

3-Formyl-2-thiopheneboronic acid (98 %), 5-formyl-2-thiopheneboronic acid (98 %) and silica gel (powder, 200 mesh) were purchased from J&K Scientific Ltd (Beijing, China). Cupric acetate (anhydrous, 97 %) was purchased from Energy Chemical Co. (Shanghai, China). SiO_2 (powder, 99.8 %) was purchased from Sinopharm Chmical Reagent Co. (Beijing, China) Organic solvent were purchased from Beijing Chemical Reagent Plant (analytical grade, 99.0+ %). All chemicals were used as received without further purification unless otherwise specified.

1.2 Synthesis[1]

The 2T3C and 2T5C were synthesized by the procedure described in reference [1] with some slight modifications.

Preparation of [2,2'-bithiophene]-3,3'-dicarbaldehyde (2T3C)

3-Formyl-2-thiopheneboronic acid (0.6017 g) and of anhydrous cupric acetate (0.3640 g) were added into 10 mL DMF. Then the reaction mixture was refluxed with stirring for 6 h (monitored by TLC). After cooling, DMF were evaporated under reduced pressure, the resulting mixture was poured into 50 mL water, extracted with dichloromethane three times (3×50 mL) and the organic layers were evaporated under reduced pressure. The crude product was purified on a silica-gel column to obtain a white powder of **2T3C** (0.135 g, 31%). 1H NMR (400 MHz, CDCl3) δ 9.86(s, 2H), 7.64(d, J=3.6Hz, 2H), 7.49(d, J=4.8Hz, 2H).

Preparation of [2,2'-bithiophene]-5,5'-dicarbaldehyde (2T5C)

5-Formyl-2-thiopheneboronic acid (0.6017 g) and of anhydrous cupric acetate (0.3640 g) were added into 10 mL DMF. Then the reaction mixture was refluxed with stirring for 6 h (monitored by TLC). After cooling, DMF were evaporated under reduced pressure, the resulting mixture was poured into 50 mL water, extracted with dichloromethane three times (3×50 mL) and the organic layers were evaporated under reduced pressure. The crude product was purified on a silica-gel column to obtain yellow powder of **2T5C** (0.098 g, 23%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.92(s, 2H), 7.72(d, J=4.4Hz, 2H), 7.42(d, J=4.4Hz, 2H).

Preparation of crystals

10 mg 2T3C or 2T5C was dissolved in 2 mL dichloromethane, by slow evaporation in refrigerator (4-6 °C) for about 2 weeks. 2T3C or 2T5C single crystal was obtained.

1.3 Instruments and methods

Total luminescence and phosphorescence spectra of solid samples, lifetime of phosphorescence and fluorescence, and absolute quantum yield were all recorded or measured on a FLS980 Spectrometer with a xenon arc lamp (Xe900) and a microsecond flash-lamp (uF900) (Edinburgh Instruments Ltd.). The absolute quantum yields of the solution samples and solid samples at room temperature were estimated by using an integrating sphere (F-M101, Edinburgh) accessory in FLS980 fluorescence spectrometer. The step, dwell time, and delay time were set at 1.00 nm, 0.1 s, and 0.1 ms, respectively. Fluorescence spectra of solution samples were obtained on a Hitachi F-4600 fluorescence spectrometer. UV absorption spectra of solution samples were collected on a Purkinje TU-1901 UV-Visible spectrophotometer. UV absorption spectra of solid samples were collected on a PerkinElmer Lambda 950 UV-Visible spectrophotometer with integrating sphere.

Single crystal X-Ray diffraction data were collected at 100 K with a SuperNova Rigaku Oxford Diffraction diffractometers with Cu−Kα radiation, $\lambda = 1.54184$ Å.

The PXRD data were collected at 298 K with a Shimadzu XRD-700 diffractometer with Cu−Kα radiation (X-ray sources, $\lambda = 1.5418$Å). Measurement range is set to $5° < 2\theta < 70°$ with the step size of $0.0330°/2\theta$.

The MS data were collected by SCIEX Triple TOF™ 5600 mass spectrometer in positive-ion mode (electrospray ionization mass spectrometry, ESI-MS).

^{1}H NMR spectra were obtained using a JEOL-400 spectrometer.

All calculations were carried out with the GAUSSIAN09[2] quantum chemistry package by the M062X[3] /aug-cc-pVDZ method. The initial structure was taken from the crystal structure, and the size of the dihedral angle was set by the GuassView software.
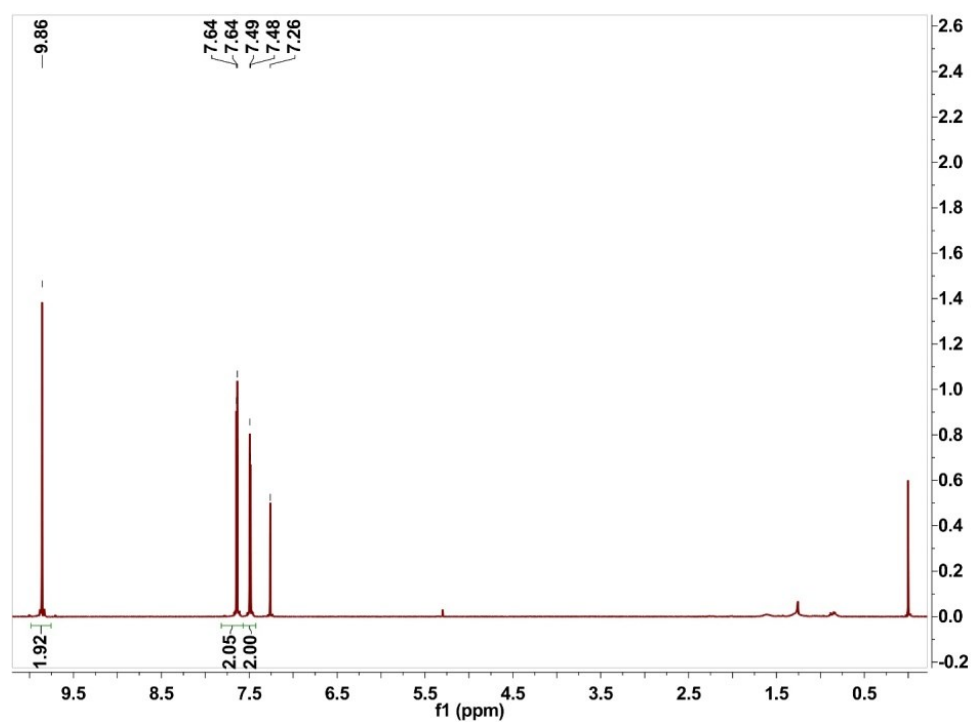
2. Result and characterization
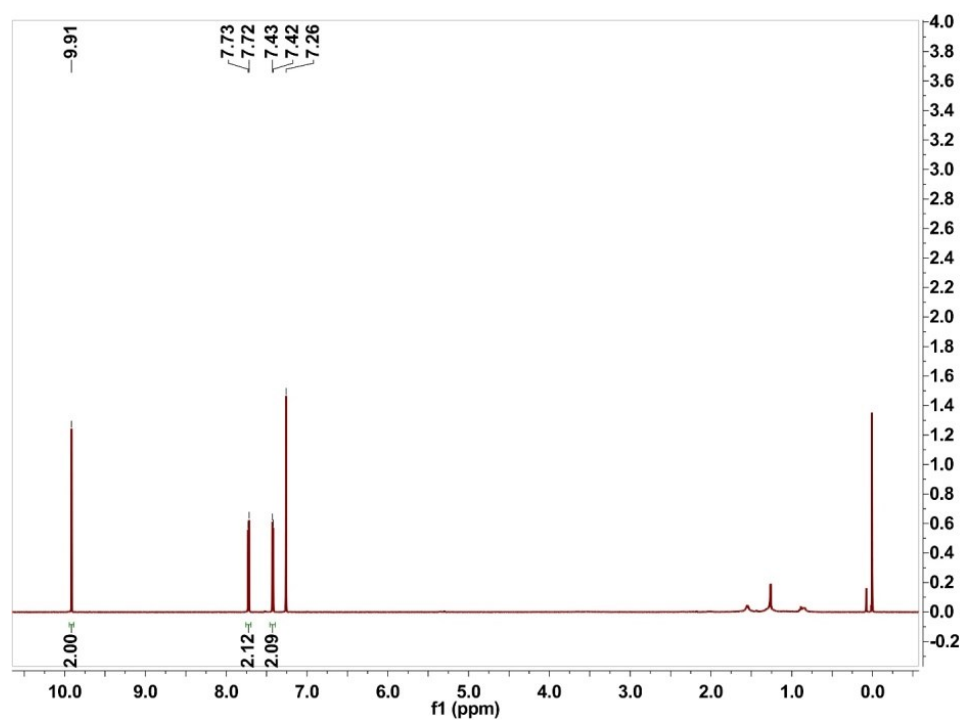

Figure S1. ^{1}H NMR spectrum of 2T3C (in CDCl$_3$).

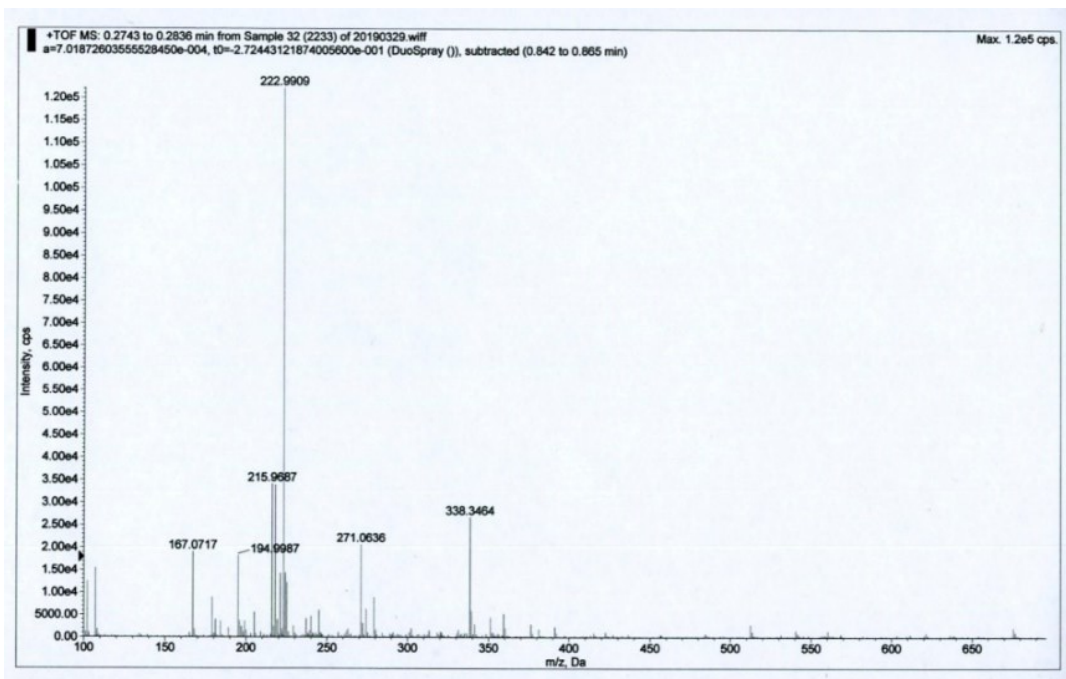**Figure S2**. ^{1}H NMR spectrum of 2T5C (in CDCl$_3$).

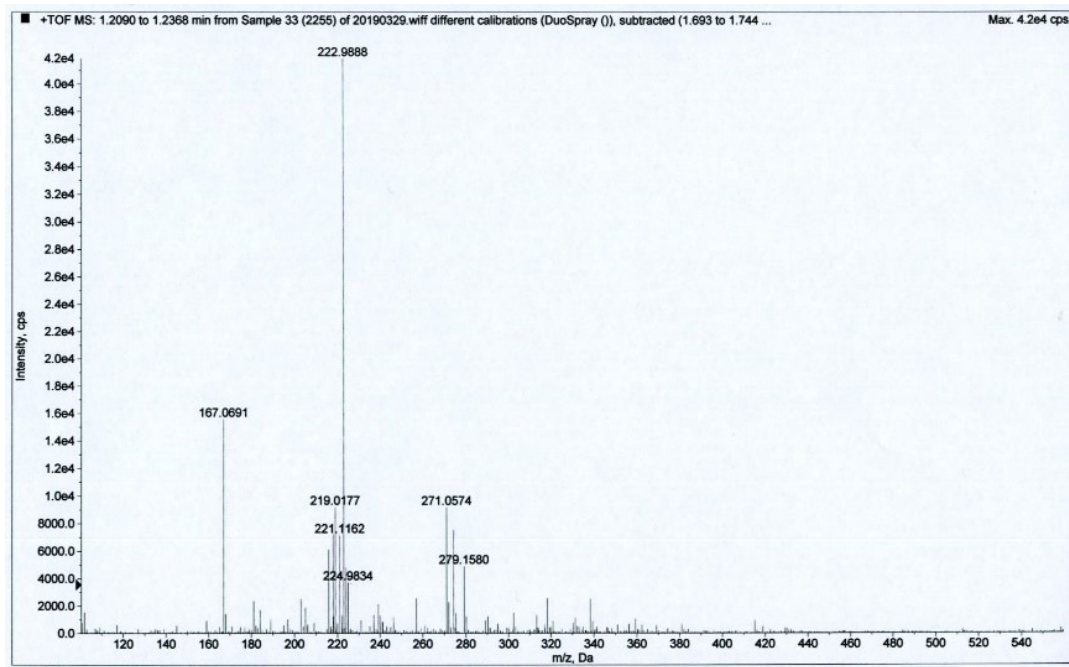**Figure S3**. Mass spectrum of 2T3C.

Figure S4. Mass spectrum of 2T5C.

In order to prove the molecular rotor properties of 2T3C and 2T5C, the fluorescence spectra and quantum yields as well as decay profiles in the methanol-glycerol mixed solvent are recorded at room temperature, the results are shown in **Fig S5a-5f** and **Table S1**. The viscosity of the solution is increased as the volume fraction of glycerol is increased (0%-70%), thus the fluorescence quantum yield and lifetime of 2T3C and 2T5C are increased, which confirm the restriction of rotation of mo-lecular rotors and suppression of non-radiative transition.[4] Further, according to the Fröster–Hoffmann equation (1),[5] correlation of fluorescence quantum yield (Φ) with the viscosity (η) of the medium are shown in **Fig S5c** and **Fig S5d**.

$$\log \Phi = C + x \log \eta \tag{1}$$

Where x is a dye-dependent constant and C is a con-centration- and temperature-dependent constant. Both 2T3C and 2T5C show a linear relationship between $\log \Phi$ and $\log \eta$. The x values of

2T3C and 2T5C are close, 0.2511 and 0.2123, respectively. The result indicates that the fluorescence of 2T3C and 2T5C have similar sensitivity to viscosity changes because they have the same number of rotatable thiophenes. The dependence of log Φ to log η does not obey the (1/3 to 2/3) power of viscosity. This implies the orientation relaxation of rotor is not a simple free-volume-dependent process and should include other intermolecular interaction process.[6]
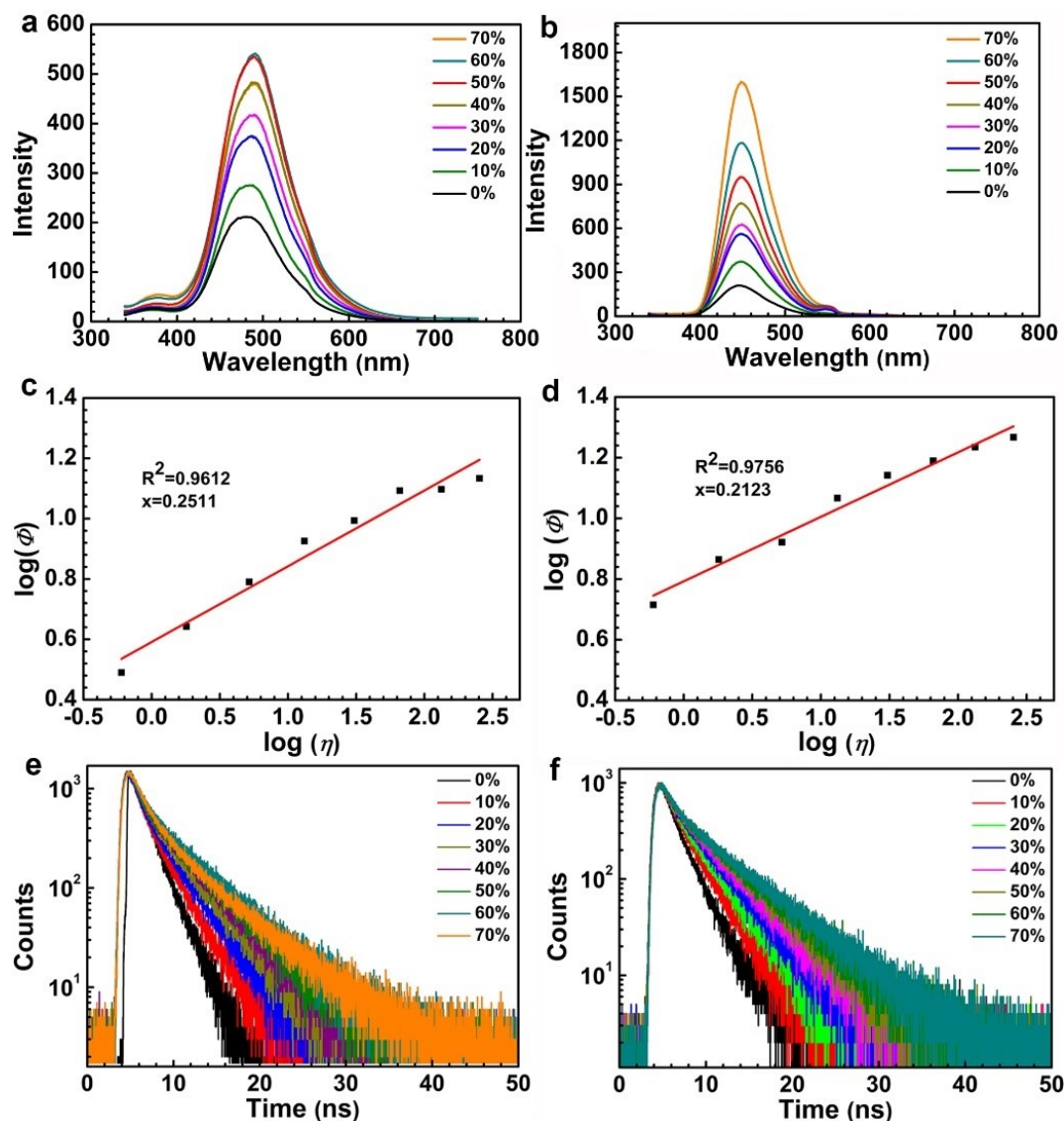

Figure S5. Normalized fluorescence spectra of 50 μM (a) 2T3C and (b) 2T5C in binary mixtures of methanol and glycerol in different volume fraction of glycerol (0-70%). Correlation of fluorescence quantum yield of (c) 2T3C and (d) 2T5C with the viscosity of the medium according to Fröster–Hoffmann equation. Fluorescence decay profiles of 50 μM (e) 2T3C and (f) 2T5C in binary mixtures of methanol and glycerol in different volume fraction of glycerol. The experiments were carried out at room temperature.

Table S1. Spectroscopic data of 50 μM 2T3C and 2T5C in binary mixtures of methanol and glycerol in different volume fraction of glycerol (0-70%).

vol (%)	η^a (cP)	λ_F (nm)	τ (ns)	Φ (%)	k_r^b (s^{-1})	k_{nr}^c (s^{-1})
			2T3C			
0	0.6	480	1.80	3.09	1.7192×10^7	5.3920×10^8
10	1.8	486	2.45	4.39	1.7896×10^7	3.8977×10^8
20	5.2	484	2.99	6.17	2.0634×10^7	3.1379×10^8
30	13.2	486	3.44	8.43	2.4524×10^7	2.6639×10^8
40	30.6	484	3.81	9.86	2.5883×10^7	2.3663×10^8
50	66.0	487	4.16	12.39	2.9811×10^7	2.1079×10^8
60	133.2	487	4.73	12.51	2.6444×10^7	1.8494×10^8
70	253.5	487	4.44	13.60	3.0658×10^7	1.9477×10^8
			2T5C			
0	0.6	450	2.11	5.19	2.4654×10^7	4.5038×10^8
10	1.8	450	2.67	7.32	2.7459×10^7	3.4766×10^8
20	5.2	451	3.18	8.35	2.6256×10^7	2.8819×10^8
30	13.2	452	3.63	11.67	3.2181×10^7	2.4357×10^8
40	30.6	451	4.17	13.87	3.3233×10^7	2.0637×10^8
50	66.0	451	4.67	15.49	3.3202×10^7	1.8114×10^8
60	133.2	450	5.07	17.18	3.3889×10^7	1.6337×10^8
70	253.5	450	5.52	18.51	3.3541×10^7	1.4766×10^8

[a] η is viscosity of methanol/glycerol mixture.

[b] $k_r = \Phi / \tau$
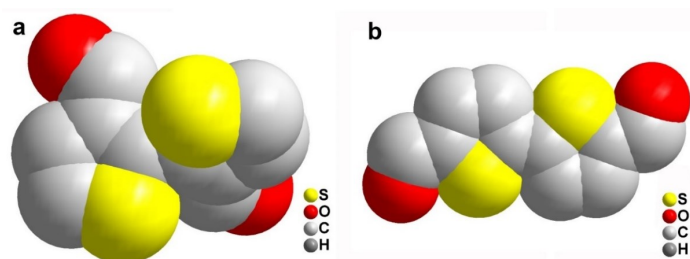
[c] $k_{nr} = (1-\Phi)/\tau$

Figure S6. Space-fill style structures of (a) 2T3C and (b) 2T5C in crystal.
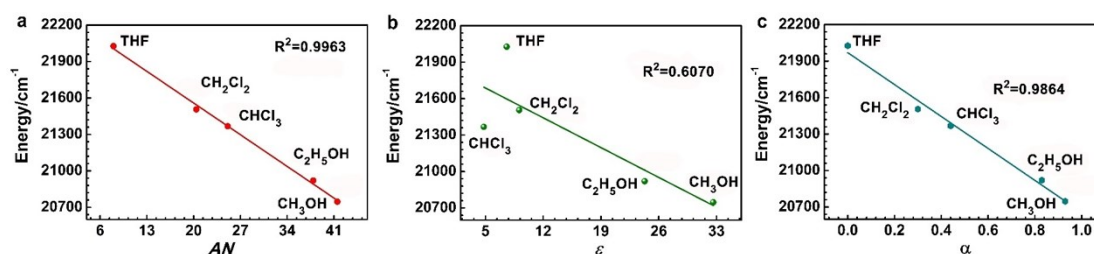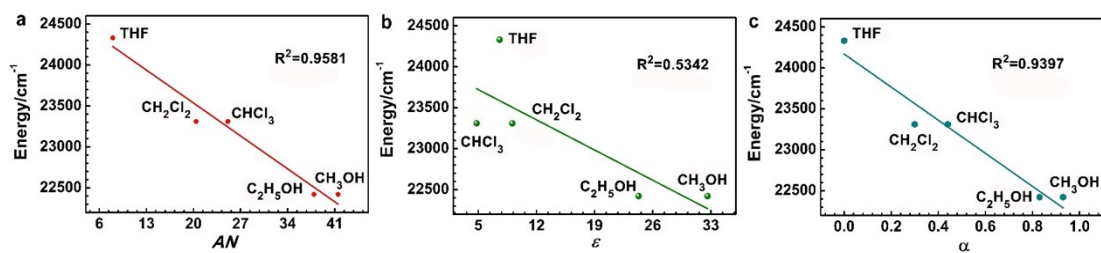

Figure S7. Correlation of 2T3C fluorescence emission energy with the solvent parameters, (a) acceptor number of solvents *AN*, (b) dielectric constant of solvents ε and (c) hydrogen bond parameters of solvents α.

Figure S8. Correlation of 2T5C fluorescence emission energy with the solvent parameters, (a) acceptor number of solvents *AN*, (b) dielectric constant of solvents ε and (c) hydrogen bond parameters of solvents α.

Table S2. Fluorescence emission energy of **2T3C** and **2T5C** in different solvents.

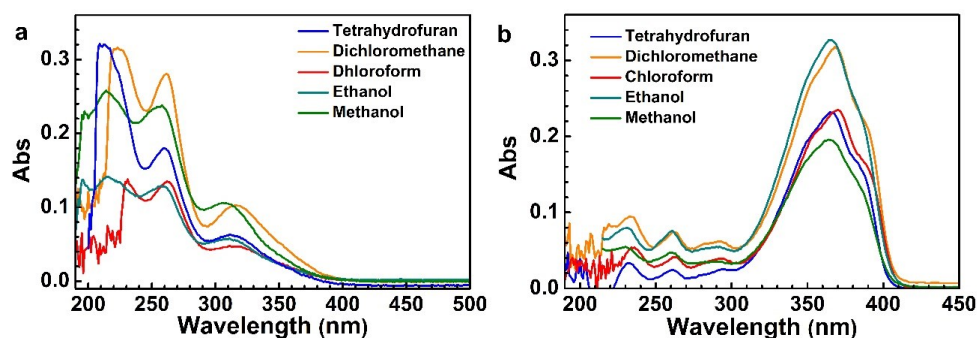| Solvents	*AN*	ε	α	$\lambda_{F\ 2T3C}$(nm)	Energy$_{2T3C}$ (cm^{-1})	$\lambda_{F\ 2T5C}$(nm)	Energy$_{2T5C}$ (cm^{-1})
Tetrahydrofuran	8.0	7.58	0	454	22026	411	24330
Dichloromethane	20.4	9.1	0.3	465	21505	429	23310
Chloroform	25.1	4.8	0.44	468	21367	429	23310
Ethanol	37.9	24.3	0.83	478	20920	446	22421
Methanol	41.5	32.6	0.93	482	20746	446	22421

Figure S9. Absorption spectra of 100 μM (a) 2T3C and (b) 2T5C in different solvents.
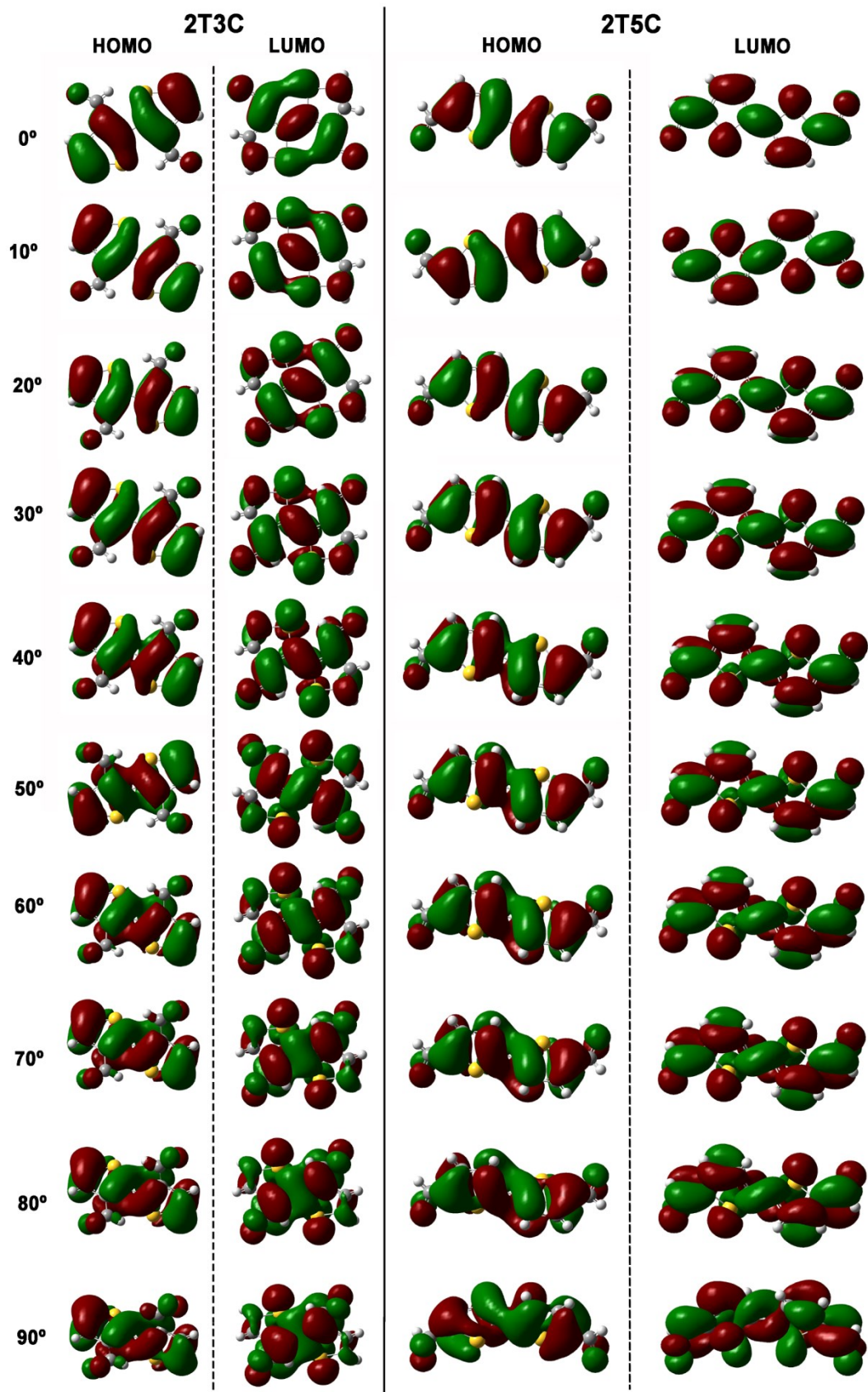
Figure S10. HOMO-LUMO orbitals obtained from 2T3C and 2T5C conformations with different dihedral angles between thiophene rings.
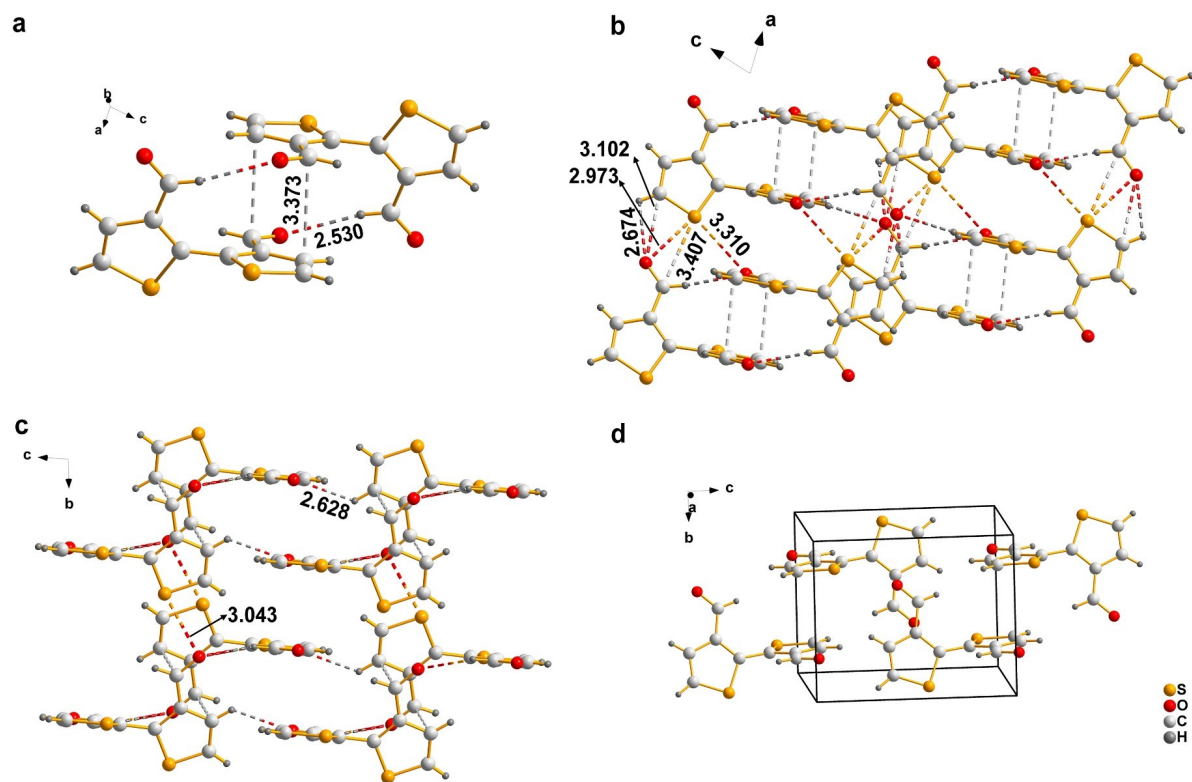
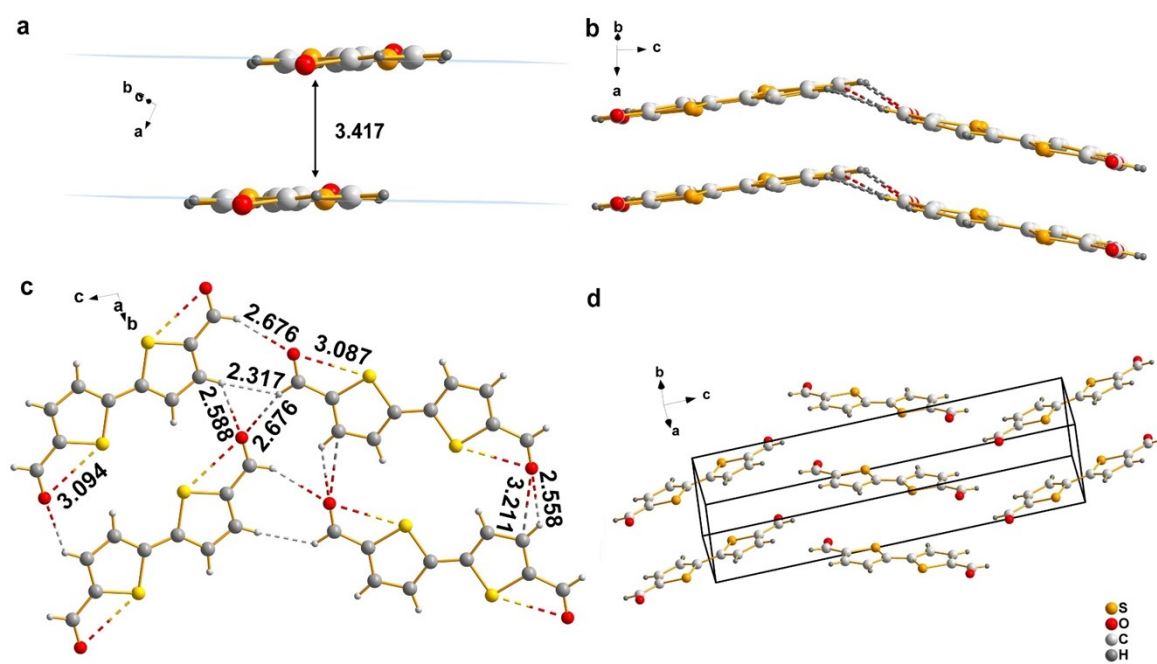**Figure S11**. Molecular stacking and interactions in 2T3C crystal (distance in Å).

Figure S12. Molecular stacking and interactions in 2T5C crystal (distance in Å).
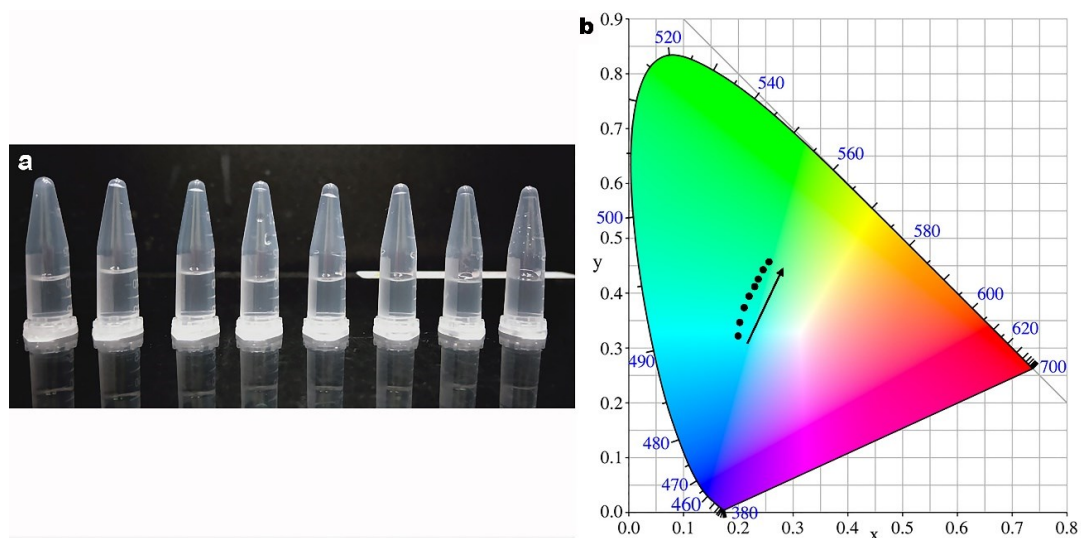
Figure S13. Photographs of the methanol/water mixtures of 50 μM 2T3C (a) under daylight and (b) CIE coordinates corresponding to **Fig 3a**.
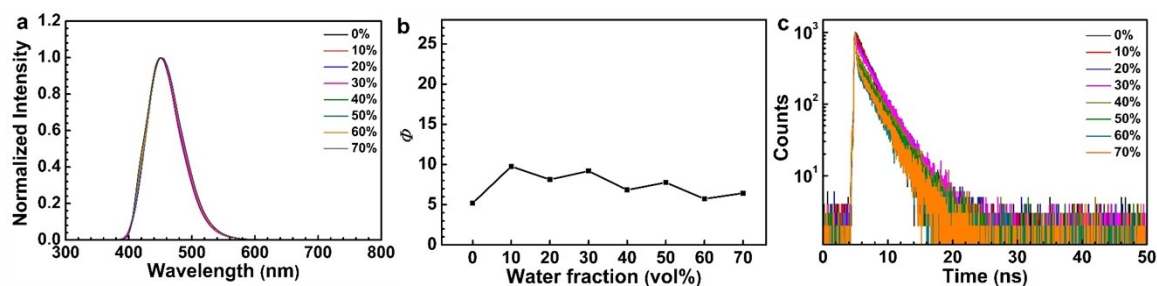

Figure S14. Normalized fluorescence spectra of 50 μM (a) 2T5C in binary mixtures of methanol and water in different volume fraction of water (0-70%). Plot of fluorescence quantum yield of (b) 2T5C with the water fraction. Fluorescence decay profiles of 50 μM (c) 2T5C in binary mixtures of methanol and water in different volume fraction of water.

Table S3. The bonding properties, geometrical parameters and the shortening percentage of van der Waals radius in 2T3C and 2T5C crystals.

Sample	Interactions[a]		d/Å	θ/°	Δr/%
2T3C	HB	C9-H9···O14	2.628	129.43	-3.4
	HB	C5-H5···O14	2.674	108.88	-1.7
	HB	C13-H13···O12	2.530	166.69	-7.0
	CB	C3-C13···S1	3.407	176.45	-2.7
	CB	C4-C5···O14	3.102	177.31	-3.7
	SB	C7-S6···O12	3.043	169.32	-8.3
	SB	C5-S1···O12	3.310	156.30	-0.3
	SB	C2-S1···O14	2.973	169.75	-10.5
	π-holeB	O12-C11···C9	3.373	86.9	-0.8
2T5C	HB	C4-H4···H9	2.317	155.26	-3.4

HB	C4-H4···O1	2.588	128.48	-4.8
HB	C9-H9···O1	2.676	158.77	-1.6
HB	C2-H2···O8	2.676	141.27	-1.6
HB	C11-H11···O8	2.558	127.53	-6.0
CB	C10-C11···O8	3.211	160.79	-0.3
SB	C14-S12···O8	3.087	140.85	-7.0
SB	C7-S6···O1	3.094	140.53	-6.8

[a] HB = hydrogen bond, SB = chalcogen bond, CB = carbon bond and π-holeB = π-hole bond

Table S4. Spectroscopic data of solid samples.

Samples[a]	λ_F (nm)	λ_P (nm)	τ_F (ns)	τ_P (μs)	Φ (%)
2T5C-cry	515/543	600	5.20	10.41	6.26
2T3C-cry	435	600	3.15	237.73	<0.01
2T3C-g	467	627	2.53	46.6	0.36
2T3C-Sg	507	604	6.04	9.51	8.43
2T3C-SiO$_2$	456	--	2.64	--	0.29
2T5C-Sg	524	577	2.79	9.61	5.27

[a] cry = crystal, g = simply ground, Sg = ground with silica gel and SiO$_2$ = ground with SiO$_2$

For the reasons, the short phosphorescence lifetime is related to the relatively flexible molecular structure (with faster vibration and rotation between two rings) of 2T3C and 2T5C, although 2T5C is planar. Moreover, it may be related to the heavy atom effect of sulfur.

Table S5. Spectroscopic data of 50 μM 2T3C and 2T5C in binary mixtures of methanol and water in different volume fraction of water (0-70%).

vol (%)	λ_F (nm)	τ (ns)	Φ (%)	k_r^a (s^{-1})	k_{nr}^b (s^{-1})
			2T3C		
0	480	1.80	3.09	1.7192×10^7	5.3920×10^8
10	488	3.21	6.99	2.1809×10^7	2.9019×10^8
20	494	4.66	10.46	2.2428×10^7	1.9199×10^8
30	498	6.37	14.60	2.2922×10^7	1.3408×10^8
40	499	7.25	15.49	2.1367×10^7	1.1658×10^8
50	501	8.14	17.05	2.0936×10^7	1.0186×10^8
60	504	8.63	19.18	2.2234×10^7	9.3687×10^7
70	508	8.95	24.50	2.7379×10^7	8.4373×10^7
			2T5C		
0	450	2.11	5.19	2.4654×10^7	4.5038×10^8
10	450	2.21	9.77	4.4128×10^7	4.0754×10^8
20	451	2.40	8.13	3.3934×10^7	3.8346×10^8
30	451	2.53	9.19	3.6366×10^7	3.5934×10^8
40	452	2.49	6.84	2.7467×10^7	3.7409×10^8

50	452	2.43	7.76	3.1953×10^{7}	3.7981×10^{8}
60	452	2.32	5.73	2.4715×10^{7}	4.0662×10^{8}
70	451	2.33	6.44	2.7624×10^{7}	4.0132×10^{8}

[a] $k_{r} = \Phi/\tau$

[b] $k_{nr} = (1-\Phi)/\tau$
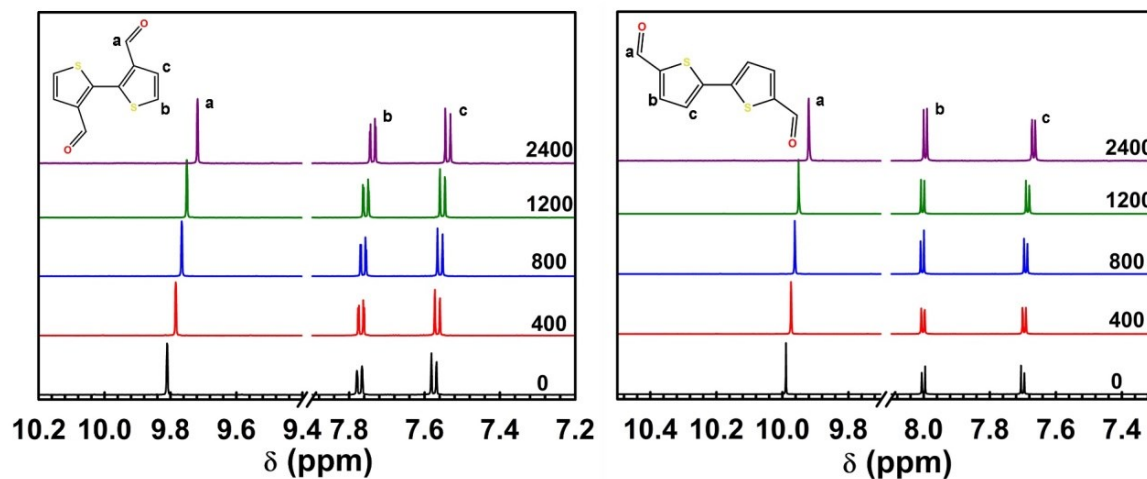
Figure S15. ^{1}H NMR spectra of 5 mM 2T3C and 2T5C with incremental water concentration in C_3D_6O ([H_2O]/[2T3C or 2T5C] = 0/400/800/1200/2400).
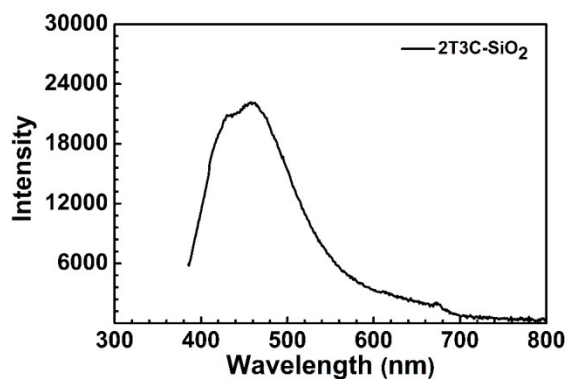
Figure S16. (a) Fluorescence spectrum of 2T3C crystal ground with SiO_2.
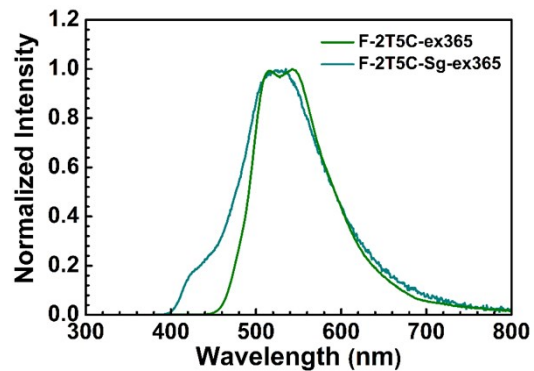

Figure S17. Normalized fluorescence spectra of 2T5C crystal and 2T5C crystal ground with silica gel.
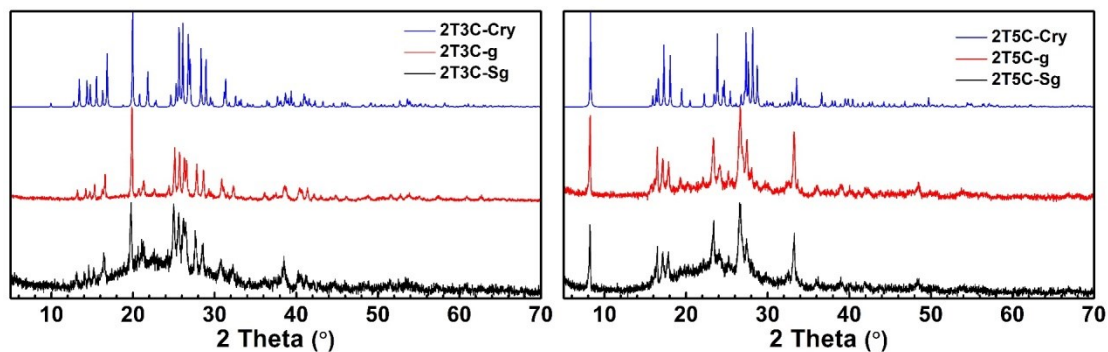
Figure S18. 2T3C and 2T5C XRD patterns in different states for crystal, only ground and ground with silica gel. (Cry = crystal, g = only ground and Sg = ground with silica gel)
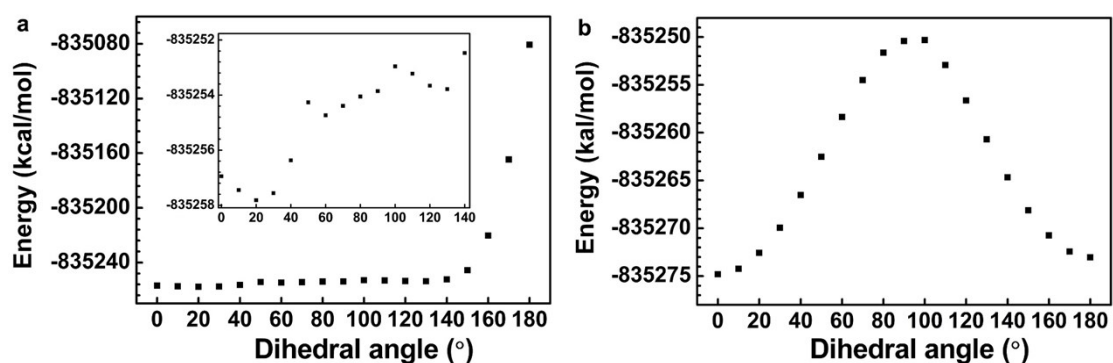

Figure S19. Plot of single-point energy with the dihedral angle between thiophene-rings (0-180°) of (a) 2T3C and (b) 2T5C.
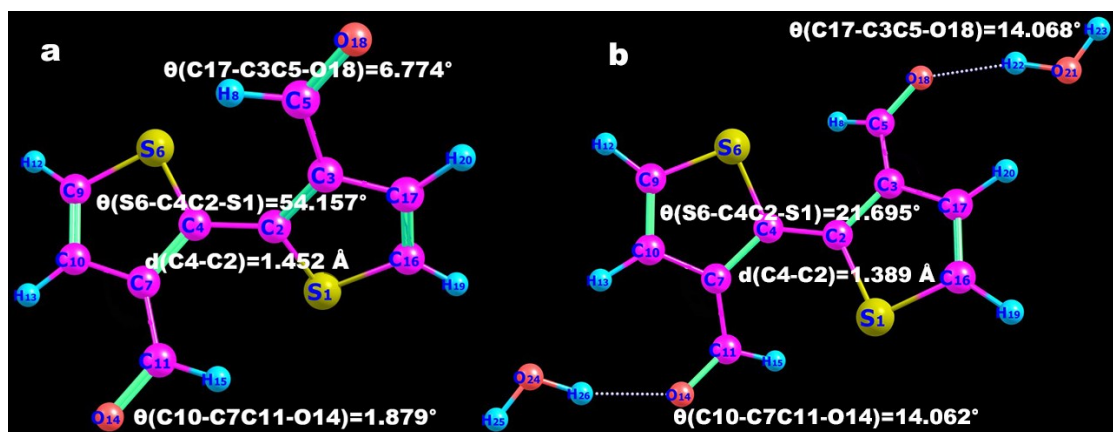

Figure S20. (a) Optimized structure of 2T3C in S_1 state. (b) Optimized structure of 2T3C in S_1 state forming hydrogen bond with water molecules.
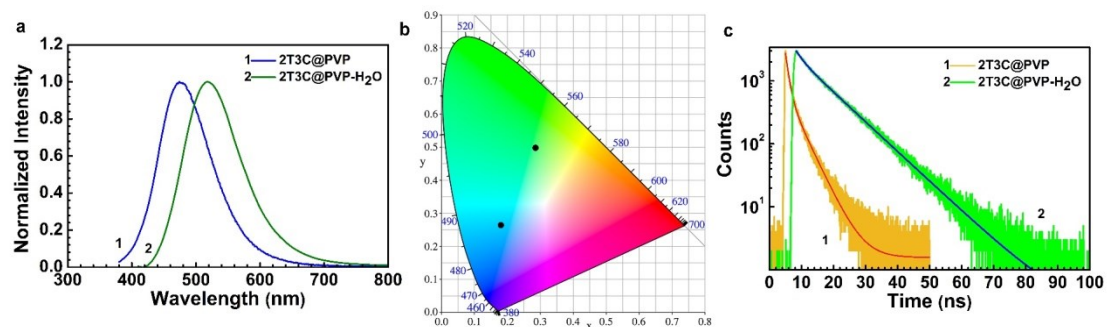
Figure S21. (a) Normalized fluorescence spectra, (b) fluorescence color coordinates (c) and fluorescence decay profiles of 1 wt% 2T3C@PVP-film and the film of dropping water.

Table S6. Quantum yield of 2T3C@PVP films with different doping concentrations.

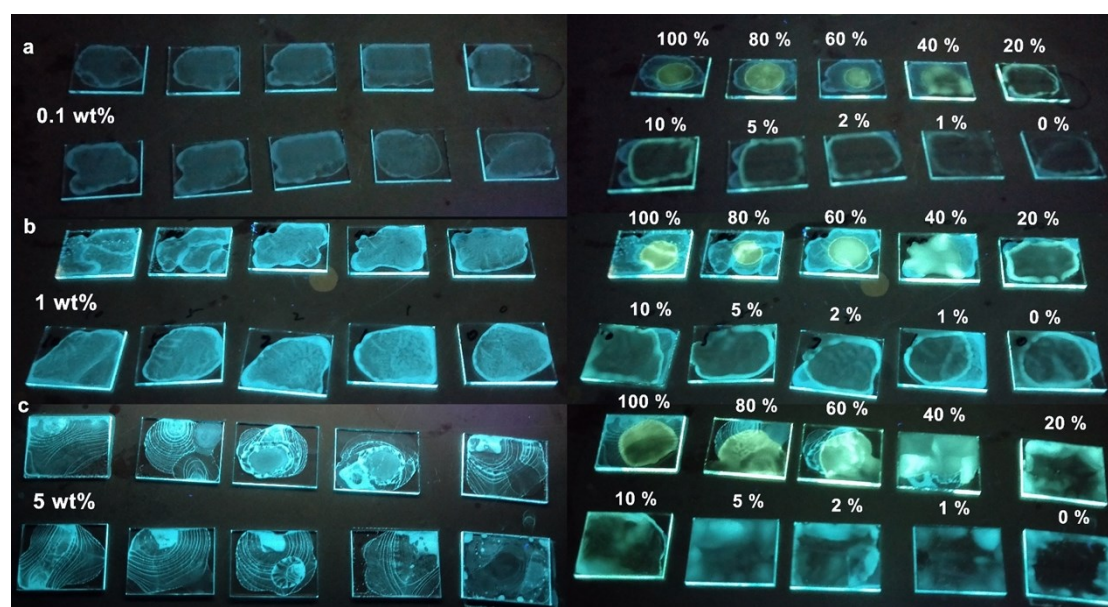| Samples	Φ (%)
0.1 wt%	5.8
0.5 wt%	4.4
1 wt%	4.3
2 wt%	3.7
5 wt%	2.8

Figure S22. Photographs of (a) 0.1 wt%, (b) 1 wt% and (c) 5 wt% 2T3C@PVP-films and dropped with water-ethanol mixtures with different water fraction under UV-365 nm radiation.

3. References

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