Supporting Information

Isomerization-induced Fluorescence Enhancement of Two New Viologen Derivatives: Mechanism Insight and DFT calculation

Xiuping Yin,[1] Xinxing Li,[1,2], Xuyi Li,[1] Malgorzata Biczysko, [*,1,2] Shourong Zhu,[1] Jiaqiang Xu[1] and Yue-Ling Bai[*,1]

[1]*College of Science, Shanghai University, 99 Shangda Road, Shanghai 200444, China*
[2] *International Center for Quantum and Molecular Structures, Department of physics, College of Science, Shanghai University, 99 Shangda Road, Shanghai 200444, China*

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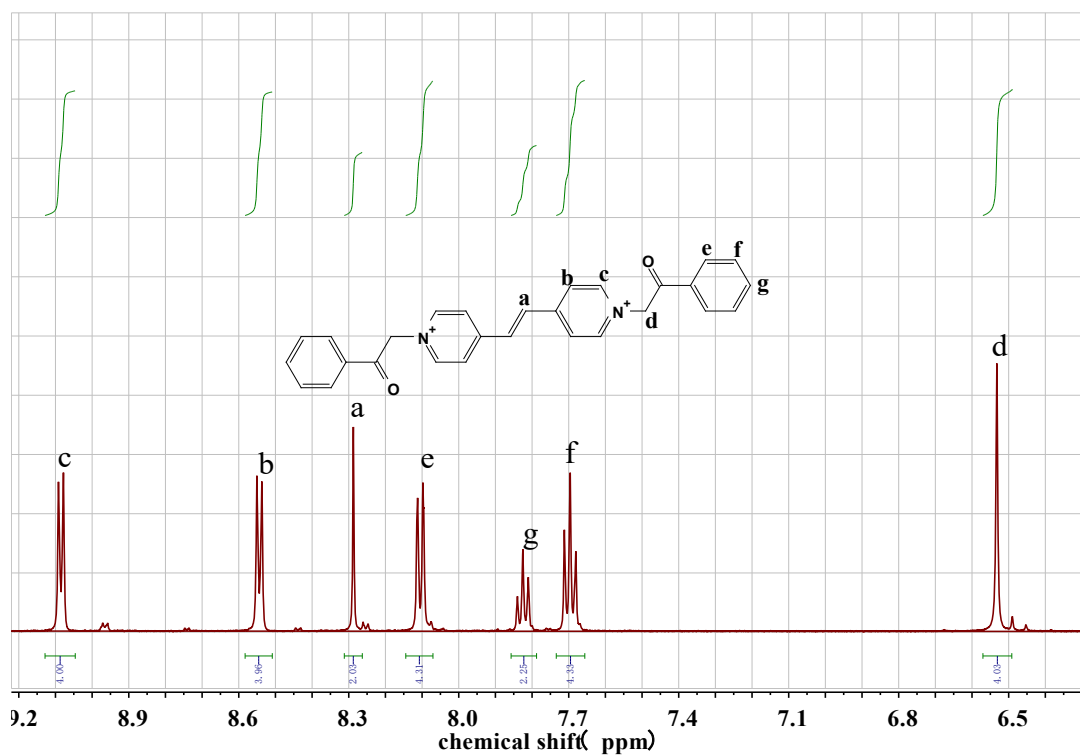
Figure S1. ^{1}H NMR of synthesized **Vio1·2Cl** powder in deuterated d-DMSO.

Figure S2. ^{13}C NMR of synthesized **Vio1·2Cl** powder in deuterated *d*-DMSO.
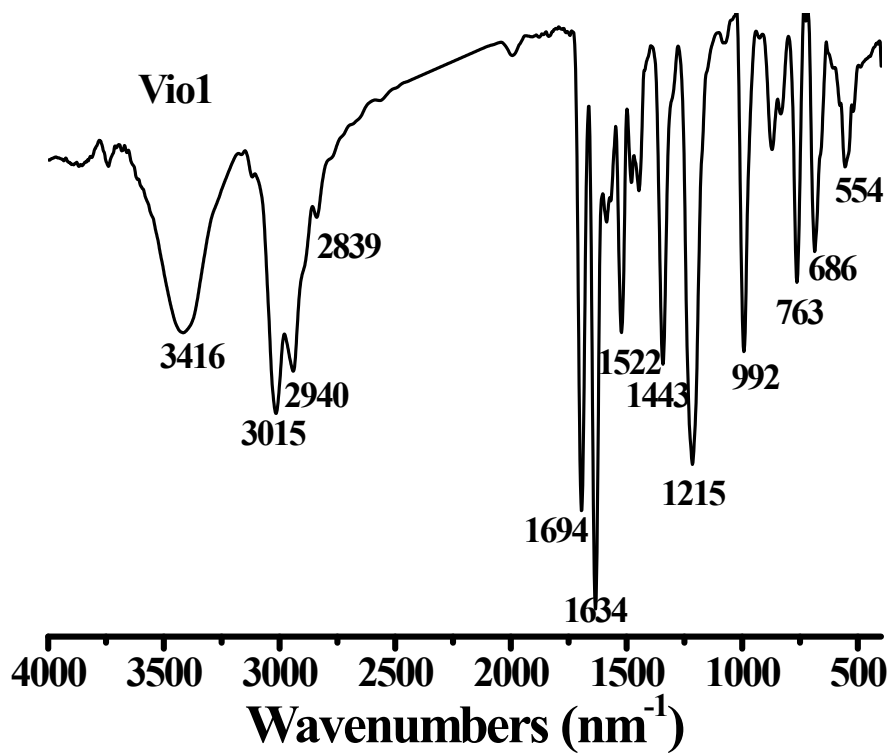
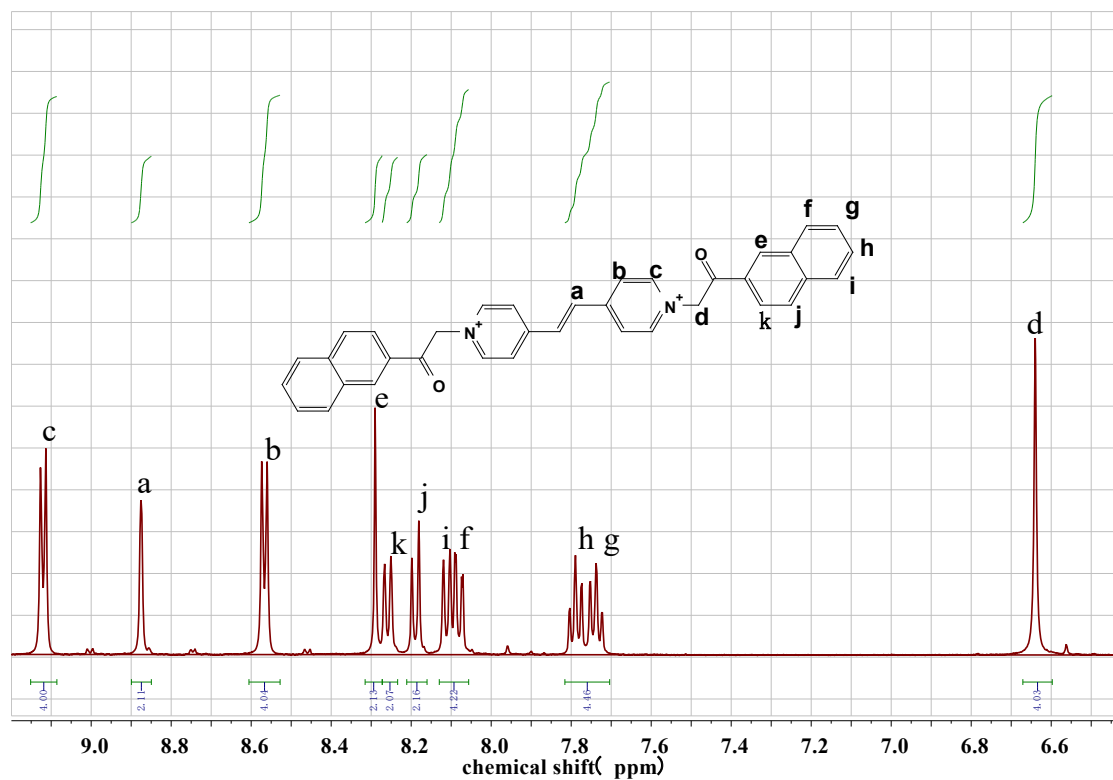**Figure S3.** IR spectra of **Vio1·2Cl** (KBr disc).

Figure S4. ¹H NMR of synthesized **Vio2·2Br** powder in deuterated d-DMSO.
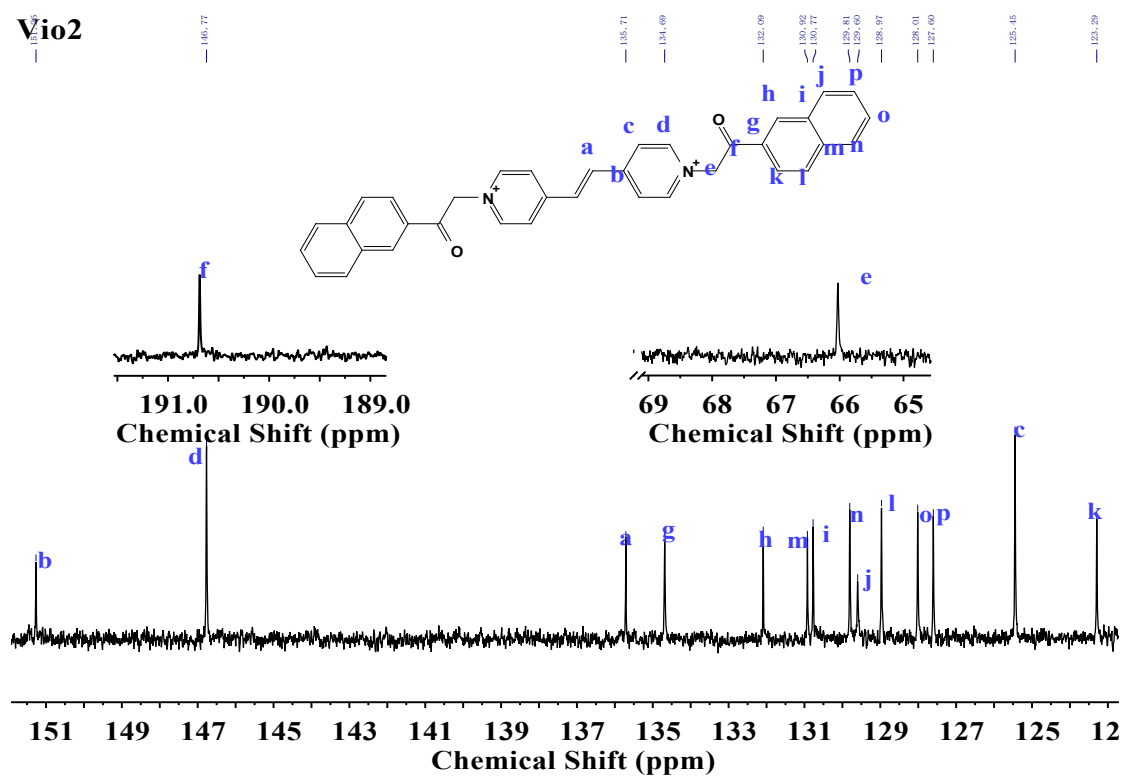
Figure S5. ^{13}C NMR of synthesized **Vio2·2Br** powder in deuterated *d*-DMSO.
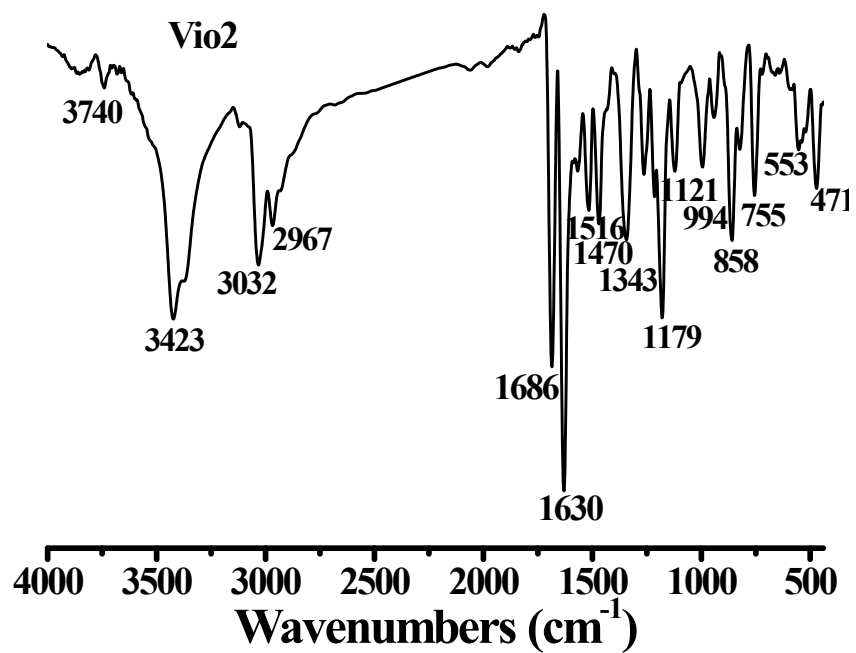
Figure S6. IR spectra of **Vio2·2Br** (KBr dis
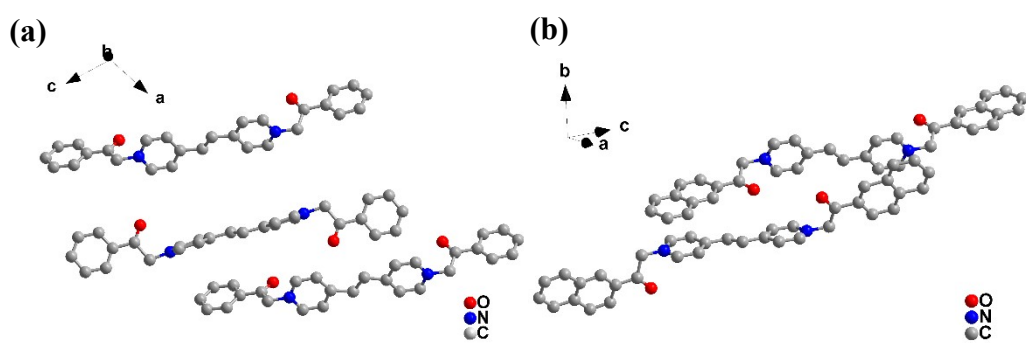
Figure S7. The crystal structure of **Vio1²⁺** (a) and **Vio2²⁺** (b).

Table S1. The crystallographic data of Vio1·2Cl and Vio2·2Br.

Compound	Vio1·2Cl	Vio2·2Br
Molecular formula	$C_{28}H_{24}N_2O_2Cl_2$	$C_{36}H_{28}N_2O_2Br_2$
Fomular weight	491.39	680.42
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$
a/(Å)	26.4051(17)	14.4466(3)
b/(Å)	11.7620(6)	18.0374(3)
c/(Å)	28.6519(12)	17.9239(3)
α (°)	90	90
β (°)	110.083(2)	98.9830(1)
γ (°)	90	90
V/Å^3	8357.6(8)	4613.31(15)
Z	12	6
Dc/mg·m^{-3}	1.172	1.469
μ/mm^{-1}	1.514	2.483
R(int)	0.0000	0.0756
F(000)	3072	2064
R_1, wR_2	R1 = 0.0937	R1 = 0.0664
	wR2 = 0.2534	wR2 = 0.1937
GOF on F^2	1.070	1.051
CCDC	2218985	2218984
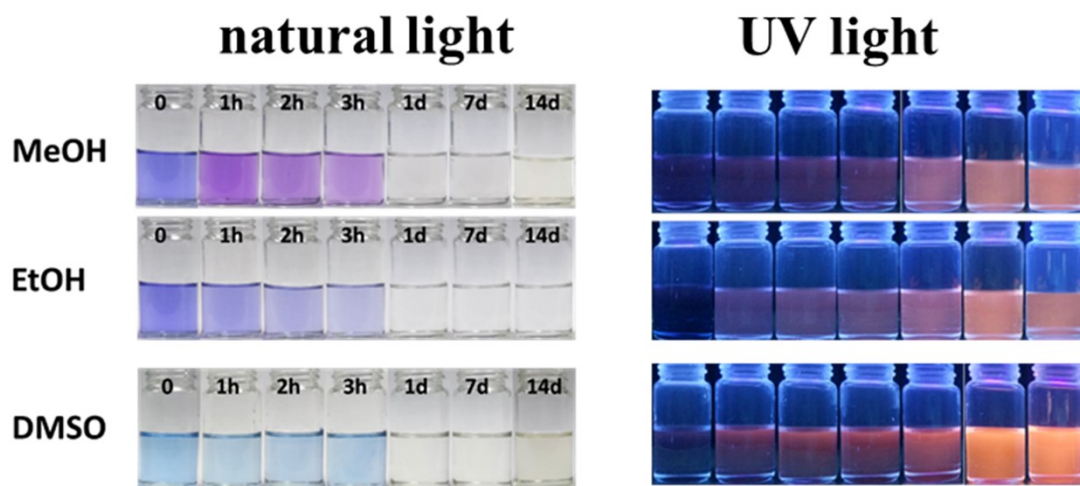
Figure S8. Photographic images of **Vio2·2Br** (2.0×10^{-4} M) in different solvents at different time (left: under natural light, right: under 365 nm UV lamp).
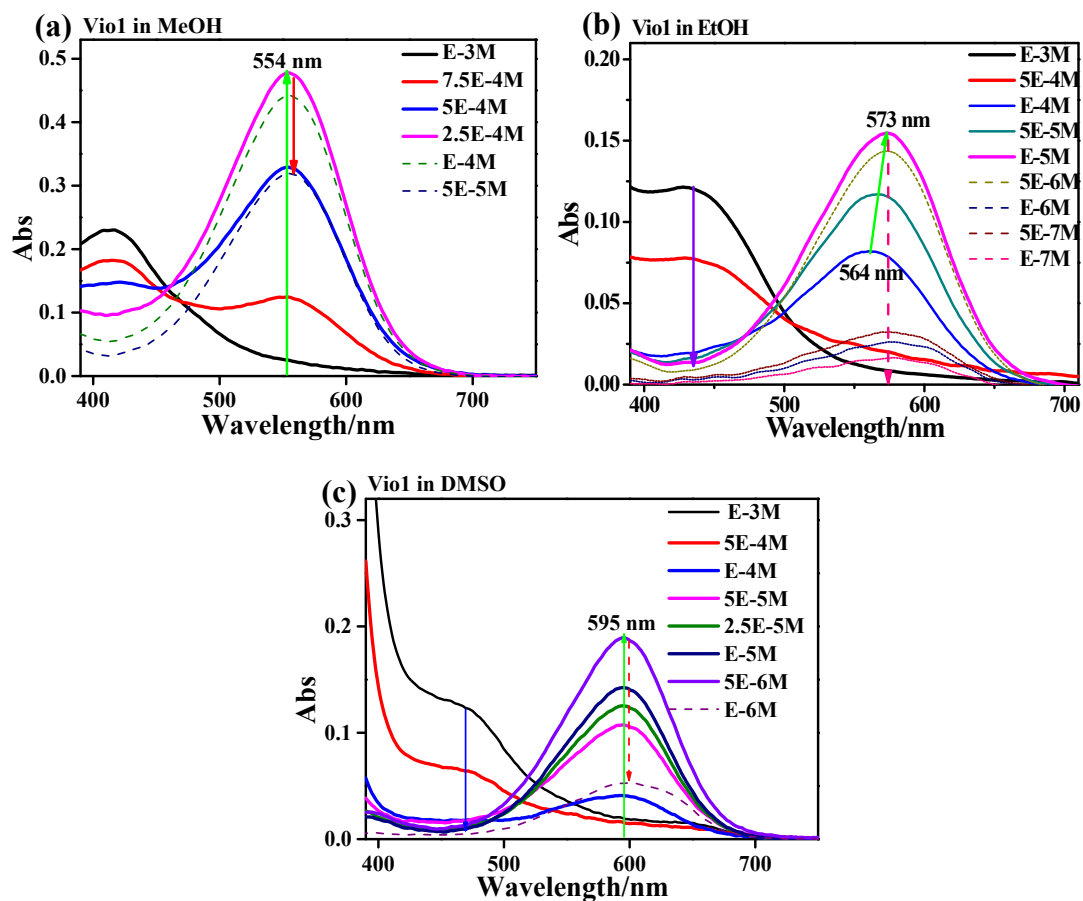
Figure S9. UV-vis spectra of **Vio1·2Cl** in different solvents at different concentration: (a) MeOH, (b) EtOH, (c) DMSO.
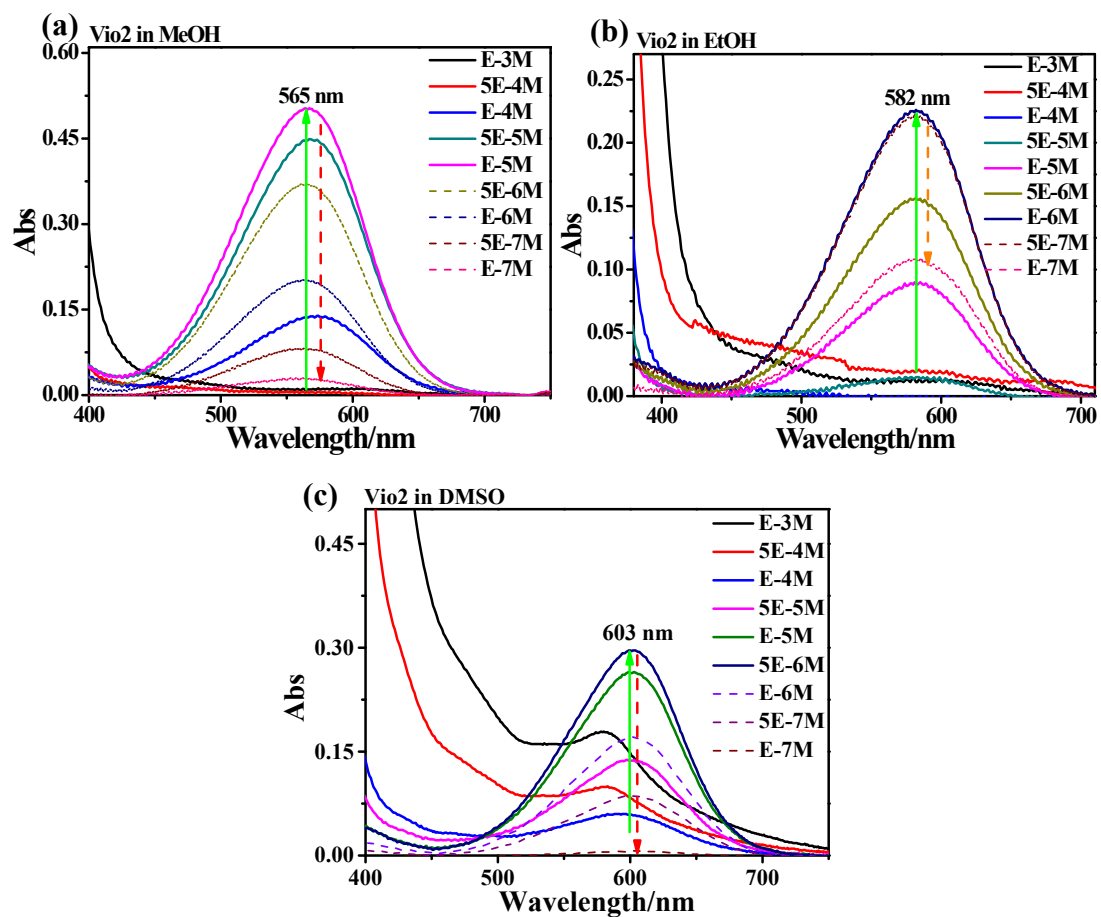
Figure S10. UV-vis spectra of **Vio2·2Br** in different solvents at different concentration: (a) MeOH, (b) EtOH, (c) DMSO.
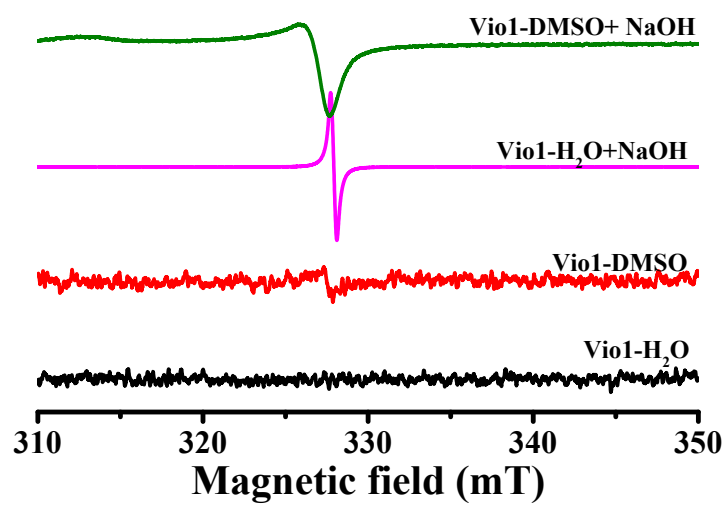
Figure S11. EPR spectra of **Vio1·2Cl** in H_2O and DMSO solutions.
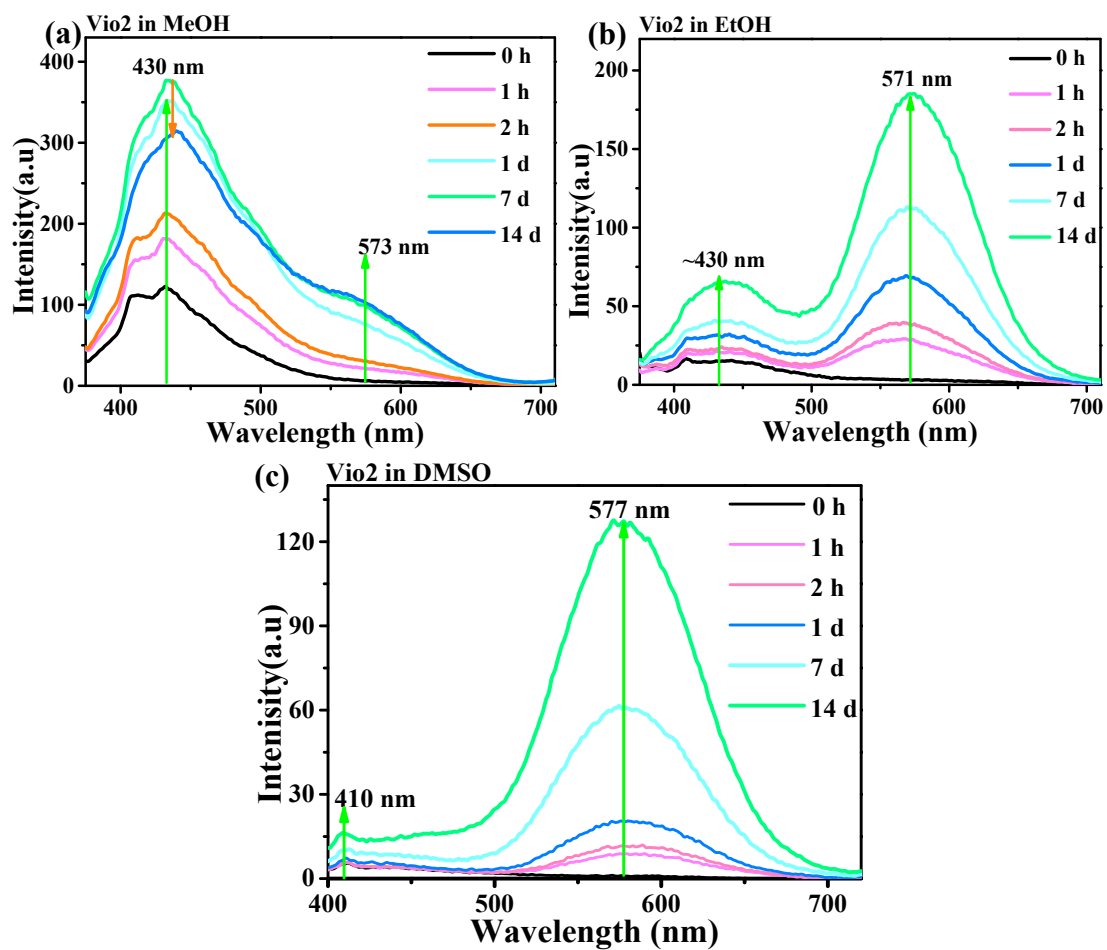
Figure S12. Fluorescence spectra of **Vio2·2Br** (2.0×10^{-4} M) in different solvents at different time: (a) MeOH, (b) EtOH, (c) DMSO.
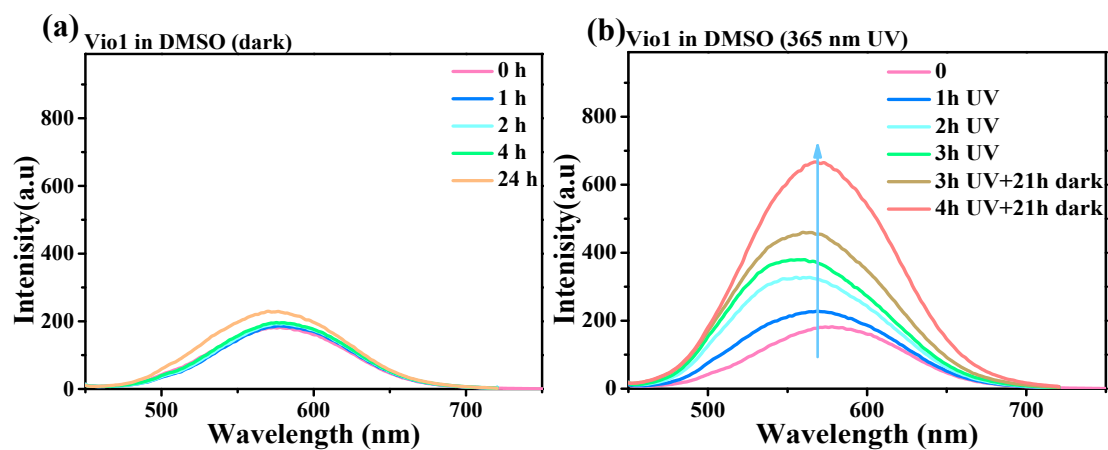
Figure S13. The Fluorescence spectra of **Vio1·2Cl** (0.2 mmol/L) in DMSO solution under the dark (a) and under the UV light irradiation (b).
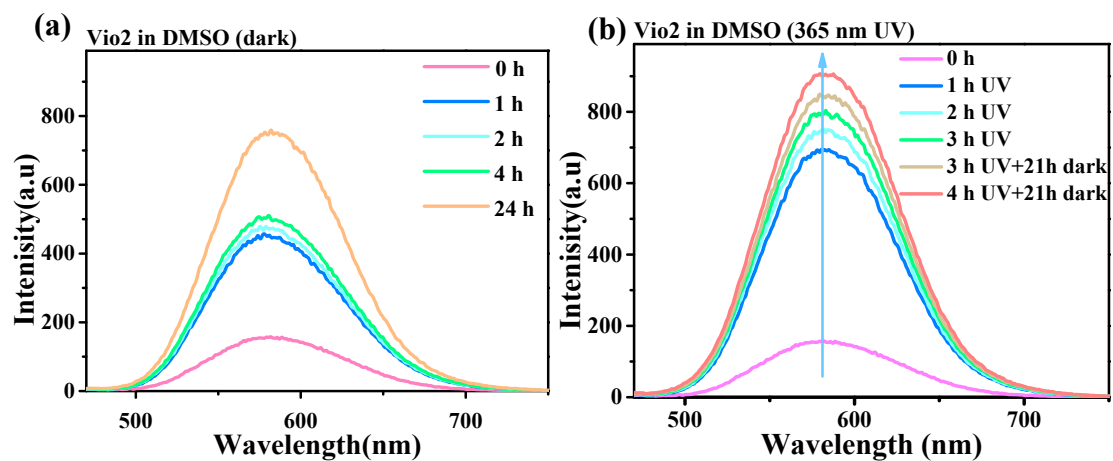
Figure S14. The Fluorescence spectra of **Vio2·2Br** (0.2 mmol/L) in DMSO solution under the dark (a) and under the UV light irradiation (b).

Table S2. The characteristic peak data of UV-vis spectrum and fluorescence spectrum in different solvents

		H$_2$O	MeOH	EtOH	DMSO
UV-vis	Vio1^{2+}	-	554 nm	564~573 nm	595 nm
	Vio2^{2+}	-	565 nm	582 nm	603 nm
PL	Vio1^{2+}	430,530 nm	430,520 nm	433,570~530 nm	410,577 nm
	Vio2^{2+}	-	430,573 nm	~430,571 nm	410,577 nm

Table S3. Absorption maxima, emission maxima, and Stokes shifts of **Vio1²⁺** and **Vio2²⁺** in different solvent.

	Solvent	λ_{abs} (max)	λ_{em} (max)	Stokes (nm)
Vio1²⁺	**MeOH**	430	520	90
	EtOH	420	530	110
	DMSO	440	577	137
Vio2²⁺	**MeOH**	361	430	69
	EtOH	368	430	62
	DMSO	460	577	117
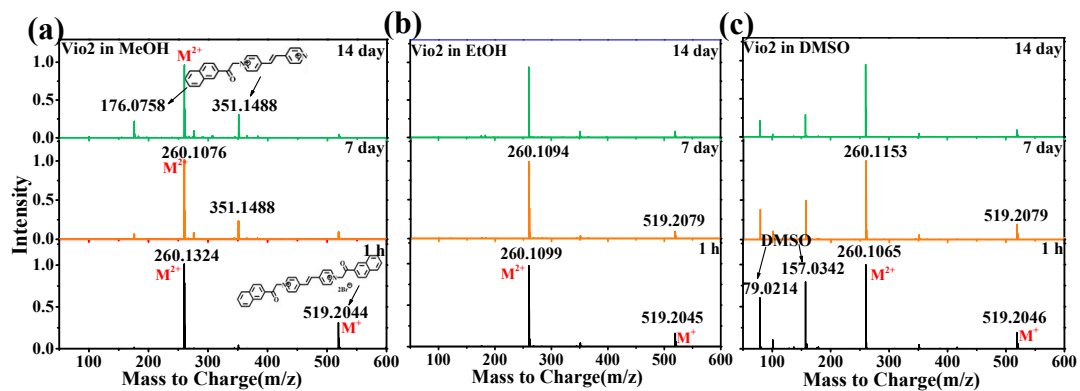
Figure S15. Mass spectra of of **Vio2·2Br** in different solvents at different time: (a) MeOH, (b) EtOH, (c) DMSO.

Table S4. Relative ion abundance of $M^{2+}/2$ in different solvents at 1h, 7 and 14 days from ESI-MS data.

	Solvent	1 h	7 day	14 day
	H$_2$O	1	0.791	0.523
Vio1·2Cl	MeOH	1	0.928	0.675
	DMSO	1	0.924	0.824
	MeOH	1	1	0.964
Vio2·2Br	EtOH	1	1	0.965
	DMSO	1	0.998	0.951
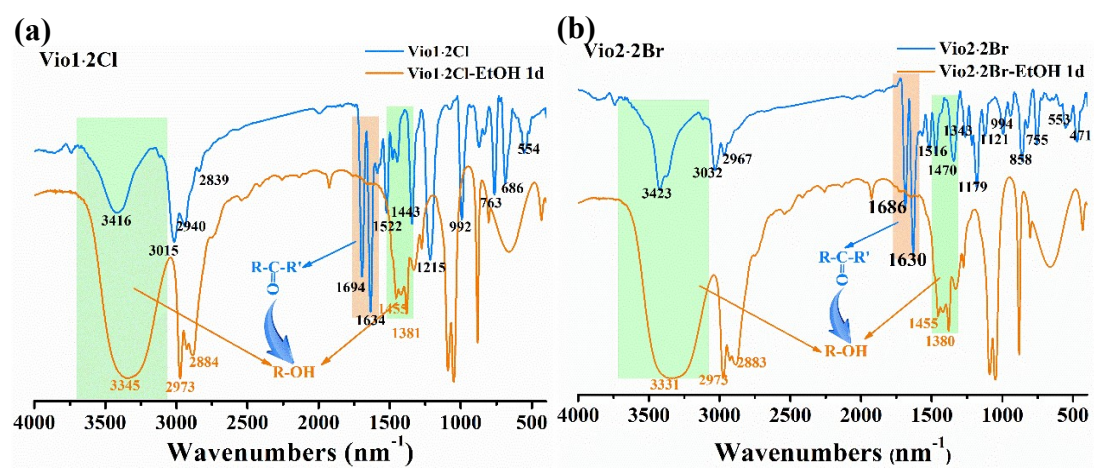
Figure S16. The FTIR spectrum of **Vio1²⁺** (a) and **Vio2²⁺** (b) in EtOH at initial state and after 1 d.
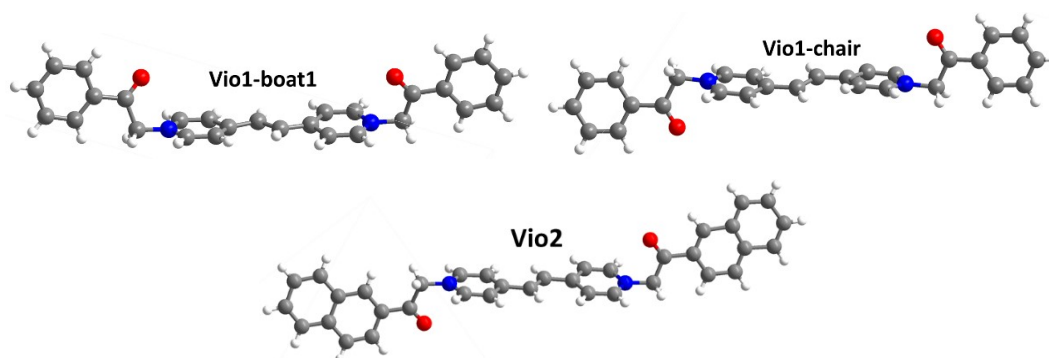
Figure S17. The molecular structure of the crystal of **Vio1²⁺** and **Vio2²⁺** (To study the spectral properties of molecules, the first step is to optimize the geometric configuration of the molecules. The molecular structure model was constructed according to the crystal cif file. Since the initial molecular model may not have the lowest energy, it is necessary to optimize its structure by software so that its energy reaches a minimum value, and the geometry is stable to do the following research).

Figure S18. Ground state optimized structures for **Vio1²⁺** and **Vio2²⁺** at CAM-B3LYP/PCM (DMSO) level of theory (There are two kinds of configuration in the structural unit of **Vio1²⁺** crystal: boat and chair configuration. **Vio2²⁺** has only one configuration of chair. The structure of the two ship types in **Vio1²⁺** is the same, so only one of them should be selected for calculation. The CAM-B3LYP functional has been chosen to calculation of the optimized ground state structure of ketone and enolic type).

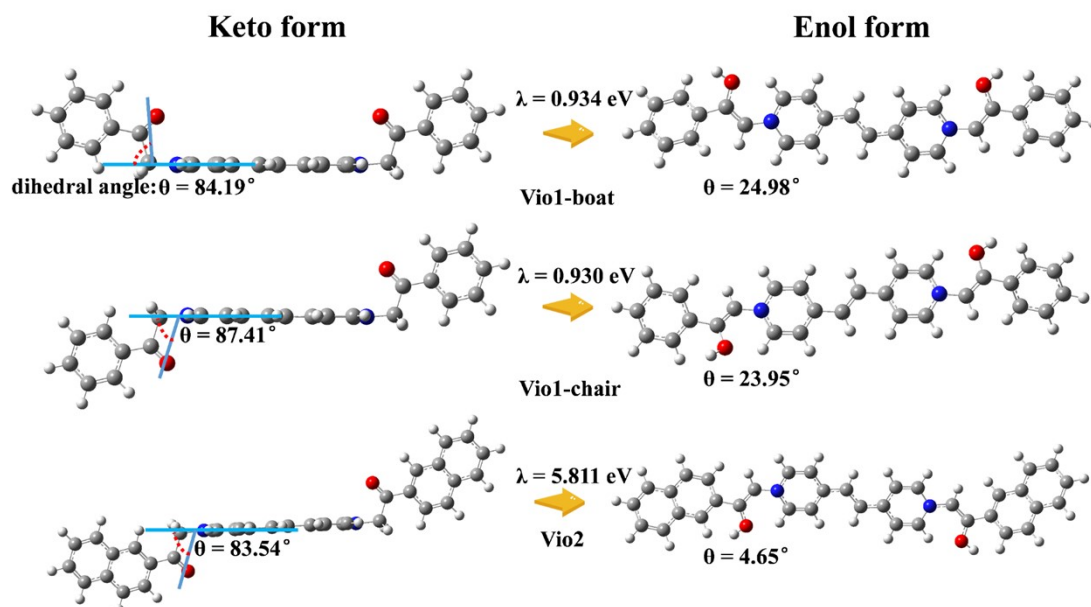**Figure S19.** Excited state optimized structures for **Vio1²⁺** and **Vio2²⁺** at CAM-B3LYP/PCM (DMSO) level of theory (There are two kinds of configuration in the structural unit of **Vio1²⁺** crystal: boat and chair configuration. **Vio2²⁺** has only one configuration of chair. The structure of the two ship types in **Vio1²⁺** is the same, so only one of them should be selected for calculation. The CAM-B3LYP functional has been chosen to calculation of the optimized ground state structure of ketone and enolic type).
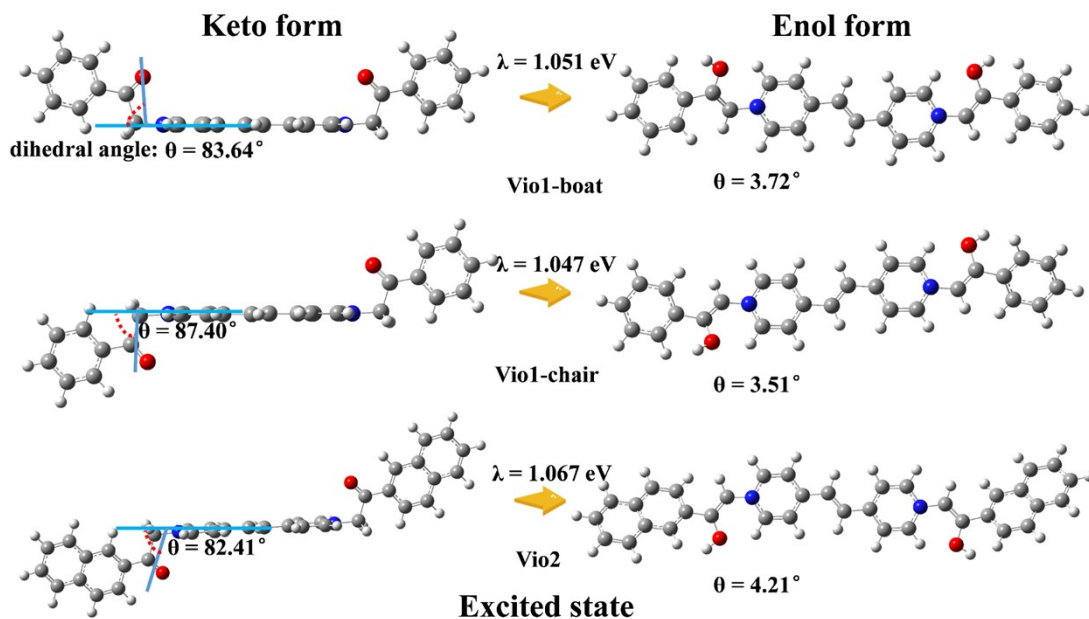
Table S5. Relative energies (and Gibbs free energies) in the ground state (S_0) structures optimized at B3LYP-D3/SNSD/PCM level.

	Vio1boat-keto	Vio1boat-enol	Vio1chair-keto	Vio1chair-enol	Vio2-keto	Vio2 enol
Energy (hartree)	-1341.32	-1341.29	-1341.32	-1341.29	-1648.67	-1648.46
Δ (eV)	0.934		0.930		5.811	
Δ (kJ/mol)	90.047		89.70		560.680	

Table S6. Selected structural parameters of **Vio1·2Cl** and **Vio2·2Br** (keto and enol) in the ground and excited electronic states and the difference of dihedral angles of the ground state (or excited state) of different structures (keto and enol).

Dihedral angle	Vio1boat	Vio1boat-enol	Vio1chair	Vio1chair-enol	Vio2	Vio2-enol
Ground state (degrees)	84.19	24.98	87.41	23.95	83.54	4.65
Excited state (degrees)	83.64	3.72	87.40	3.51	82.41	4.21
Δθ	0.55	21.26	0.01	20.44	0.1	0.44
Ground state (Δθ)	**Vio1boat**	59.21	**Vio1chair**	63.46	**Vio2（**	78.89
Excited state (Δθ)	**（k-e）**	79.92	**（k-e）**	83.89	**k-e）**	78.2

Table S7. Emission wavelengths and relative oscillator strengths for **Vio1·2Cl** and **Vio2·2Br** calculated at TD-CAM-B3LYP/SNSD level.

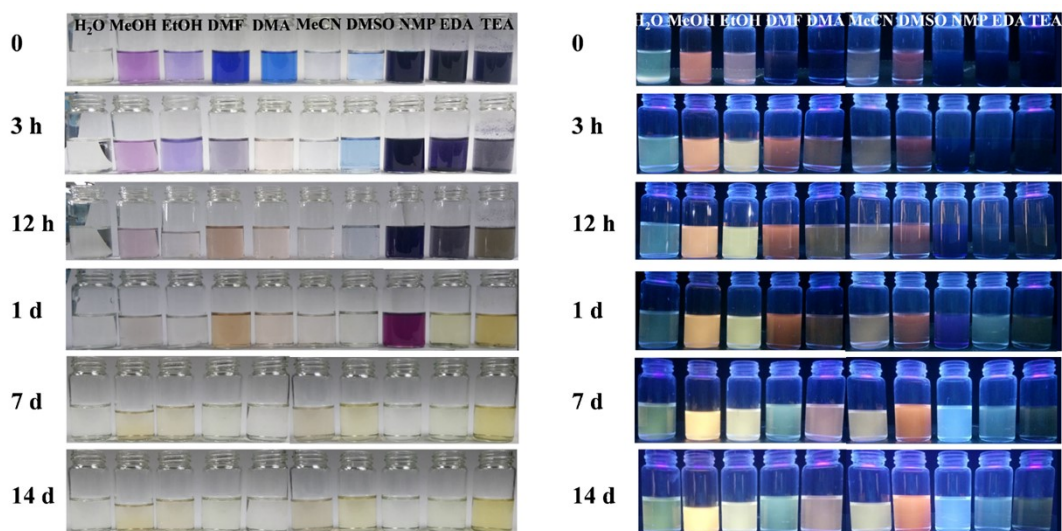|		Vio1-boat	Vio1-boat-enol	Vio1-chair	Vio1-chair-enol	Vio2	Vio2-enol
	E/eV	2.98	2.20	2.98	2.20	2.98	2.13
DMSO	λ/nm	417	564	416	563	417	582
	f	1.53	2.58	1.53	2.65	1.62	2.81

Figure S20. The solvatochromism (Left) and photoluminescence (Right) of **Vio1·2Cl** (2×10^{-4} M) in different solvents with increasing time (solvents left to right: H_2O, MeOH (Methanol), EtOH (Ethanol), DMF (N, N-Dimethylformamide), DMA (N, N-Dimethylacetamide), MeCN (Acetonitrile), DMSO (Dimethyl sulfoxide), NMP (N-methyl-2-pyrrolidone), EDA (Ethylenediamine), and TEA (Triethylamine).
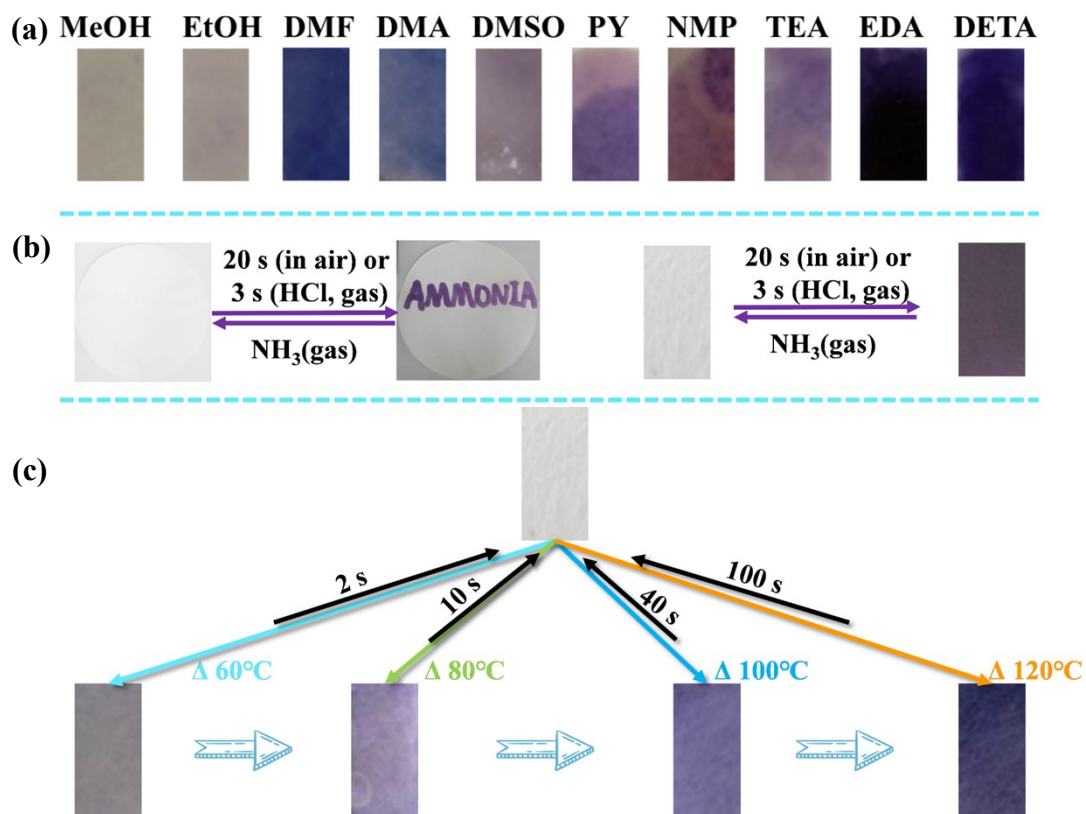
Figure S21. (a) Photographs of the **Vio1·2Cl** impregnated test papers after treatment with different organic solvent. (b) Photographs of the **Vio1·2Cl** impregnated test papers after treatment with NH$_3$ and HCl. (c) Photographs of the **Vio1·2Cl** impregnated test papers after treatment with different temperature.