Supporting Information for

Novel Indoloquinoxaline-Tetraphenylethylene Star-like Conjugated Isomers: Aggregation-Induced Emission and Acidichromism for Versatile Fluorescent Applications

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Contents

1. General methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-600 (600 MHz for ^{1}H and 151 MHz for ^{13}C) spectrometer ($CHCl_3$: δ 7.26 ppm and δ 76.82~77.25 ppm respectively). The following abbreviations were used to explain multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on Applied Biosystems-Sciex 5800 MALDI FT-ICR Mass Spectrometer. The density functional theory (DFT) calculations were performed with the Gaussian 09 Rev. D.01 employing the B3LYP/6-31g(d) level. UV-Vis spectra were measured by Shanghai Jinghua UV1800PC UV-Vis spectrophotometer. Emission spectra were obtained on a FluoroMax-4 fluorescence spectrophotometer. The thickness of the films was measured by Thickness gauge SD-201. Cyclic voltammetry (CV) was tested on the Ingsens IGS1130 electrochemical analyzer, which had a three-electrode cell, and was carried out in the deoxygenated anhydrous acetonitrile solution of *tetra*-*n*-butylammonium-hexafluorophosphate (0.1 M) under nitrogen environment. Platinum disk electrode, platinum wire electrode, and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively, with the Tetra-8-IQ or Tetra-9-IQ thin film for evaluation coated on the surface of the platinum disk electrode. The CV curves were calibrated using the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an external standard, which was measured under the same condition before and after the measurement of samples. The energy level of Fc/Fc^+ was assumed at -4.8 eV to vacuum. The half-wave potential of Fc/Fc^+ was found to be 0.44 V, related to the Ag/AgCl reference electrode.

2. Supporting data

2.1. NMR spectra of Tetra-8-IQ and Tetra-9-IQ

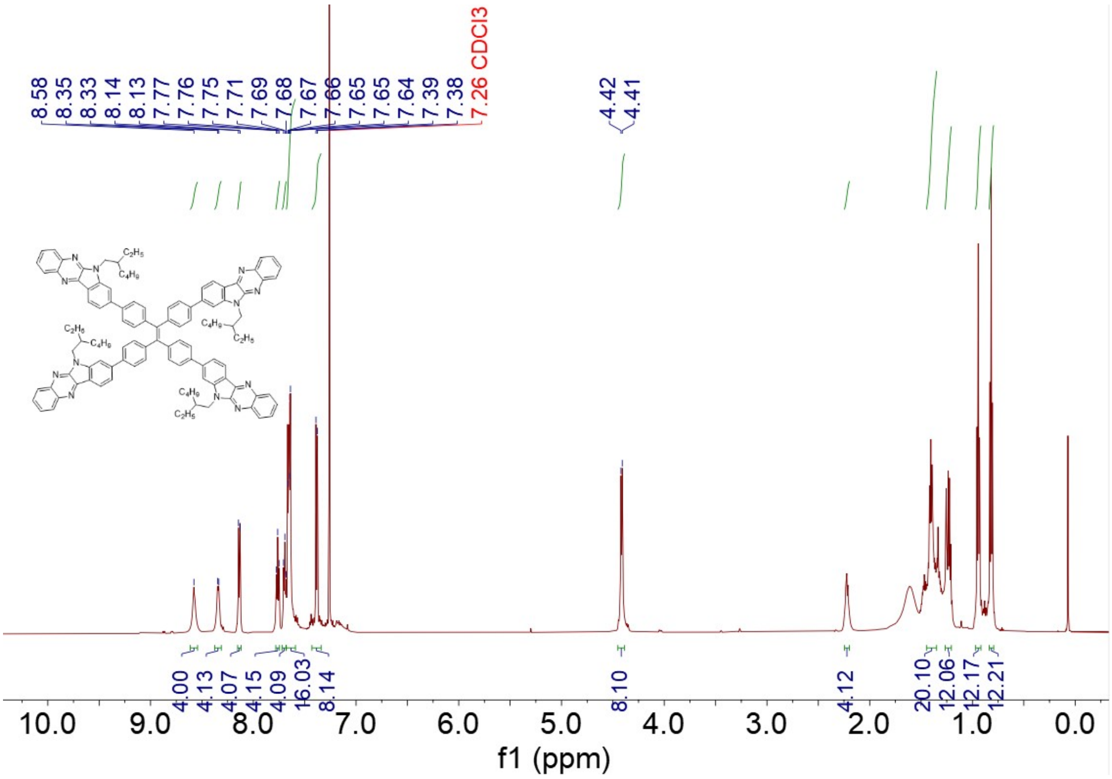


Figure S1. ^{1}H NMR spectrum of Tetra-8-IQ (CDCl$_3$, 25 ^{o}C)

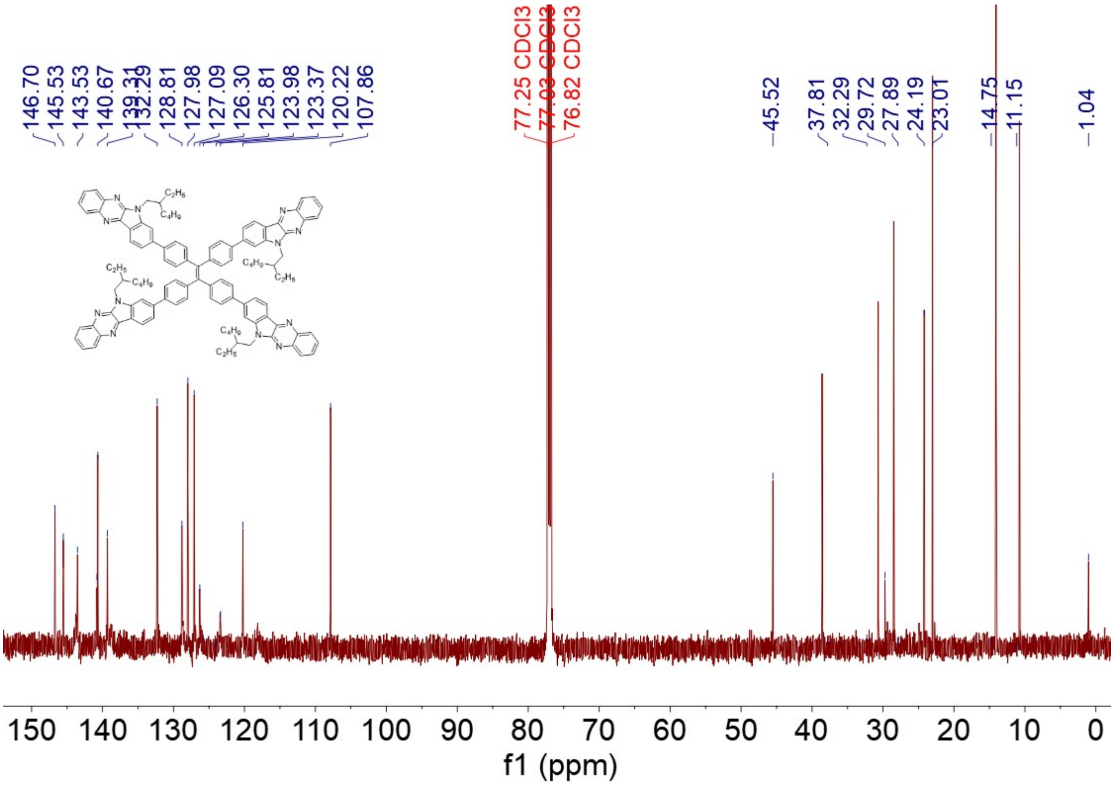


Figure S2. ^{13}C NMR spectrum of Tetra-8-IQ (CDCl$_3$, 25 ^{o}C)

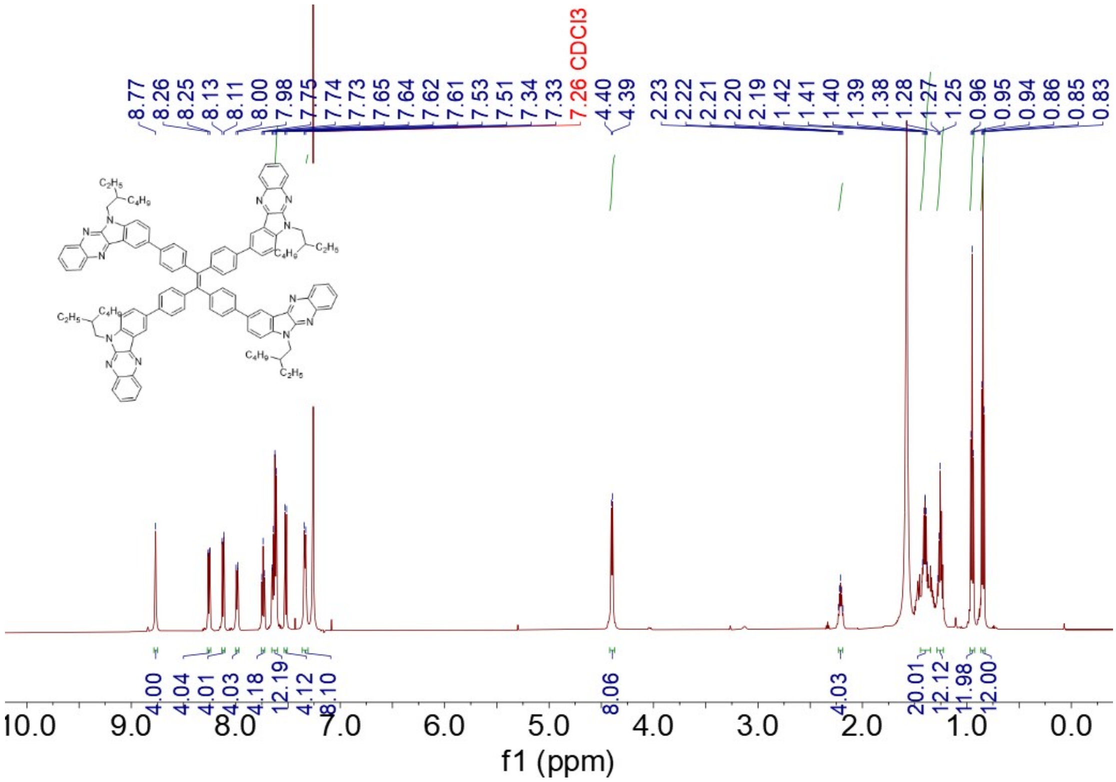


Figure S3. ^{1}H NMR spectrum of Tetra-9-IQ ($CDCl_3$, 25 ^oC)

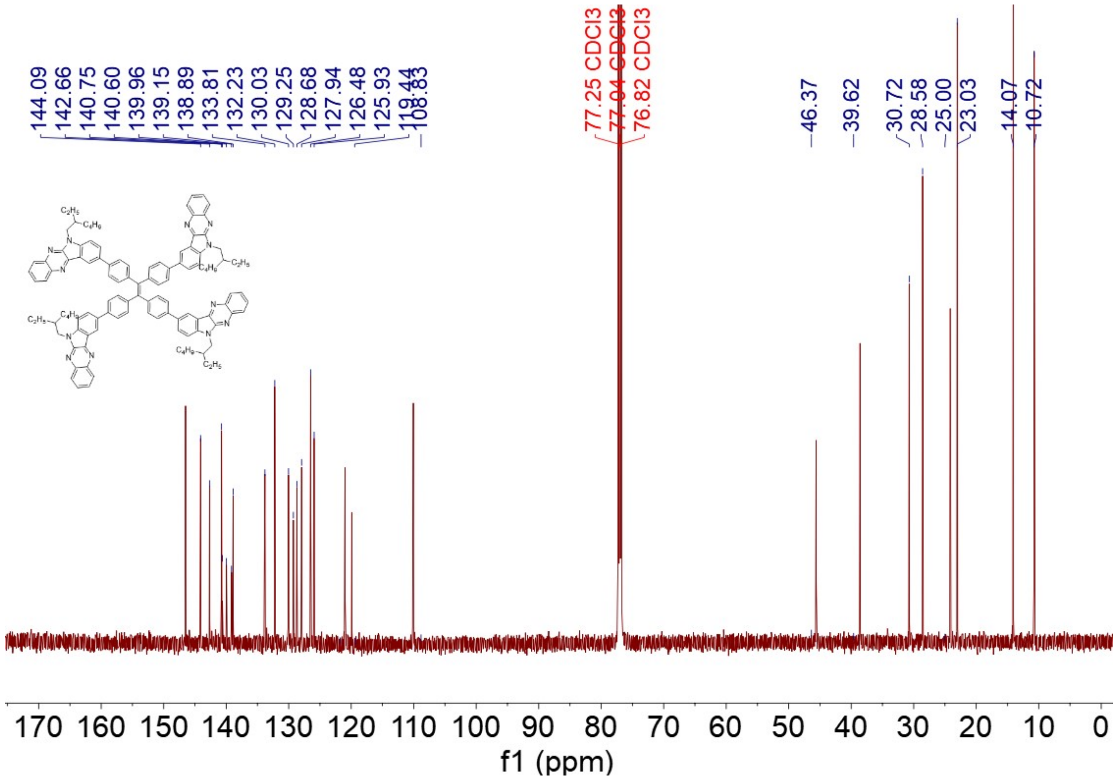
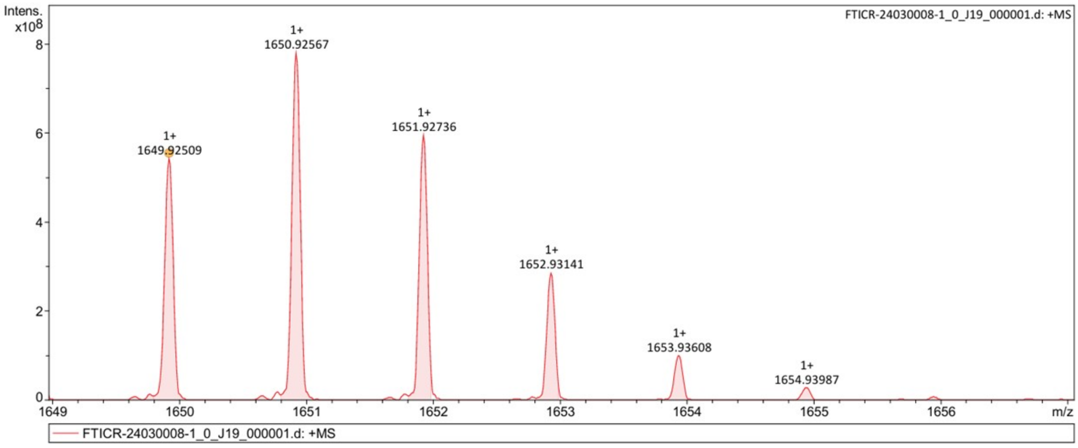


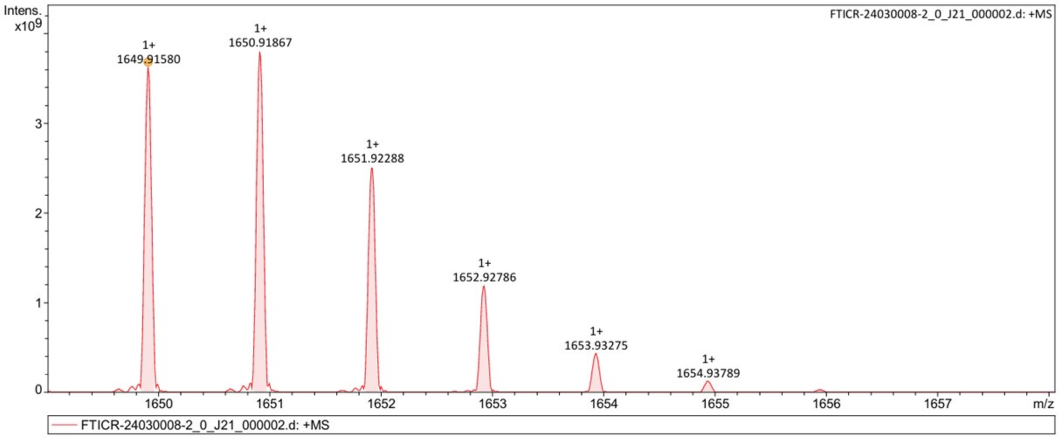
Figure S4. ^{13}C NMR spectrum of Tetra-9-IQ ($CDCl_3$, 25 ^oC)

2.2. HR-MS spectra of Tetra-8-IQ and Tetra-9-IQ



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1649.925092	1	C114H113N12	100.00	1649.920568	-2.7	-1.4	73.8	65.0	even	ok

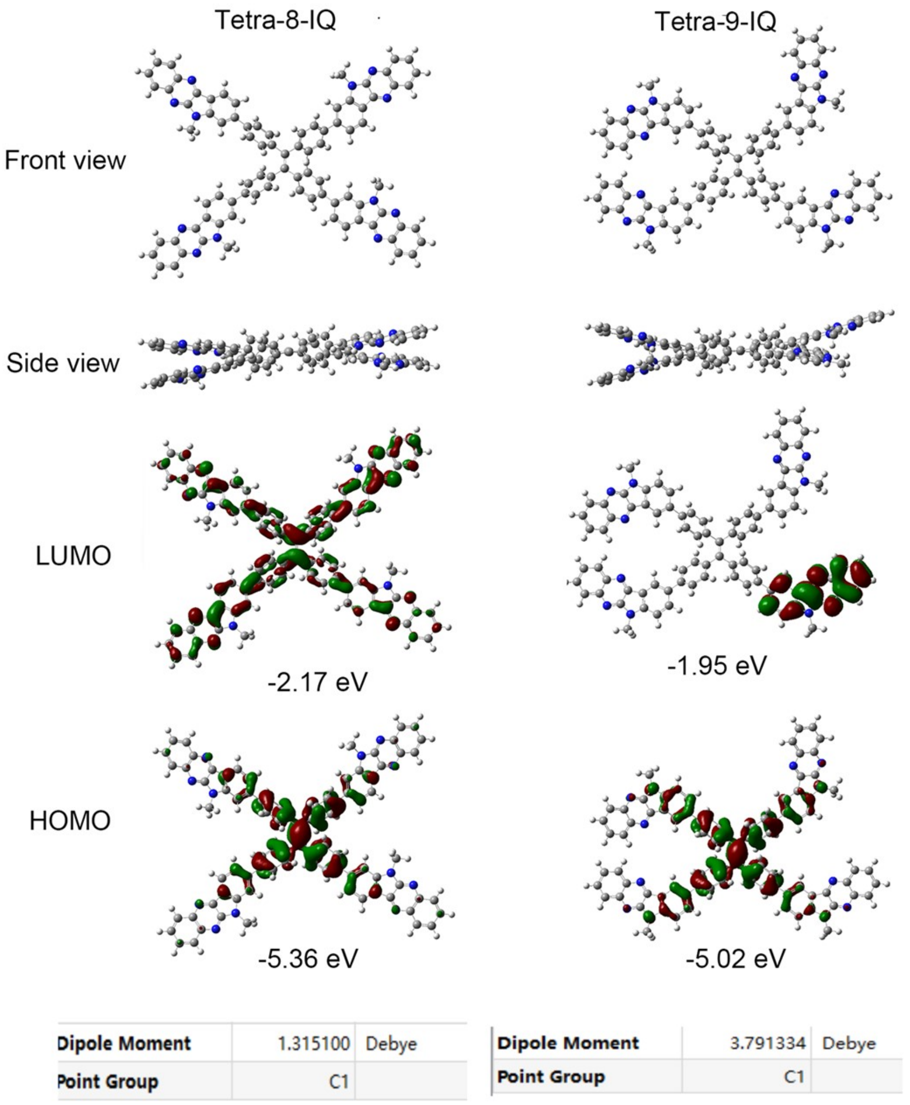
Figure S5. High-resolution mass spectra of compound Tetra-8-IQ.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1649.915802	1	C114H113N12	100.00	1649.920568	2.9	2.0	76.3	65.0	even	ok

Figure S6. High-resolution mass spectra of compound Tetra-9-IQ.

2.3. The results of DFT theoretical calculations of Tetra-8-IQ and Tetra-9-IQ



Dipole Moment	1.315100	Debye
Point Group	C1	

Dipole Moment	3.791334	Debye
Point Group	C1	

Figure S7. Optimized structures and frontier molecular orbital profiles of Tetra-8-IQ and Tetra-9-IQ

2.4. Photophysical properties of Tetra-8-IQ and Tetra-9-IQ in different solutions

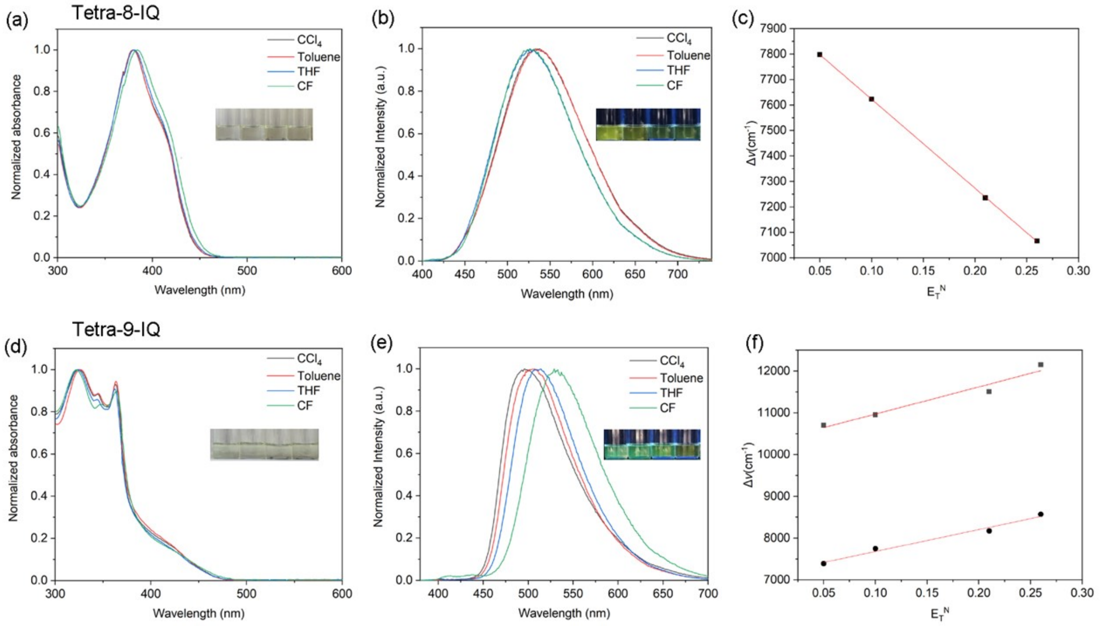


Figure S8. Normalized UV-Vis absorption spectra of Tetra-8-IQ (a) and Tetra-9-IQ (d); photoluminescence spectra of Tetra-8-IQ (b) and Tetra-9-IQ (e) in solvents of different polarities; (c)stokes shift (Δv) of Tetra-8-IQ (c) and Tetra-9-IQ (f) relationship with the solvent polarity parameter E_T^N. (Notes: No data was obtained for solvents with greater polarity (such as DMF and DMSO), as the solubility of the compounds in these solvents was limited.)

Table S1 Solvochromic properties of Tetra-8-IQ in different solvents

Solvent	$E_T^{N\ a}$	$\lambda_{ab}{}^{b}$(nm)	$\lambda_{em}{}^{c}$(nm)	Δ v(cm^{-1})	PLQY(%)
CCl_4	0.05	379	538	7798	10.1
Toluene	0.10	379	533	7623	4.1
THF	0.21	381	526	7235	3.5
Chloroform	0.26	384	527	7066	2.7

[a] E_T^N is the normalized value of the Dimroth and Reichardt solvent polarity parameter E_T on a scale from TMS (0.00) to water (1.00)，data from Ref[Reichardt C. Solvatochromic dyes as solvent polarity indicators[J]. Chemical Reviews, 1994, 94(8): 2319-2358.]

[b] λ_{ab} =absorption maximum; [c] λ_{em}=emission maximum; [d] Δv=Stokes shift.

[e] Absolute PLQYs were measured with an excitation wavelength of 380 nm.

Table S2 Solvochromic properties of Tetra-9-IQ in different solvents

Solvent	E_T^{N} [a]	λ_{ab}[b](nm)	λ_{em}[c](nm)	Δ ν(cm^{-1})	PLQY(%)
CCl_4	0.05	324/363	496	10703/7387	10.6
Toluene	0.10	326/364	507	10951/7749	13.2
THF	0.21	323/362	514	11505/8169	18.3
Chloroform	0.26	322/364	529	12152/8569	2.4

[a] E_T^N is the normalized value of the Dimroth and Reichardt solvent polarity parameter E_T on a scale from TMS (0.00) to water (1.00)， data from Ref[Reichardt C. Solvatochromic dyes as solvent polarity indicators[J]. Chemical Reviews, 1994, 94(8): 2319-2358.]

[b] λ_{ab} =absorption peak; [c] λ_{em}=emission maximum; [d] $\Delta\nu$=Stokes shift.

[e]Absolute PLQYs were measured with an excitation wavelength of 360 nm.

2.5. Mechanistic investigation through ¹H NMR spectra

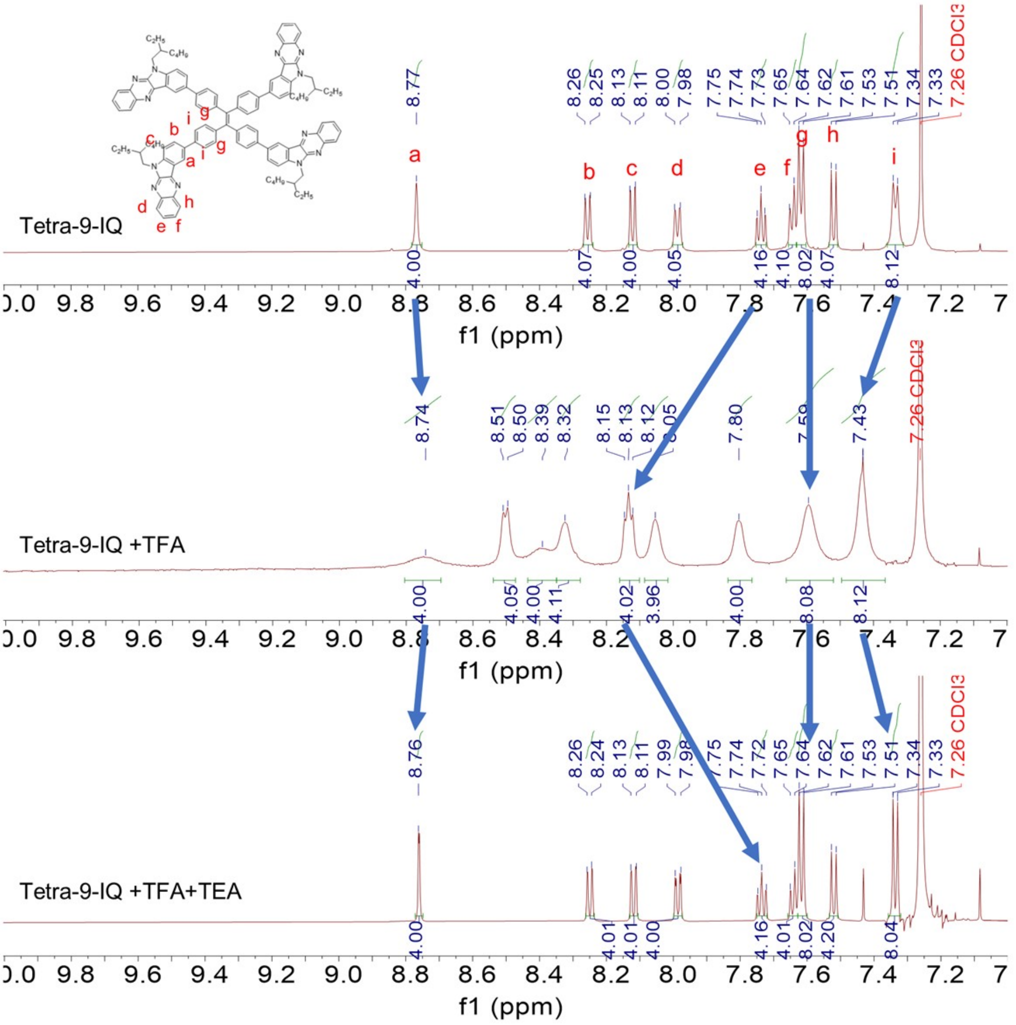


Figure S9. Partial ¹H NMR spectra of Tetra-9-IQ, Tetra-9-IQ with addition of TFA (Tetra-9-IQ+TFA), and Tetra-9-IQ with addition of TFA and subsequent addition of TEA (Tetra-9-IQ+TFA+TEA).

2.6. Solid-state emission spectra of compound/PMMA films

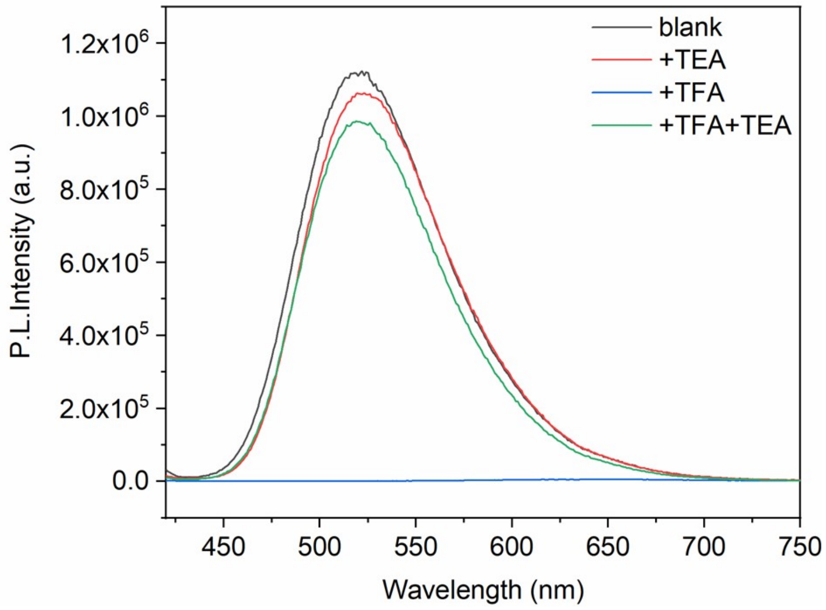


Figure S10. Solid-state emission spectra of Tetra-8-IQ/PMMA film (**thickness: 0.058 mm**). Black line: the pristine Tetra-8-IQ/PMMA film; red line: the Tetra-8-IQ/PMMA film dipped in TEA and methanol solution; blue line: the Tetra-8-IQ/PMMA film dipped in TFA and methanol solution; green line: the Tetra-8-IQ/PMMA film dipped in TFA and methanol solution, then dipped in TEA and methanol solution. Excitation wavelength: 390 nm.

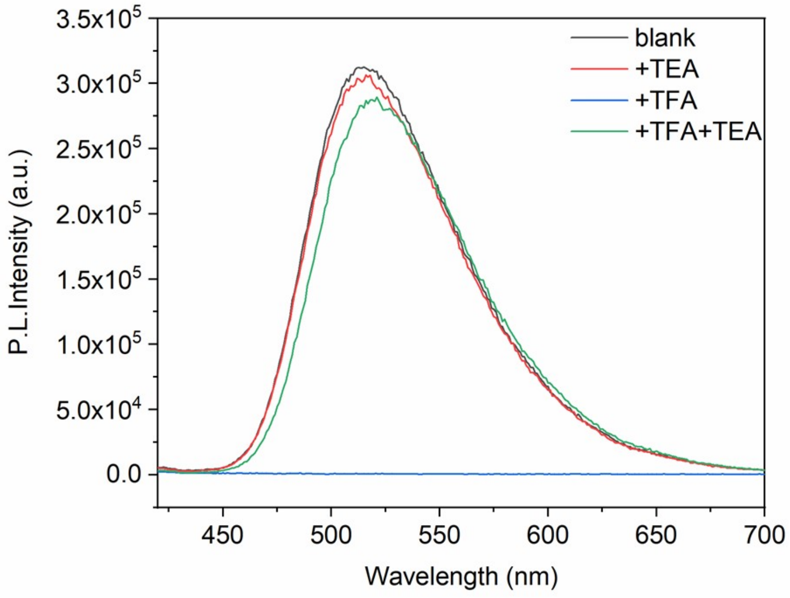


Figure S11. Solid-state emission spectra of Tetra-9-IQ/PMMA film (**thickness: 0.045 mm**). Black line: the pristine Tetra-9-IQ/PMMA film; red line: the Tetra-9-IQ/PMMA film dipped in TEA and methanol solution； blue line: the Tetra-9-IQ/PMMA film dipped in TFA and methanol solution; green line: the Tetra-9-IQ/PMMA film dipped in TFA and methanol solution, then dipped in TEA and methanol solution. Excitation wavelength: 366 nm.

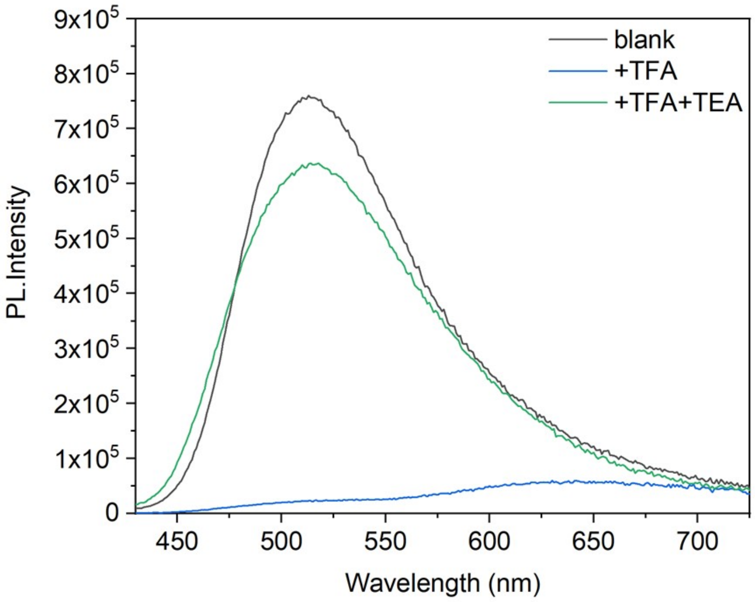


Figure S12. Solid-state emission spectra of Tetra-8-IQ/PMMA film (**thickness: 0.116 mm**). Black line: the pristine Tetra-8-IQ/PMMA film; blue line: the Tetra-8-IQ/PMMA film dipped in TFA and methanol solution; green line: the Tetra-8-IQ/PMMA film dipped in TFA and methanol solution, then dipped in TEA and methanol solution. Excitation wavelength: 390 nm.

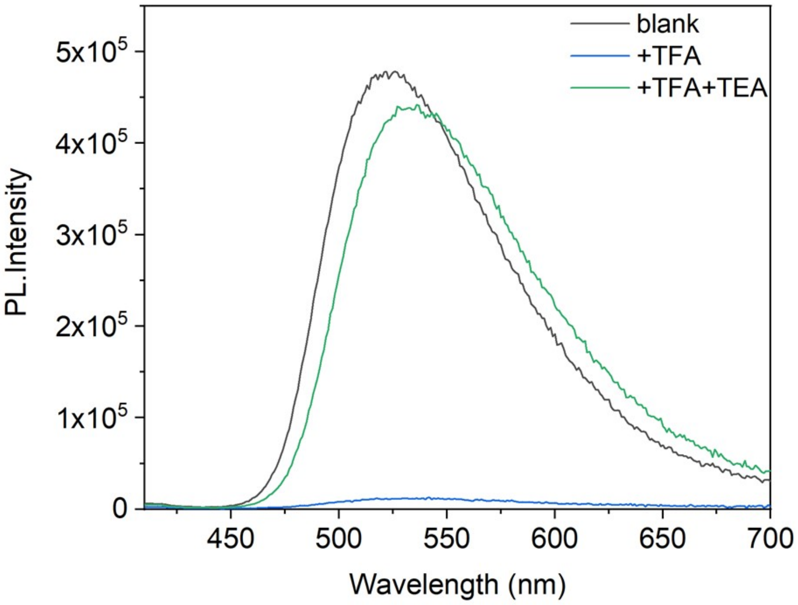


Figure S13. Solid-state emission spectra of Tetra-9-IQ/PMMA film (**thickness: 0.131 mm**). Black line: the pristine Tetra-9-IQ/PMMA film; blue line: the Tetra-9-IQ/PMMA film dipped in TFA and methanol solution; green line: the Tetra-9-IQ/PMMA film dipped in TFA and methanol solution, then dipped in TEA and methanol solution. Excitation wavelength: 366 nm.

For Tetra-8-IQ/PMMA, when the film thickness is 0.058 nm, immersing it in TFA/MeOH for 30 seconds can induce the complete quenching of the film's fluorescence. Subsequently, upon immersing this film in TEA/MeOH for 30 seconds, the fluorescence of the film can be fully restored. When the film thickness increases from 0.058 nm to 0.116 mm, submerging the film in TFA/MeOH for 90 seconds will lead to the complete quenching of the film's fluorescence. Nevertheless, after submerging this film in TEA/MeOH for 30 seconds once again, the fluorescence of the film can be entirely recovered. For Tetra-9-IQ/PMMA, when the primal film thickness is 0.045 nm, upon being dipped in TFA/MeOH for 30 seconds, the complete quenching of the film's fluorescence can be observed as well. Subsequently, when this film is immersed in TEA/MeOH for 30 seconds, the fluorescence of the film can also be fully restored. When the film thickness increases from 0.045 nm to 0.131 mm, after the film is dipped in TFA/MeOH for 120 seconds, the complete quenching of the film's fluorescence can be witnessed too. Subsequently, after this film is immersed in TEA/MeOH for 30 seconds once again, the fluorescence of the film can also be completely recovered.