

Supporting Information

Chromism Based on Supramolecular H-bonds

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1. Instruments and methods

The UV-visible absorption spectra were measured with a Shimadzu UV-1601PC double-beam spectrophotometer. All spectroscopic measurements were carried out at room temperature. Fluorescence spectra were measured using F-4500 (Hitachi). For the measurements of absorption spectra, we used a quartz cell with a typical optical length of 1 cm. And the fluorescence spectra were measured using a quartz cell with an optical length of 1 cm and a reflection measurement along the 45° direction relative to the excitation light direction was used to eliminate re-absorbing phenomena from high concentrations. Fluorescence kinetics were measured using a picosecond timeresolved fluorescence apparatus.¹ ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 or AVANCE 600 spectrometer and referenced to solvent signals. COSY, NOESY, HSQC and HMBC spectra were recorded on a Bruker AVANCE 600 spectrometer and referenced to solvent signals. For NMR experiments, the *d*₂-TFA instead of the normal TFA was used, mixing with 1ml of *d*₂-DCM. The electrochemical cyclic voltammetry (CV) was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dichloromethane (DCM) solution with a scan speed at 0.1 V/s. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively.

2. DFT calculations

Computational details are presented as follows:

Density functional theory (DFT) calculations were performed using the Gaussian 03 program² with the B3LYP exchange-correlation functional.³ All-electron triple- ξ valence basis sets with polarization functions (6-311G**) are used for all atoms. Geometry optimizations were performed with full relaxation of all atoms. Calculations were performed in gas phase without solvent effects. Charge distribution of the molecules was calculated by natural population analysis.⁵

3. Supporting figures

Fig. S1. Absorption spectra of the 1×10^{-5} M DCM solution of PDIs **1** (a), **2** (b) and **3** (c) upon titration of TFA.

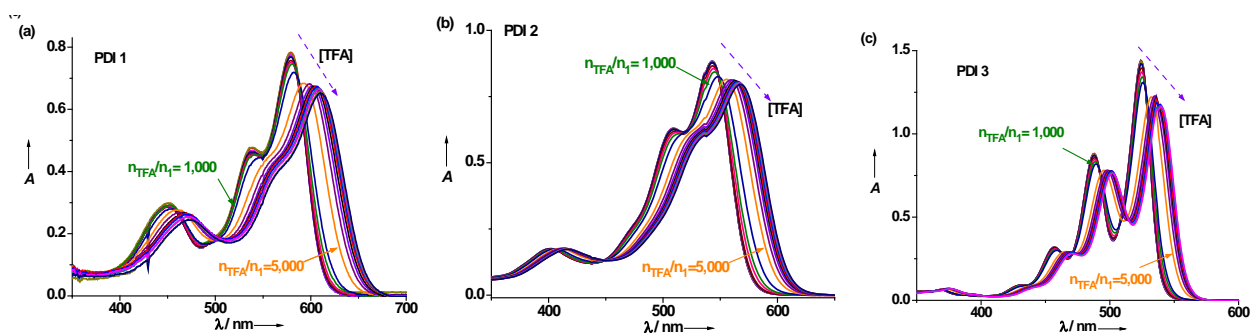


Fig. S2. Fluorescence spectra of the 1×10^{-5} M DCM solution of PDIs **1** (a), **2** (b) and **3** (c) upon titration of TFA.

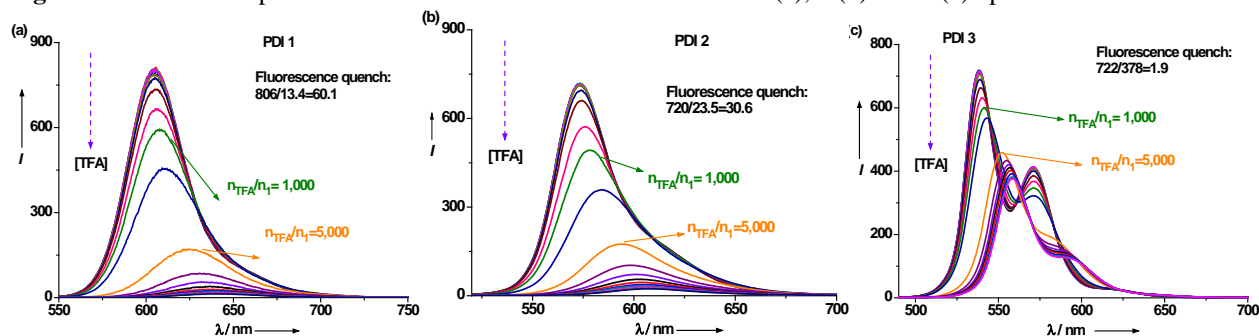
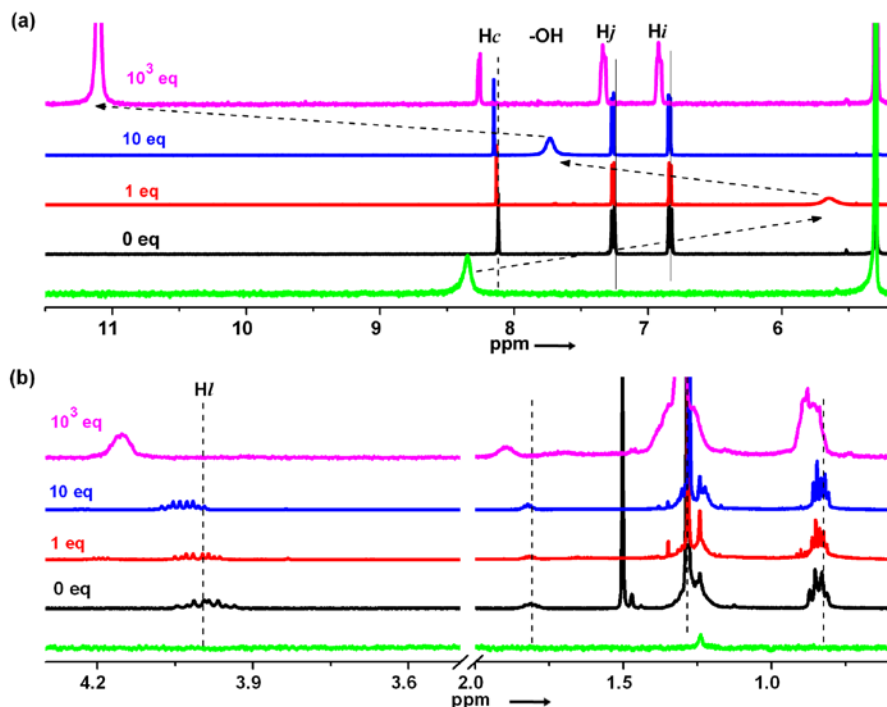
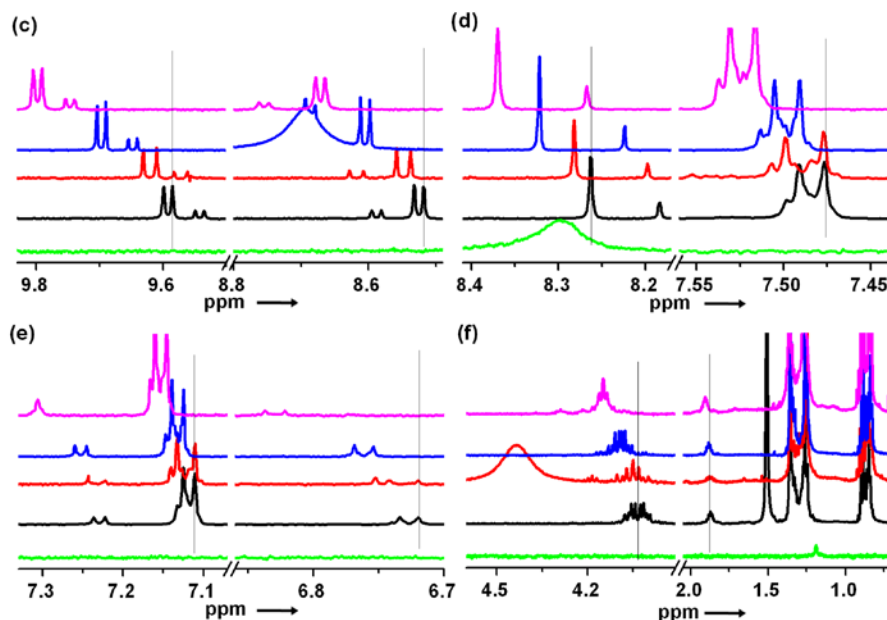


Fig. S3. ^1H NMR spectra of the $\text{DCM-}d_2$ solution of TFA (green line, $[\text{TFA}] = 1 \times 10^{-3} \text{ M}$) and PDIs **1** (a and b), **2** (c-f) and **3** (g and h) ($[\text{PDI}] = 1 \times 10^{-3} \text{ M}$) as 0 (black line), 1 (red line), 10 (blue line) and 1000 (pink line) equivalents of TFA was added, respectively. Assignments of the perylene-Hs are supported by the COSY, H-H NOE, HSQC and HMBC spectra of PDI **1** (Figure S5), **2** (Figure S6) and **3** (Figure S7) in d_2 -DCM.

PDI 1



PDI 2: The set of the weak signals are originated from the 1,6-4-*tert*-butylphenoxy PDI derivatives.



PDI 3

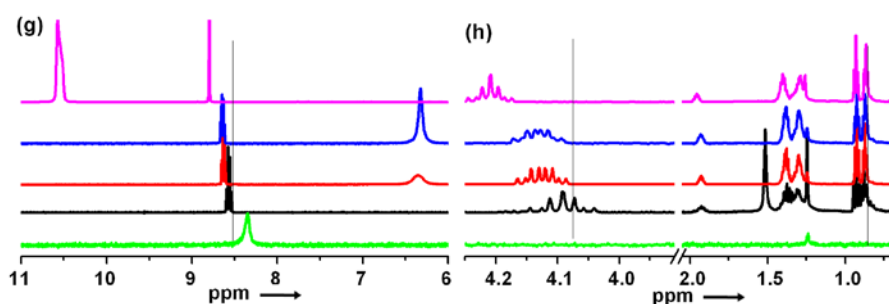
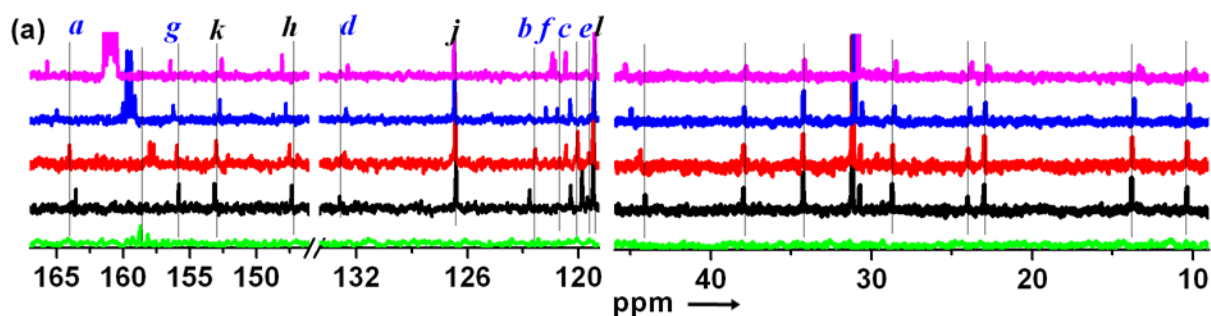
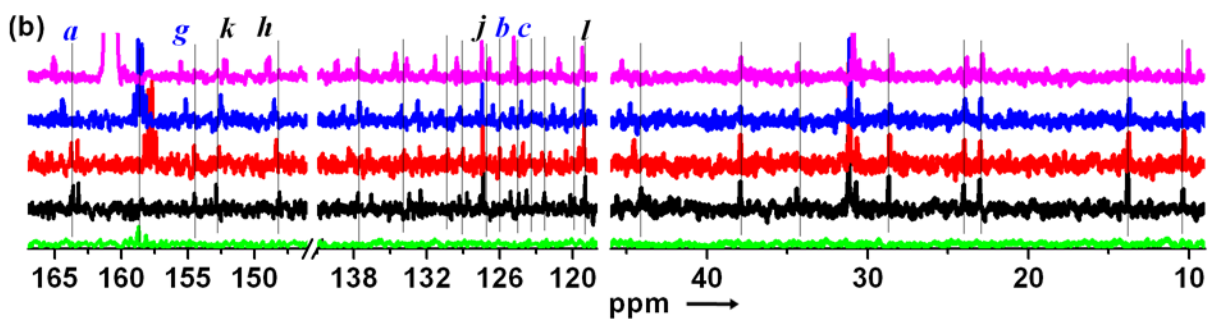


Fig. S4. ^{13}C NMR spectra of the $\text{DCM-}d_2$ solution of TFA (green line, $[\text{TFA}] = 1 \times 10^{-3} \text{ M}$) and PDIs **1** (a), **2** (b), and **3** (c) ($[\text{PDI}] = 1 \times 10^{-3} \text{ M}$) as 0 (black line), 1 (red line), 10 (blue line) and 1000 (pink line) equivalence of TFA is added, respectively. Assignments of the perylene carbons are supported by the COSY, H-H NOE, HSQC and HMBC spectra of PDI **1** (Figure S5), **2** (Figure S6) and **3** (Figure S7) in d_2 -DCM.

PDI 1



PDI 2



PDI 3

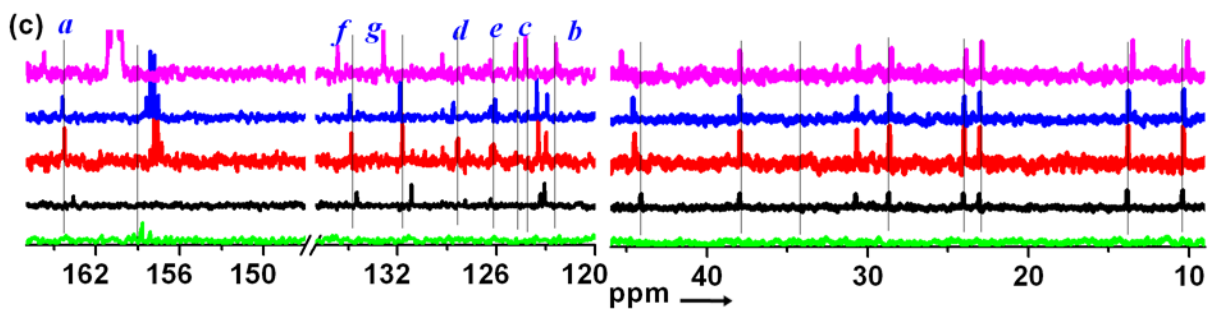
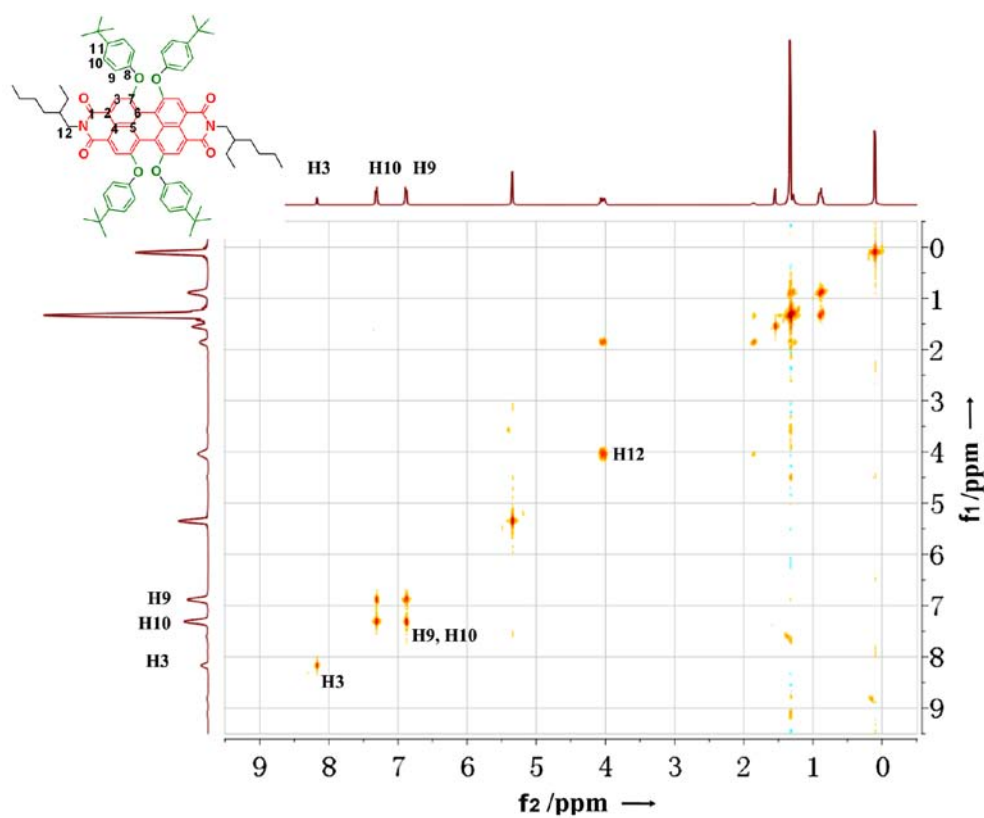
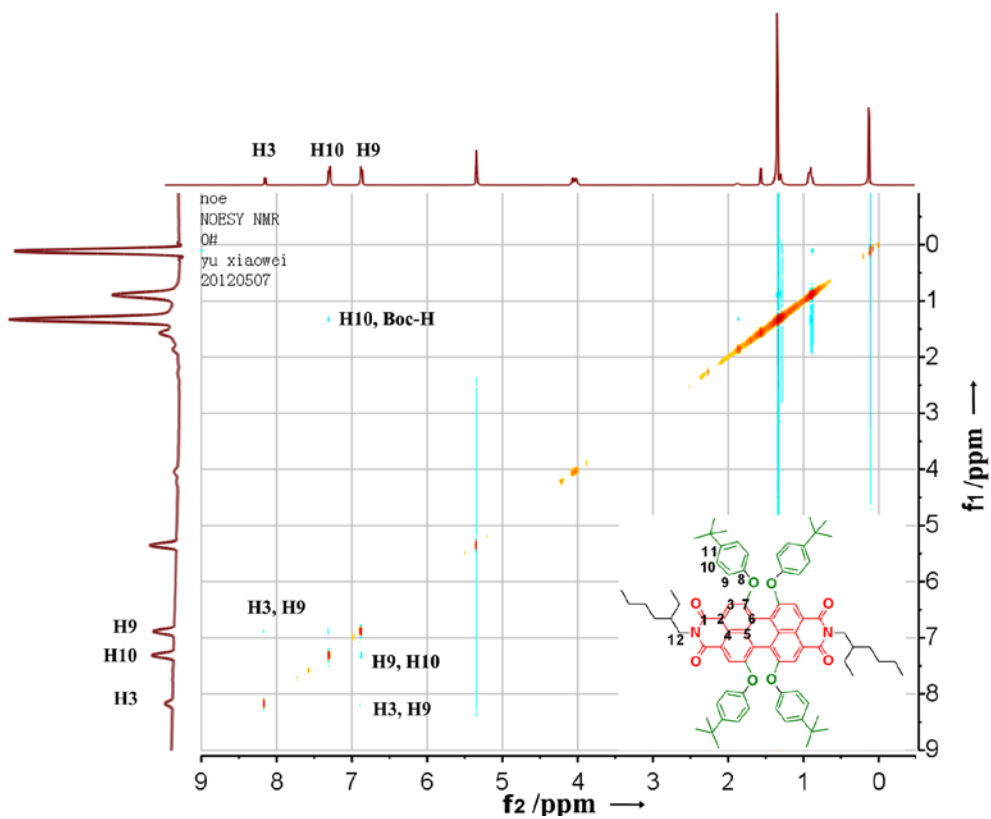


Fig. S5. COSY, H-H NOESY, HSQC and HMBC spectra of the DCM-*d*₂ solution of PDI **1** ($[1]=1\times 10^{-3}$ M).

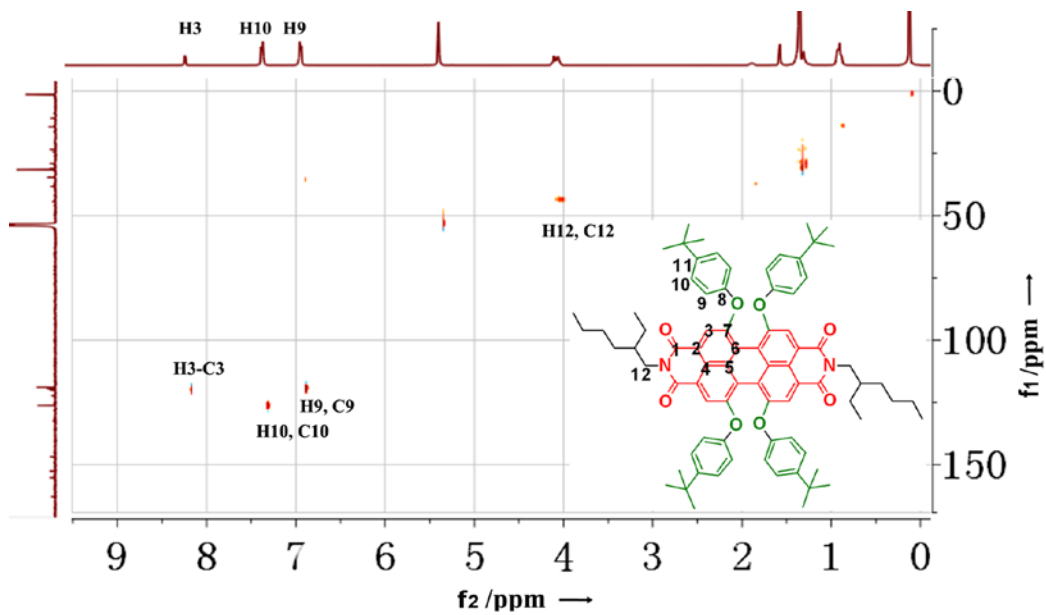
COSY



NOE



HSQC



HMBC

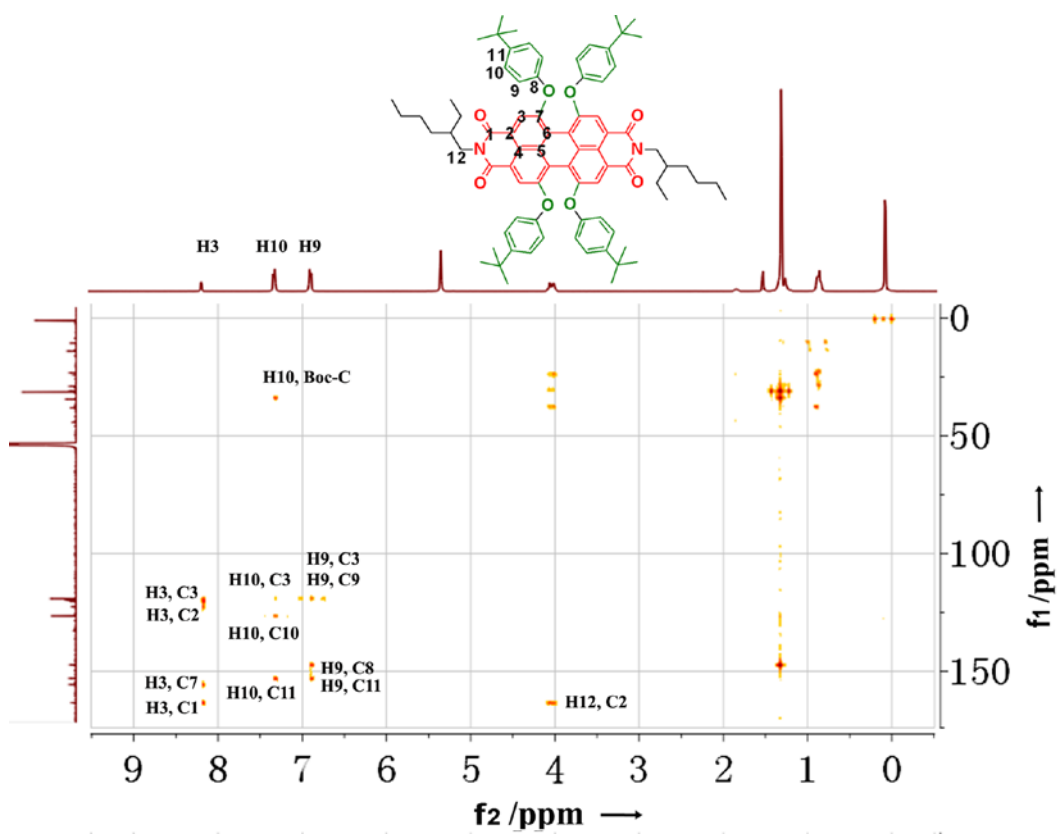
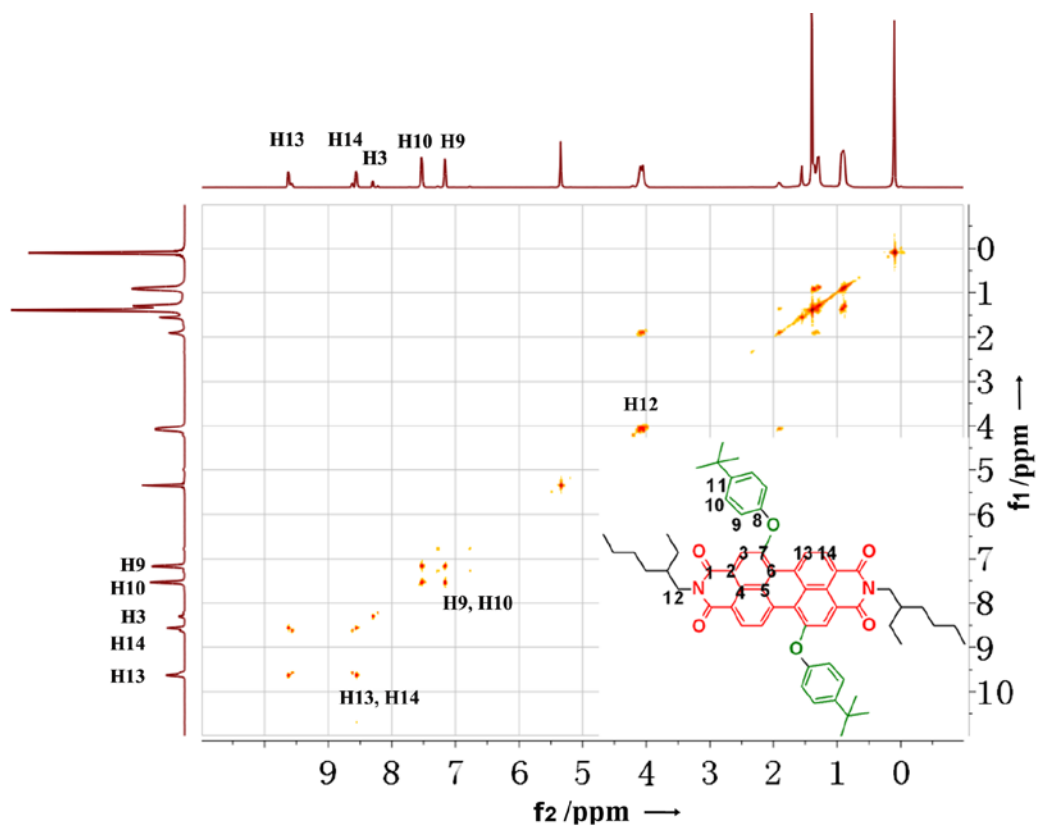
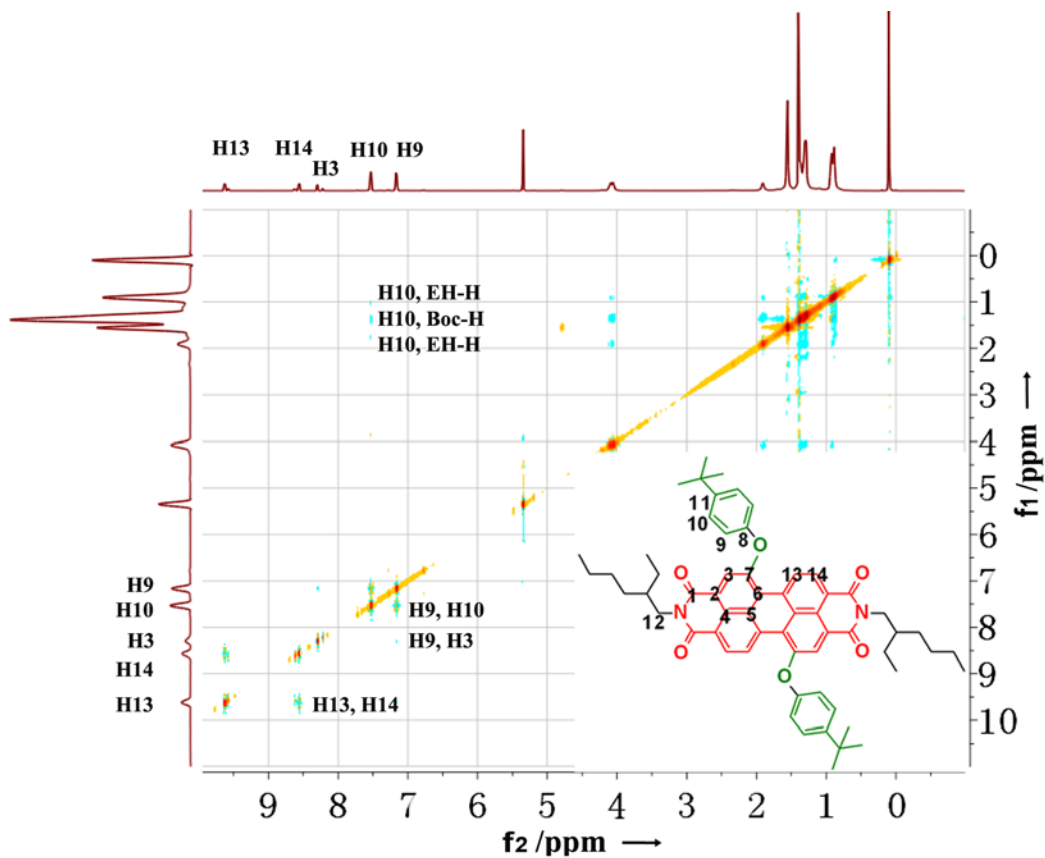


Fig. S6. COSY, H-H NOESY, HSQC and HMBC spectra of the DCM- d_2 solution of PDI **2** ($[2]=1\times 10^{-3}$ M).

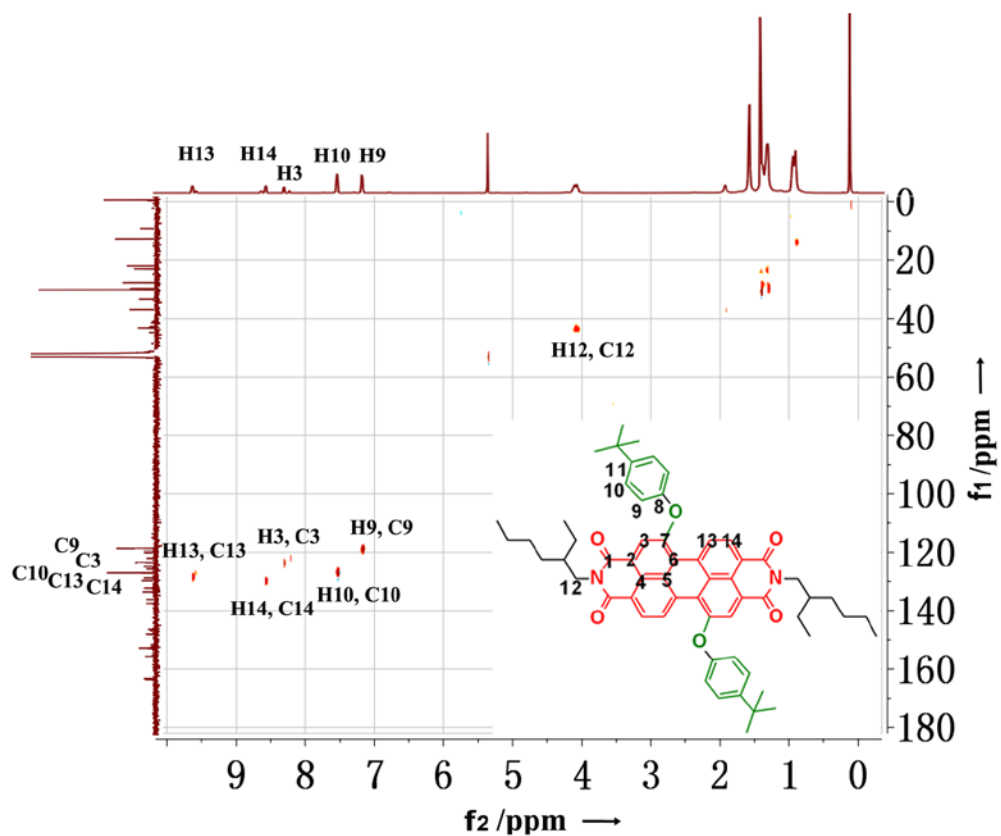
COSY



NOE



HSQC



HMBC

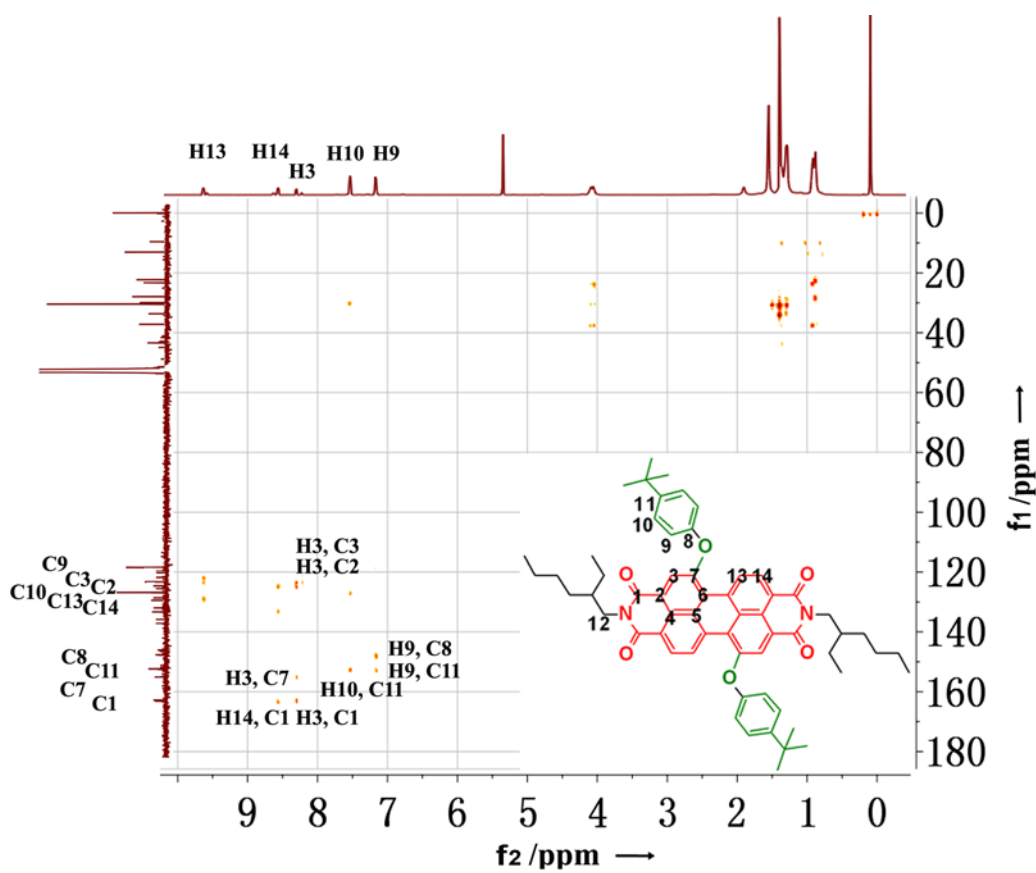
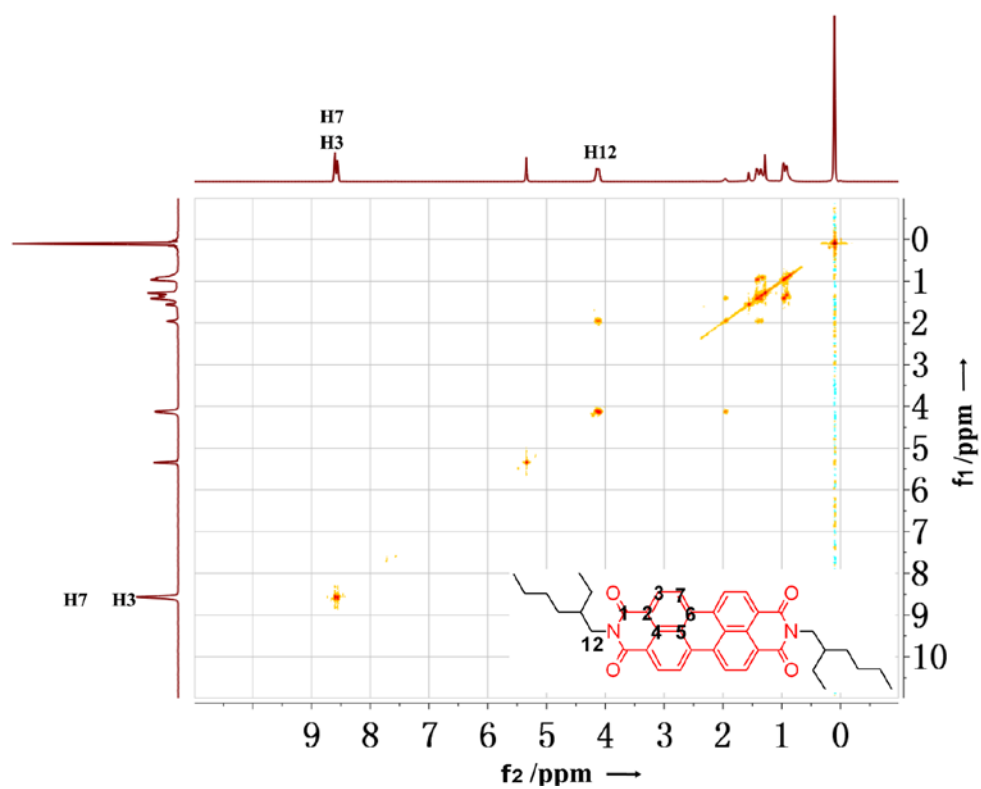
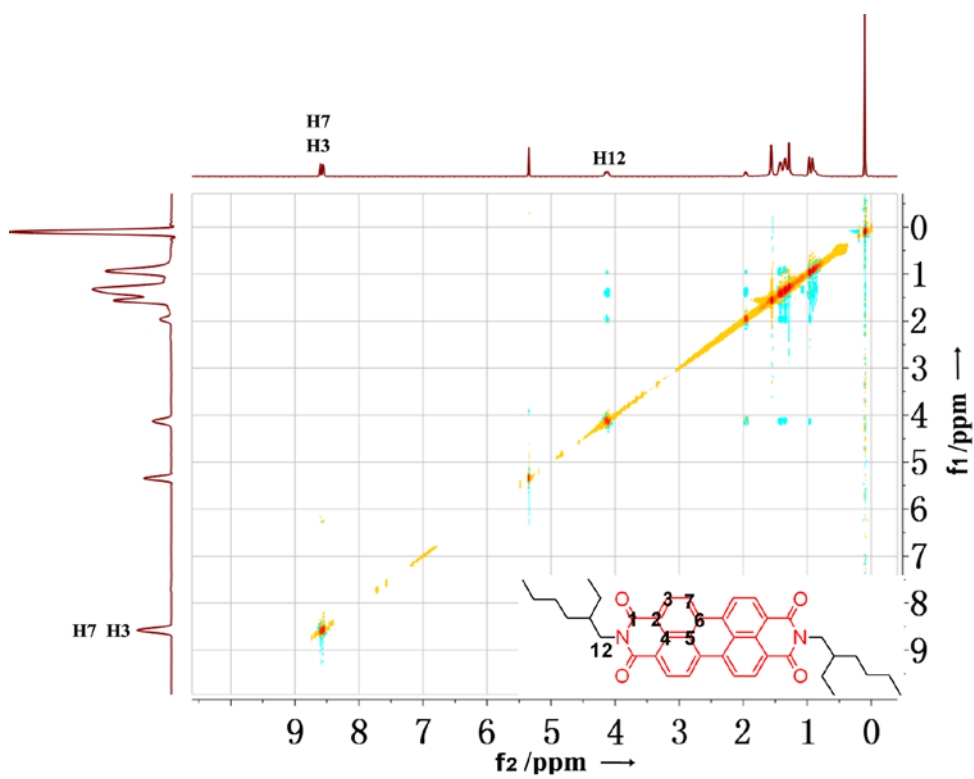


Fig. S7. COSY, H-H NOESY, HSQC and HMBC spectra of the DCM- d_2 solution of PDI **3** ($[3]=1\times 10^{-3}$ M).

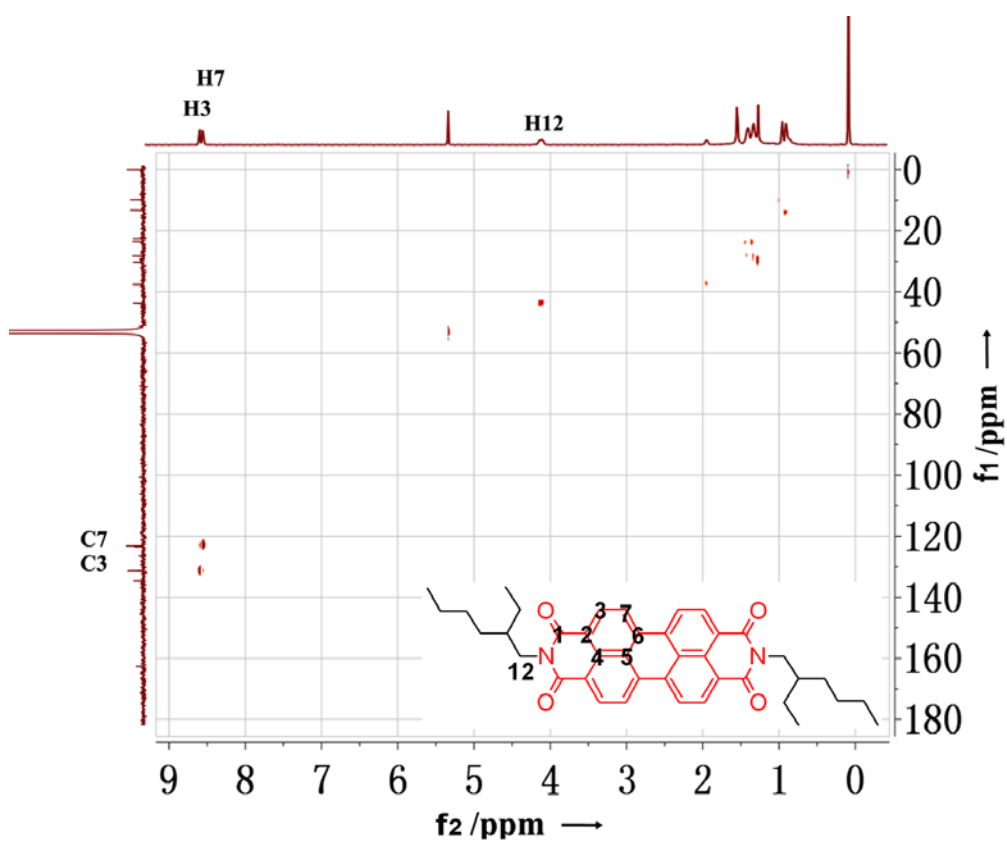
COSY



NOE



HSQC



HMBC

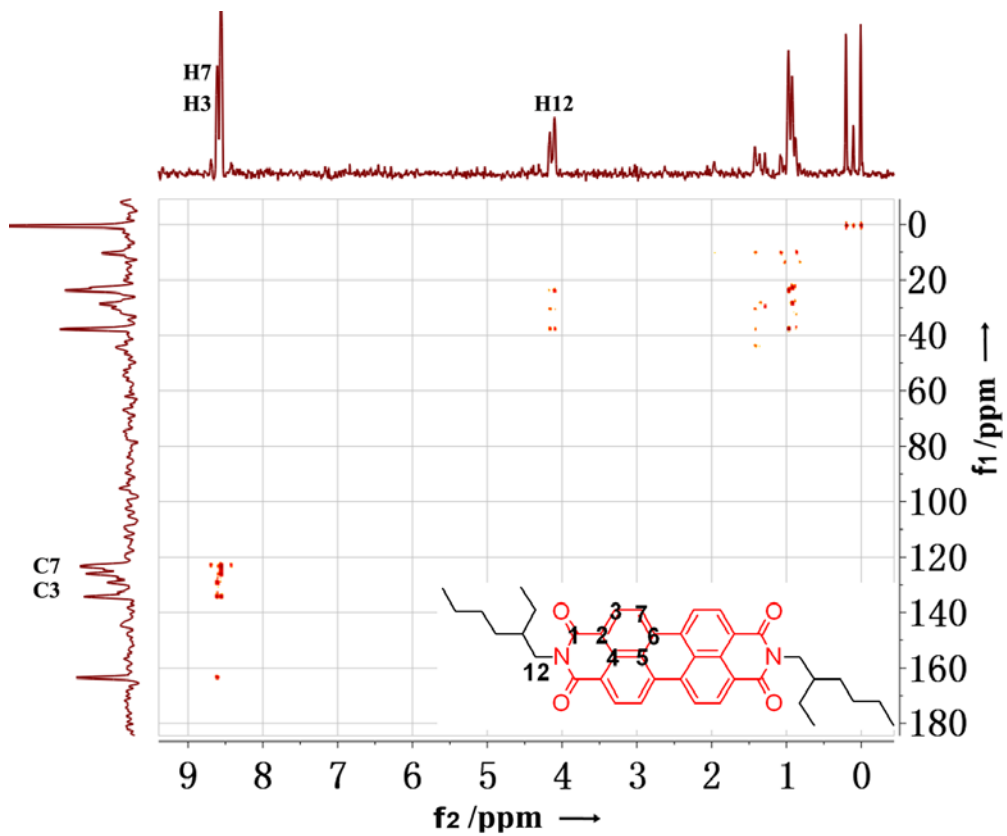


Fig. S8. The static potential out of the PDI **1** molecule: More red means more easily H-bonding with the TFA molecule. This figure shows that the imide C=O is more red than the bridged -O- atom, indicating that the imide C=O is more easily H-bonded with the TFA molecule.

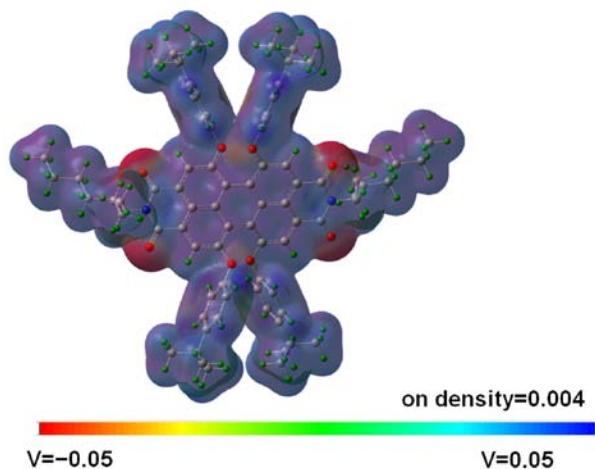


Fig. S9. Cyclic voltammetry of PDIs **1**, **2**, and **3** after addition of 0, 1, and 10 equivalence of TFA into the 1×10^{-4} M solution in DCM with 0.1 M Bu_4NPF_6 and a scanning rate of 0.1 V/s.

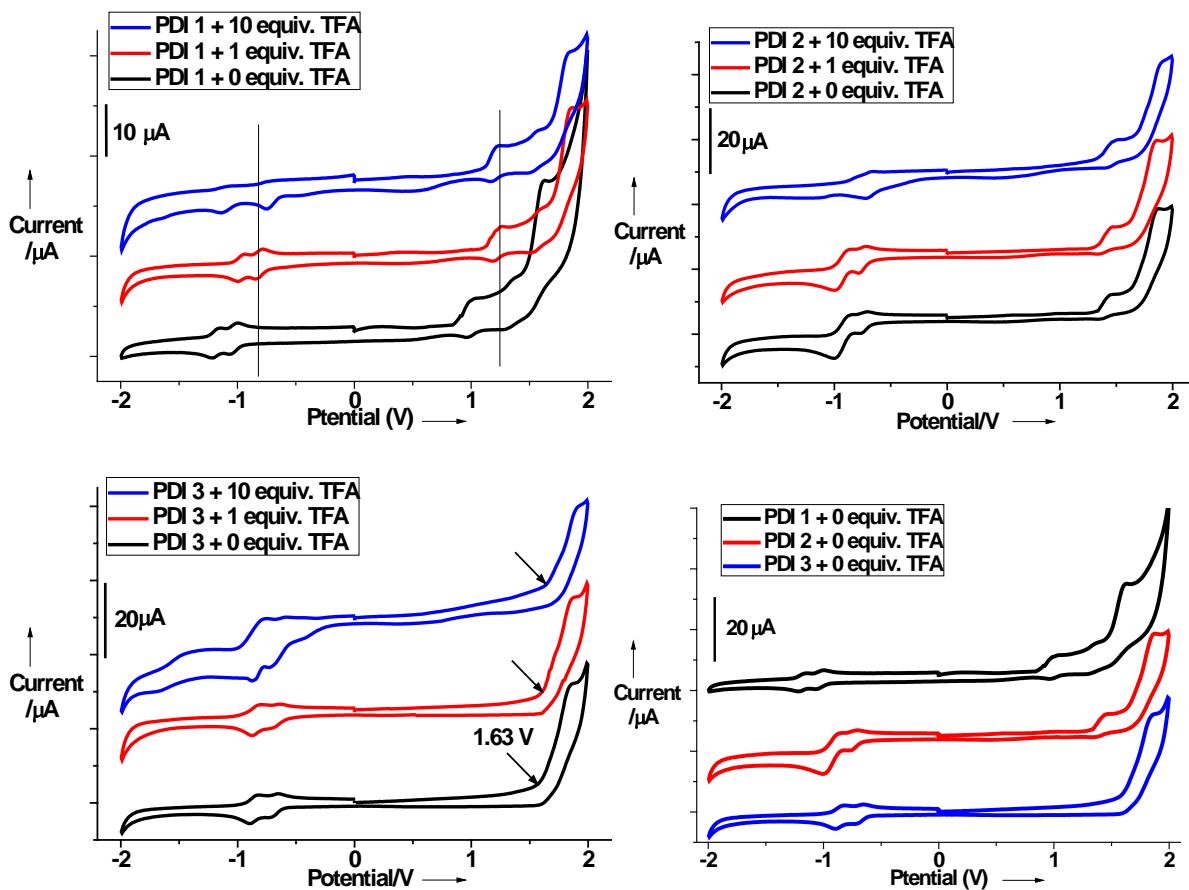


Fig. S10. Absorption spectra of the 1×10^{-5} M DCM solution of PDI **1** (a), PDI **2** (b), and PDI **3** (c) without or with addition of 50,000 equivalence of TFA, TCIA, AA, TFAOH, and EtOTFA, respectively.

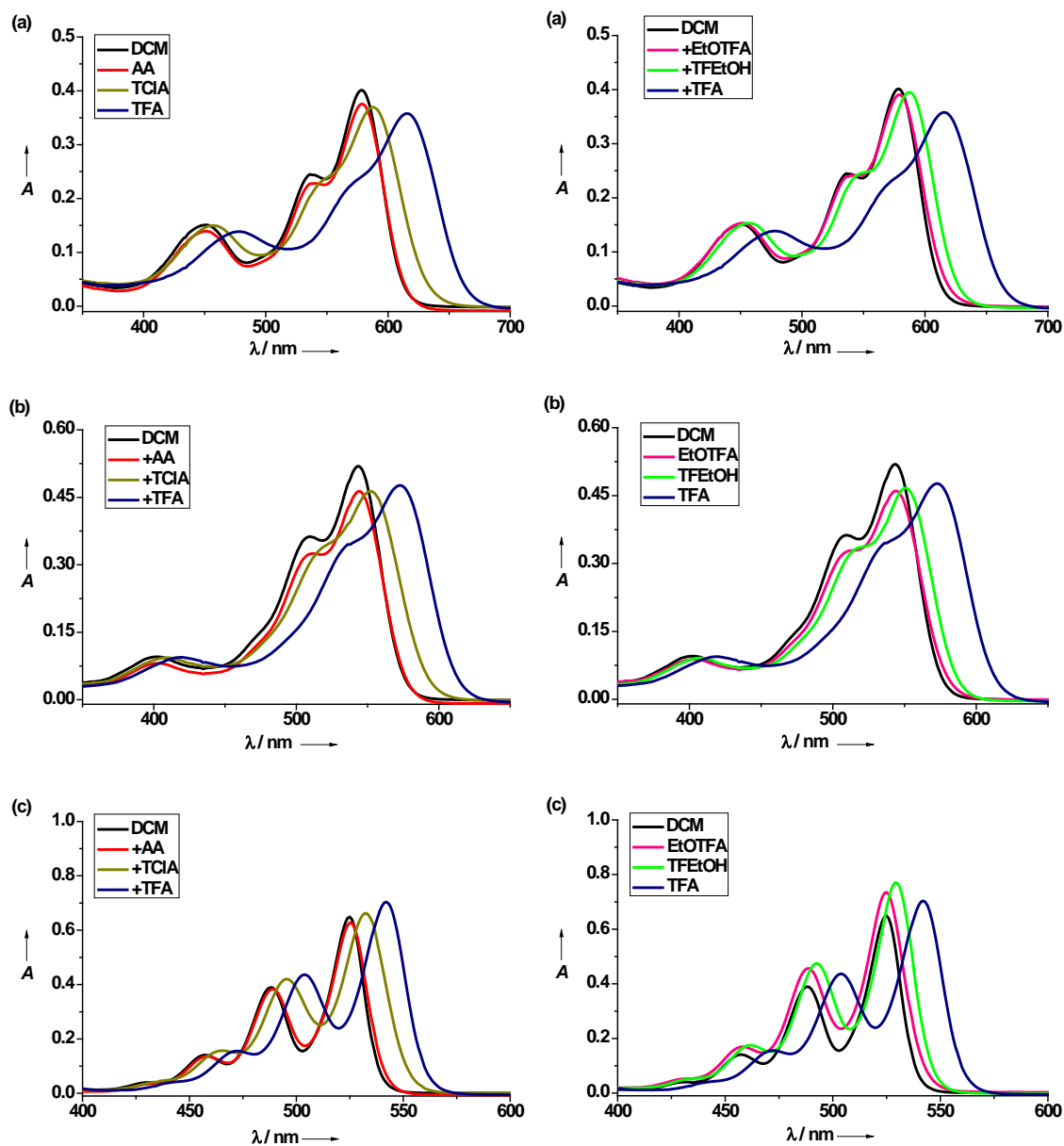


Fig. S11. Fluorescence spectra of the 1×10^{-5} M DCM solution of PDI **1** (a and b), PDI **2** (c and d), and PDI **3** (e and f) without or with addition of 50,000 equivalence of TFA, TCIA, AA, TFAOH, and EtOTFA, respectively.

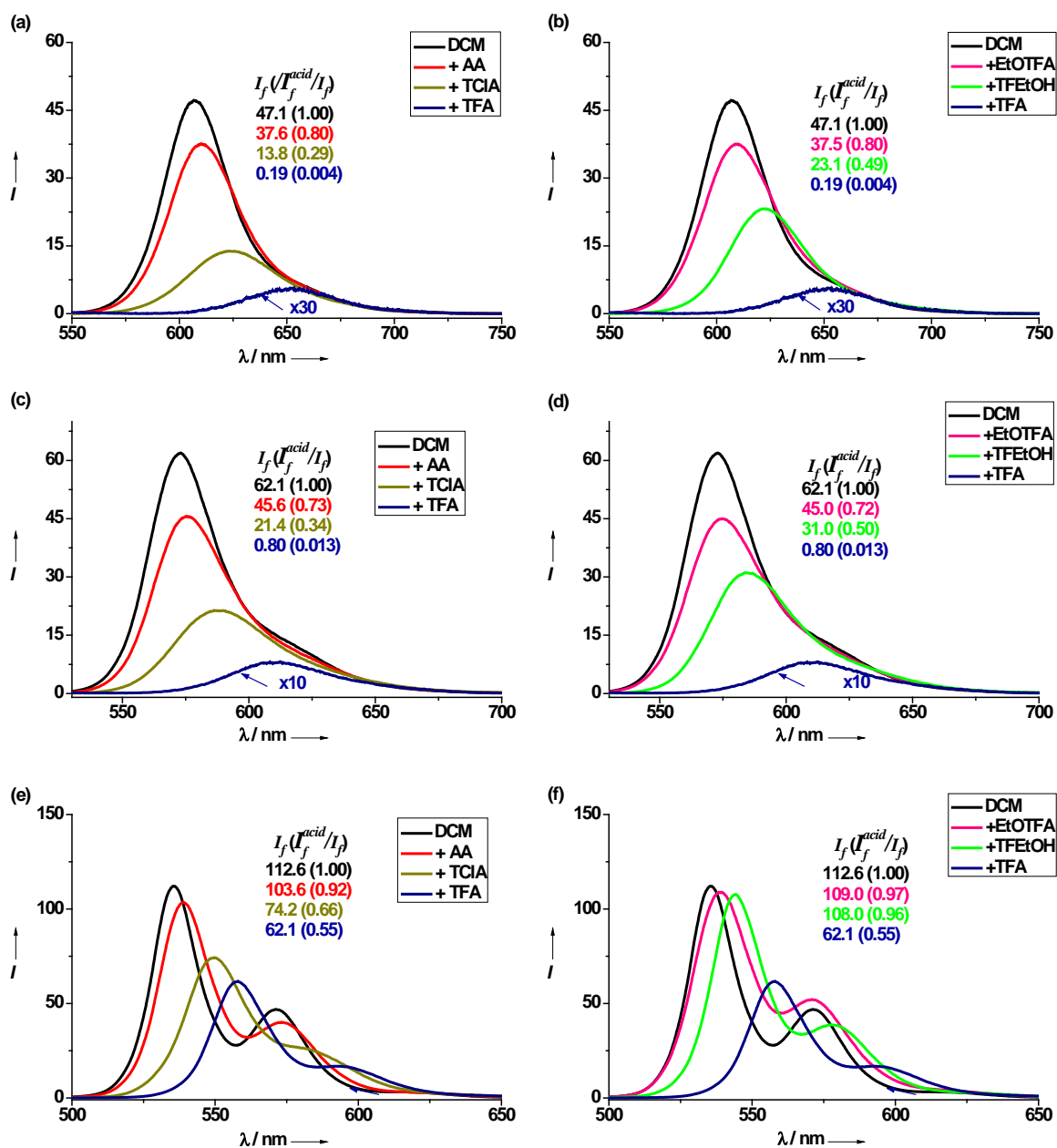


Fig. S12. Fluorescence decay curves measured from the 1×10^{-5} M DCM solution of PDIs **1** (a), **2** (b) and **3** (c) upon addition of 0, 1,000, 5,000 and 50,000 equiv. of TFA inside, respectively.

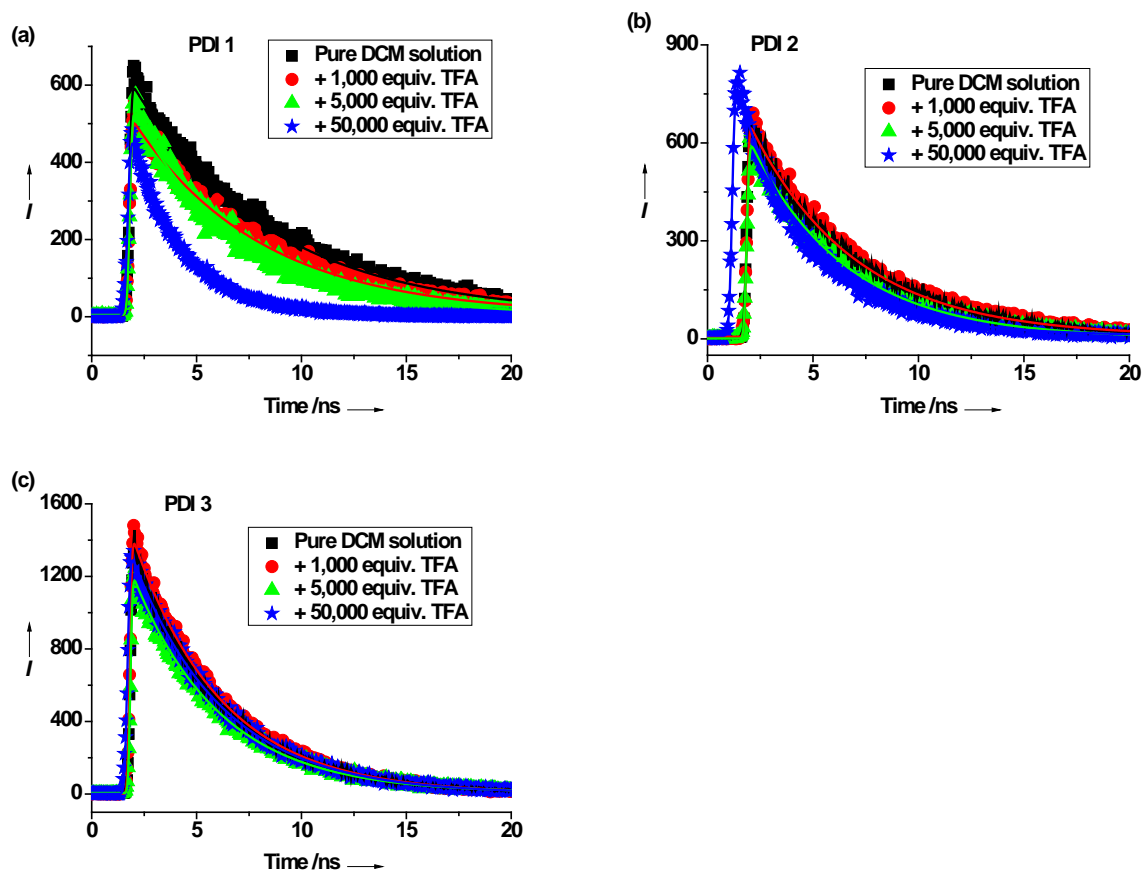
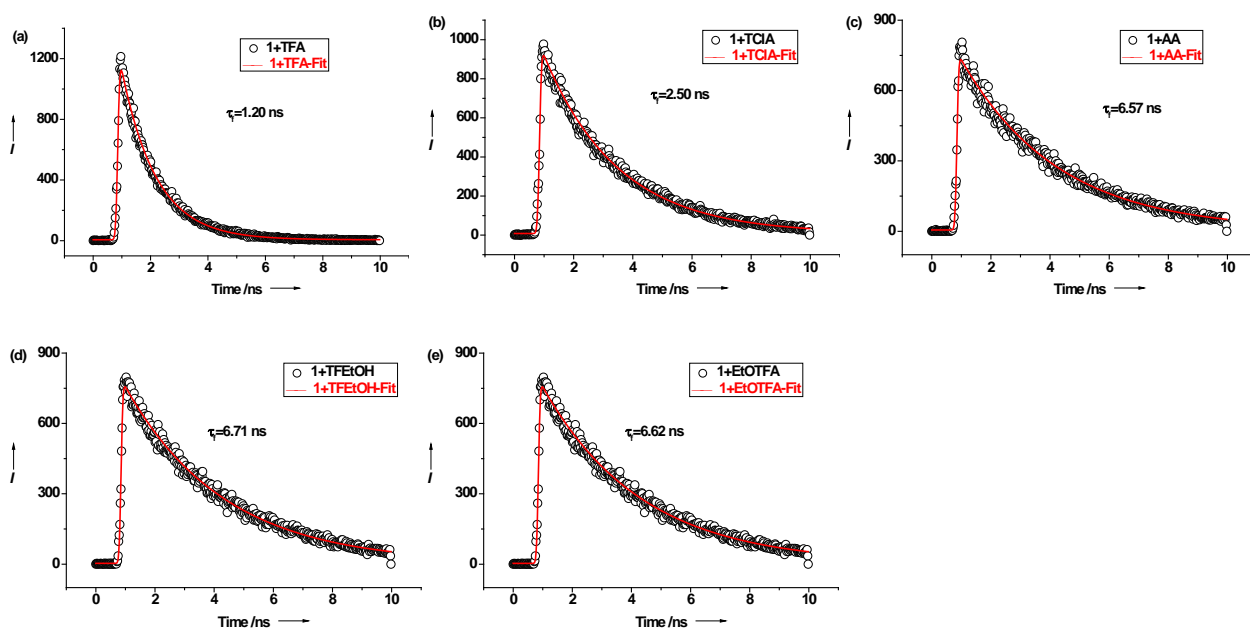


Fig. S13. Fluorescence decay curves measured from the 1×10^{-5} M DCM solution of PDI **1** after addition of 50,000 equiv. of TFA (a), TCIA (b), AA (c), TFEtOH (d) and EtOTFA (e) inside, respectively.



4. Supporting tables

Table S1. Calculated H-bonding energy (eV) of one or two TFA molecules onto the H-bonding sites of the imide C=O, imide N atom, and the bridged –O– atom of PDI **1**, respectively.

TFA molecules	H-bonding site	Imide C=O	Bridged –O–	Imide N
One TFA molecule	Energy (eV)	0.60	0.40	0.08
Two TFA molecule	H-bonding site	Imide C=O + C=O	Imide C=O + Bridged –O–	/
	Energy (eV)	1.19 \approx 2*0.60	1.00 = 0.60 + 0.40	/

Table S2. Electrochemical data of PDIs **1**, **2**, and **3** after addition of 0, 1, and 10 equivalences of TFA, respectively.

$n_{\text{TFA}}/n_{\text{PDI}}$	PDI 1		PDI 2		PDI 3	
	E_{Red} (V)	E_{Ox} (V)	E_{Red} (V)	E_{Ox} (V)	E_{Red} (V)	E_{Ox} (V)
0	-1.22, -1.08	1.05, 1.36, 1.61	-0.98, -0.75	1.45, 1.86	-0.87, -0.69	/, /, 1.86 (1.63 ^[a])
1	-0.98, -0.83	1.25, 1.58, 1.86	-0.97, -0.75	1.45, 1.86	-0.87, -0.69	/, /, 1.86 (1.63)
10	-1.13, -0.76, -0.46 ^[b]	1.25, 1.58, 1.83	-1.14, -0.71, -0.46 ^[b]	1.47, 1.87	-0.87, -0.68, -0.45 ^[b]	/, /, 1.86 (1.63)

^[a] This value was estimated from the on-set of the oxidation potential (Figure S9) and was used to calculate the energy gap of PDI **3** because the calculated energy gap (2.32 eV/534 nm) was consistent well with the experimental data from the absorption maximum (2.36 eV/525 nm without addition of any TFA inside, Figure S1c and Table 1). ^[b] this potential is originated from the added TFA.

Table S3. Calculated HOMO and LUMO energy levels (eV), energy gap (eV), absorption maximum ($\lambda_{\text{max}}^{\text{a}}$, nm) and absorption red-shifting ($\Delta\lambda_{\text{max}}^{\text{a}}$, nm) after H-bonding one or two TFA molecules onto the imide C=O functions of PDI **1**.

	DFT					First excited state calculated by time-dependent DFT ^[c]		
	HOMO (eV)	LUMO (eV)	E_{g} (eV)	$\lambda_{\text{max}}^{\text{a}}$ (nm)	$\Delta\lambda_{\text{max}}^{\text{a}}$ (nm)	E_{g} (eV)	$\lambda_{\text{max}}^{\text{a}}$ (nm)	$\Delta\lambda_{\text{max}}^{\text{a}}$ (nm)
PDI 1	-5.423	-3.103	2.320	534.405	0.000	2.122	584.252	0.000
+TFA- Ot ^[a]	-5.549	-3.299	2.250	551.014	16.609	2.061	601.602	17.350
+TFA- Ot-Ot ^[b]	-5.690	-3.490	2.201	563.413	29.008	2.011	616.440	32.188
+TFA- Ot-Ob ^[d]	-5.712	-3.421	2.291	541.132	6.727	2.085	594.680	10.428

Note: ^[a] one TFA molecule H-bonds onto the imide C=O; ^[b] Two TFA molecules with one H-bonded onto one C=O of the imide and the other H-bonded onto another C=O of the imide. H-bonding of the second TFA molecule onto the imide C=O accumulates (1) the reduction of the energy gap and further the red-shifting of the absorption, as revealed from the time-dependent DFT calculation results and (2) the depressions of the HOMOs' and LUMOs' energy levels, as revealed from the DFT calculation results; ^[c] Time-dependent DFT (TD-DFT) calculations support the observations of red-shifting for absorption spectra when TFA is H-bonded, and the red-shifting degree agrees well with the data calculated from the HOMO and LUMO values (and also the experimental values). The values 584.252 and 616.440 nm by TD-DFT is more consistent with the experimental values than 534.405 and 563.413 nm that are calculated from the HOMO and LUMO values. ^[d] Although H-bonding and the second TFA molecule onto the bridged –O– atom enlarges the energy gap, E_{g} , yielding the blue-shifting of the absorption, sum of the effects

from the H-bonding of the TFA molecules onto the imide C=O and onto the bridged –O– atom both reduce the energy gap, resulting in the red-shifting.

Table S4. Fluorescent lifetime (τ_f) of PDI **1** after addition of 50,000 equivalences of TFA, TCIA, AA, TFEtOH, and EtOTFA, respectively.

	In pure DCM	+TFA	+TCIA	+AA	+TFEtOH	+EtOTFA
τ_f (ns)	6.62±0.13	1.20±0.01	2.50±0.04	6.57±0.14	6.71±0.12	6.62±0.11
6,62/ τ_f	1.00	5.56	2.63	1.01	0.99	1.00
I_f^{acid}/I_f	1	0.004	0.29	0.80	0.49	0.80

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