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

Supporting information

Direct Evidence of Solvent Polarity Governing the Intramolecular Charge and Energy Transfer: Ultrafast Relaxation Dynamics of Push-Pull Fluorene Derivative

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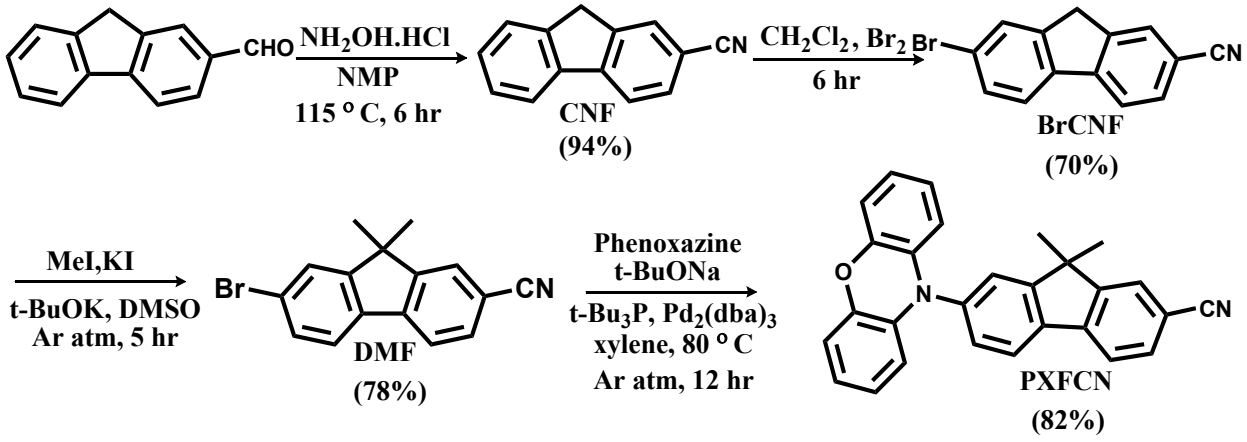

NMP : N-Methyl-2-pyrrolidone
t- Bu_3P : Tri (*tert*- butyl) phosphine
$Pd_2(dba)_3$:Tris(dibenzylideneacetone)dipalladium(0)

Scheme S1 Synthesis of 2-cyano-9-phenoxazine -9,9-dimethylfluorene (**PXFCN**)

Synthetic procedure of PXFCN

Synthesis of 9H-Fluorene-2-carbonitrile (FCN):

In a 100 mL RB 9H-fluorene-2-carbaldehyde (1 equiv), N-methylpyrrolidone (8 mL) and $H_2NOH.HCl$ (1 equiv.) was taken and heated to 115 °C for 5-6 hr. On completion of the reaction, the reaction mixture was poured into cold water and stirred for some time. A light yellowish precipitate was formed which was collected by filtration, dried and was recrystallized from ethanol/water mixture. Yield: 94%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86-7.83 (m, 2H), 7.82 (s, 1H), 7.68 (d, J = 8 Hz, 1H), 7.60 (d, J = 7 Hz, 1H), 7.45-7.40 (m, 2H), 3.96 (s, 2H). ^{13}C NMR (125 MHz): 146.24, 143.91, 143.64, 139.91, 131.20, 128.64, 128.59, 127.31, 125.33, 120.98, 120.39, 109.67, 36.78. HRMS (EI) (m/z): [M]+ calcd. for: $C_{14}H_9N$ 191.07 found 192.08159.

Synthesis of 7-Bromo-9H-fluorene-2-carbonitrile (BrCNF):

In a 100 mL RB FCN (1 equiv.) and dry CH_2Cl_2 (6 mL) was stirred for some time. Br_2 (4 equiv.) was added drop wise and was stirred for 6 hr. The condenser was connected to a trap filled with NaOH solution through which the HBr evolving from the mixture was passed. The mixture was poured into a solution of 5% $NaHSO_3$ in water and stirred for some time. A light brown precipitate was obtained which was dried and recrystallized from DMF/water mixture. Yield 70%. ^{1}H (500 MHz, $CDCl_3$): 7.83-7.81 (m, 2H), 7.74 (s, 1H), 7.70-7.68 (m, 2H,), 7.57 (d, J = 8 Hz, 1H), 3.95 (s, 2H). ^{13}C NMR (125 MHz): 144.68, 144.07, 142.18, 137.79, 130.31, 129.51, 127.53, 121.61, 121.12, 119.42, 118.40, 109.06, 35.53. HRMS (EI) (m/z): [M]+ calcd. for: $C_{14}H_8BrN$ 268.98 found 269.99132.

Synthesis of 2-Bromo-7-cyano-9,9-dimethyl-9*H*-fluorene (DMF) : A mixture of BrCNF (1 equiv.), KI (0.2 equiv.), and t-BuOK (4 equiv.), were taken in a 100 mL two neck RB and vacuum was applied for 10 minutes. In the presence of argon, DMSO was added to the mixture and was kept for stirring. MeI (2 equiv.) was added drop wise to the solution. The reaction mixture was kept for stirring for 5 hr, after which it was poured to water. The product was separated by filtration and dried. Yield 78%. ^{1}H (500 MHz, $CDCl_3$): δ 7.76 (d, J =7.5 Hz, 1H), 7.68 (s, 1H), 7.65-7.63 (m, 2H), 7.61 (d, J = 6 Hz, 1H), 7.52, (d, J =7 Hz, 1H), 1.50 (s, 6H). ^{13}C NMR (125 MHz): 156.12, 153.78, 142.76, 136.28, 131.64, 130.75, 126.52, 126.50, 123.23, 122.44, 120.65, 119.48, 110.59, 47.44, 26.69. HRMS (EI) (m/z): [M]+ calcd. for: $C_{16}H_{12}BrN$ 297.02 found 298.02359.

Synthesis of 2-cyano-7-phenoxazine -9,9-dimethyl-9*H*-fluorene (PXFCN):

Phenoxazine (1.2 equiv.), DMF, (1 equiv.) sodium tert-butoxide (4.5 equiv.), $Pd_2(dba)_3$[(tris(dibenzylidineacetone) dipalladium(0))] (0.15 equiv.), and tri(tert-butyl)phosphine (0.13 equiv.) were dissolved in 200 mL of xylene, and refluxed at 80°C for 12 hr under Ar atmosphere. On completion of the reaction, the reaction mixture was cooled to room temperature and was extracted by adding 200 mL of distilled water in a volume ratio of xylene to water of 1:1. The organic phase was collected, dried using $MgSO_4$ and then concentrated under vacuum. The concentrated product was refined using silica gel column chromatography using hexane:ethyl acetate in a volume ratio of 1:3 as an eluent. The product was then concentrated under vacuum and dried to obtain 100 mg of compound with a yield of 82 %. ^{1}H NMR (500 MHz,$CDCl_3$):δ 7.97 (d, *J* = 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.74 (s, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.37 (d, *J* = 8Hz, 1H), 6.72 (d, *J* =7 Hz, 2H), 6.66 (t, J = 7.5 Hz, 2H), 6.60 (t, J = 8Hz, 2H), 5.96 (d, J = 7.5 Hz, 2H), 1.53 (s, 6H). ^{13}C NMR (125 MHz): 157.32, 154.50, 143.99, 142.79, 139.64, 137.46, 134.32, 131.70, 130.14, 126.66, 125.41, 123.51, 123.31, 121.52, 120.90, 119.50, 115.58, 113.15, 110.71, 47.54, 26.78. HRMS (EI) (m/z): [M]+ calcd. for: $C_{28}H_{20}N_2O$ 400.16 found 400.15743

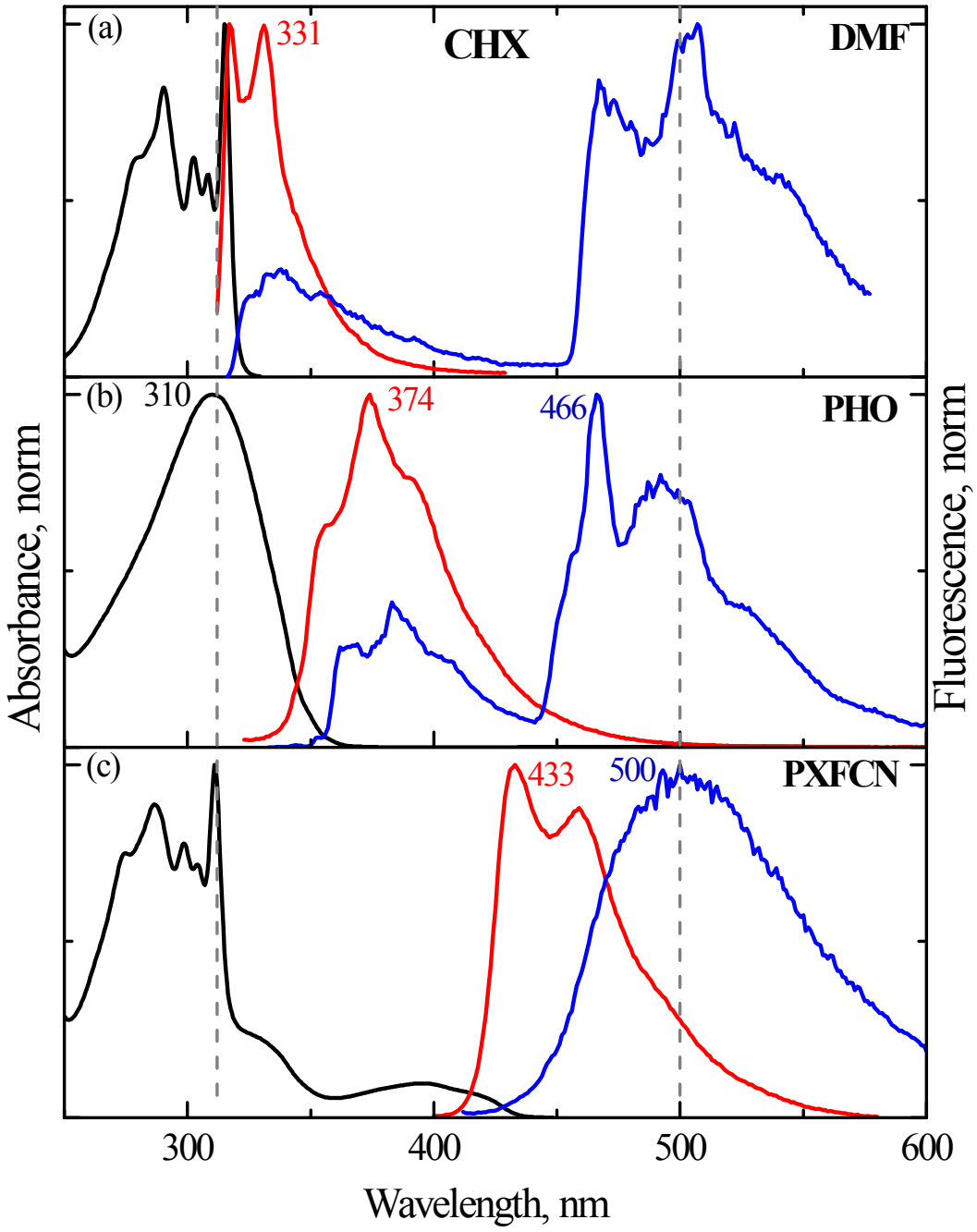

Figure S1 Steady state absorption (black) and emission (red) spectra of DMF (a), PHO (b) and **PXFCN** (c) in CHX at room temperature. The emission spectra measured at 77 K are provided in blue colour.

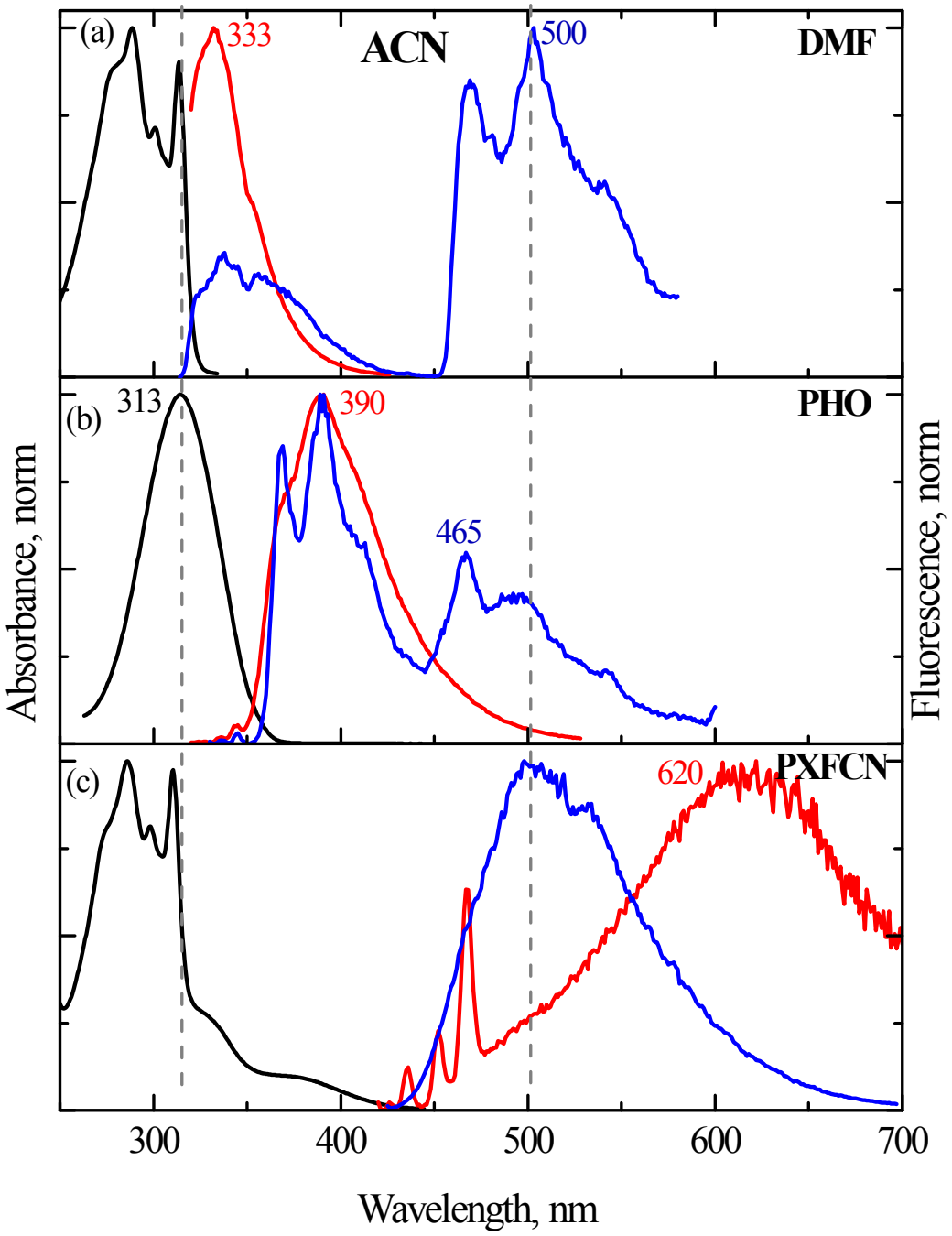

Figure S2 Steady state absorption (black) and emission (red) spectra of DMF (a), PHO (b) and **PXFCN** (c) in ACN at room temperature. The emission spectra measured at 77 K are provided in blue color.

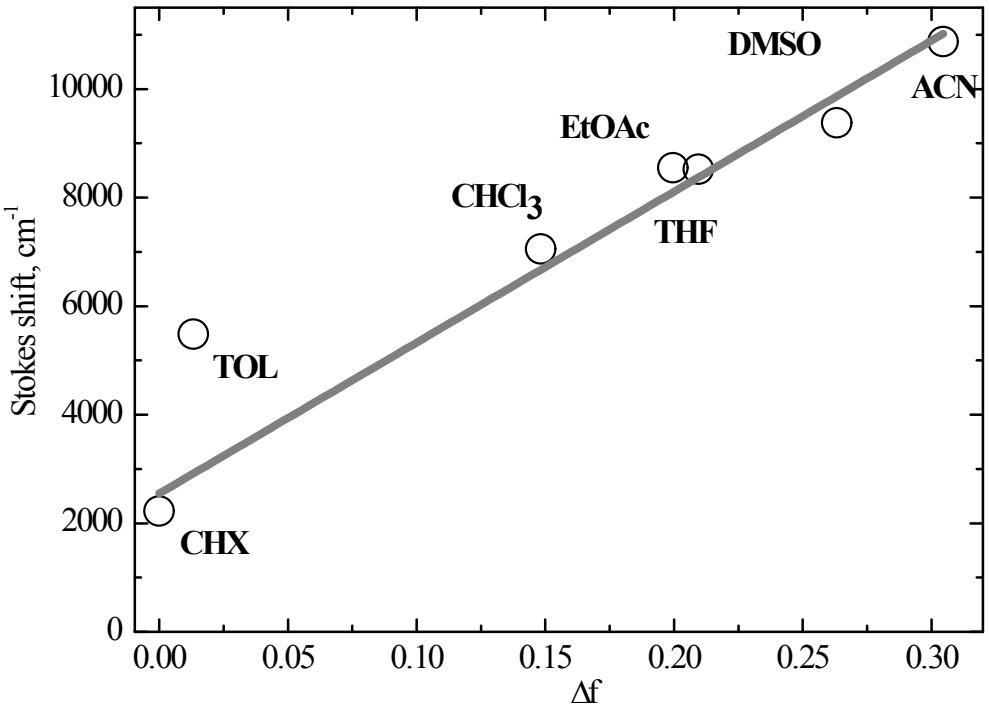

Figure S3 Plot of Stokes shift versus the orientational polarizability (Δf) of **PXFCN** in various solvents.

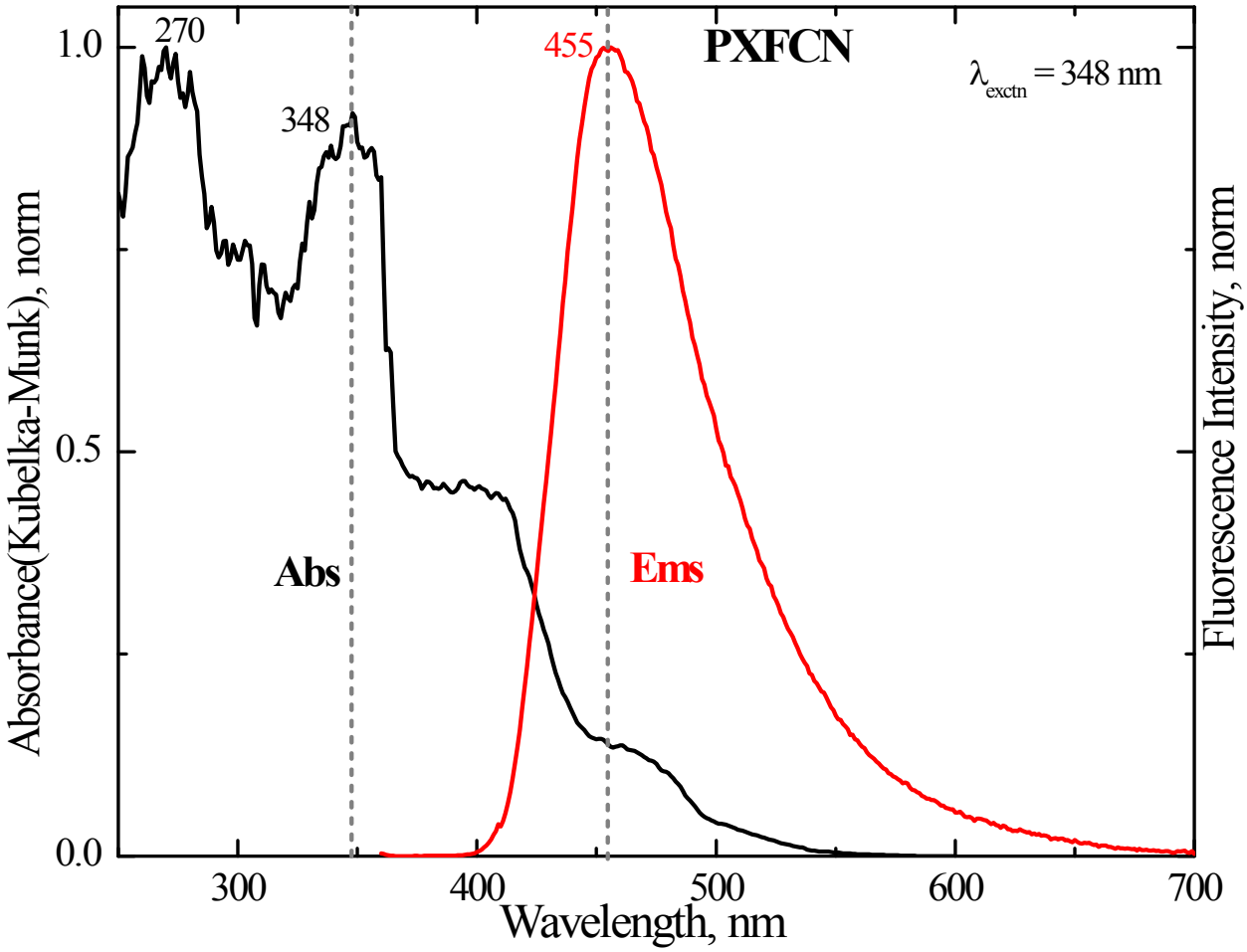

Figure S4 Steady state absorption (black) and emission (red) spectra of **PXFCN** in the solid state.

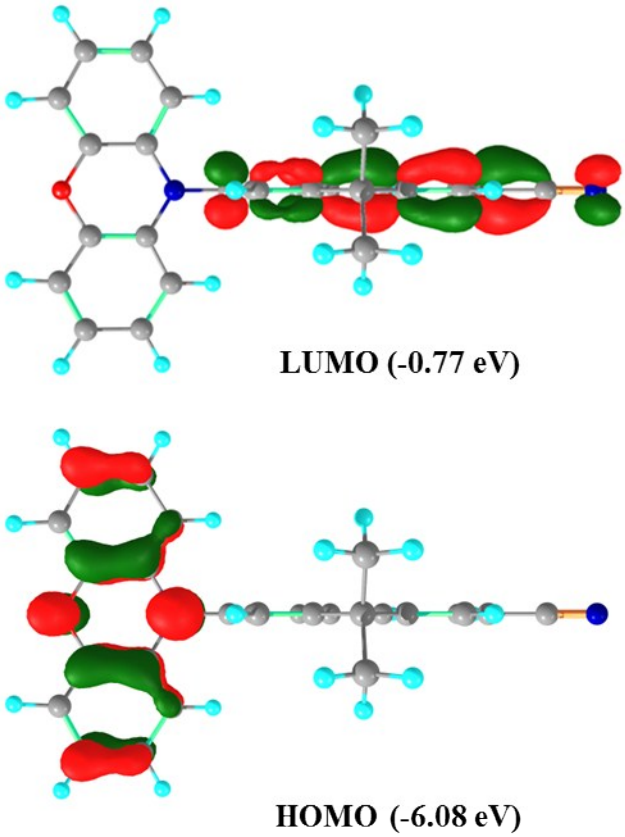

Figure S5 Frontier molecular orbitals of **PXFCN** with the corresponding energy level.

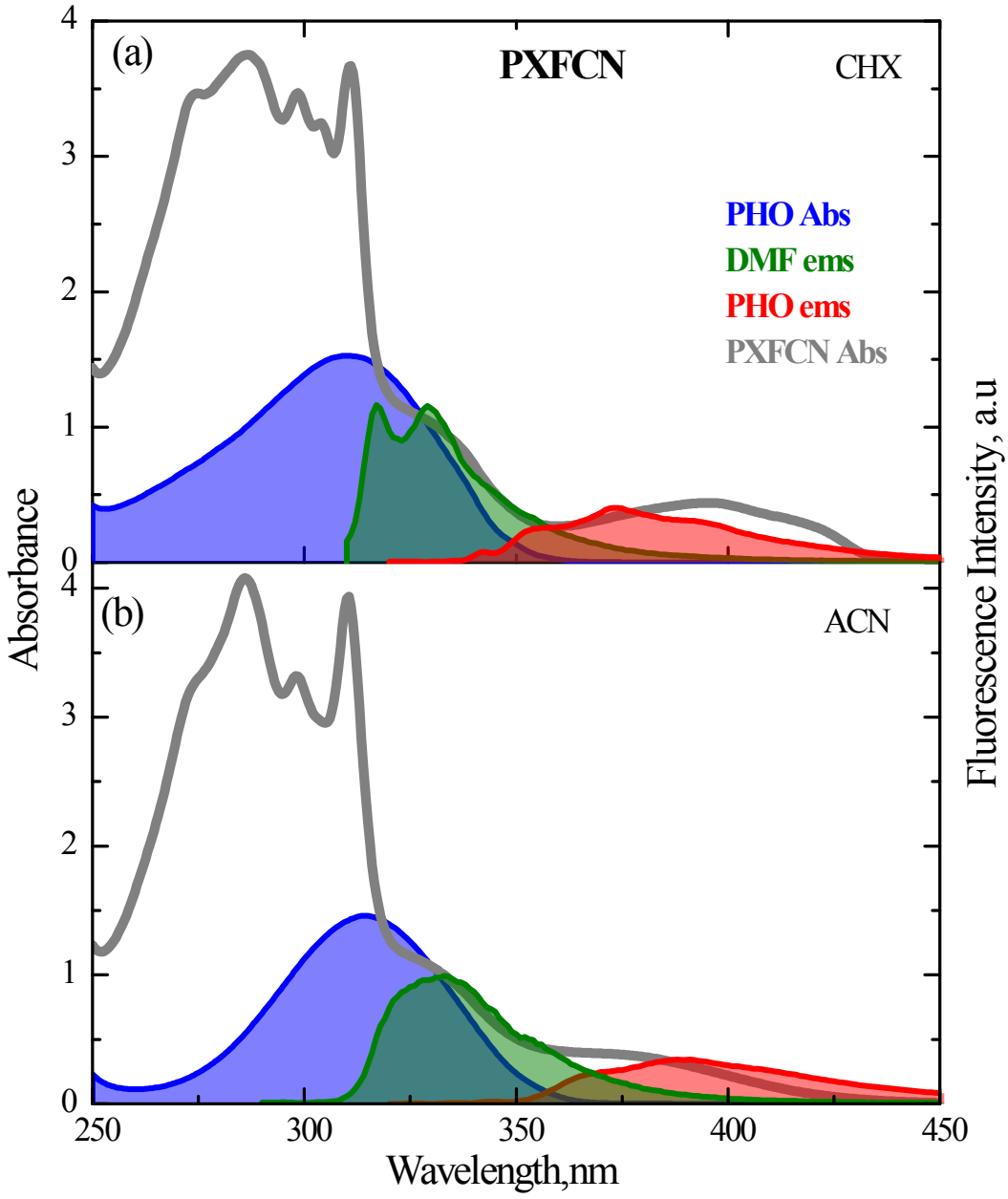

Figure S6 Absorption spectra of PHO (blue) and **PXFCN** (grey) and emission spectra of DMF (green) and PHO (red) in CHX (a) and ACN (b) are compared to show the overlap region. The spectra are normalized arbitrarily for clarity.

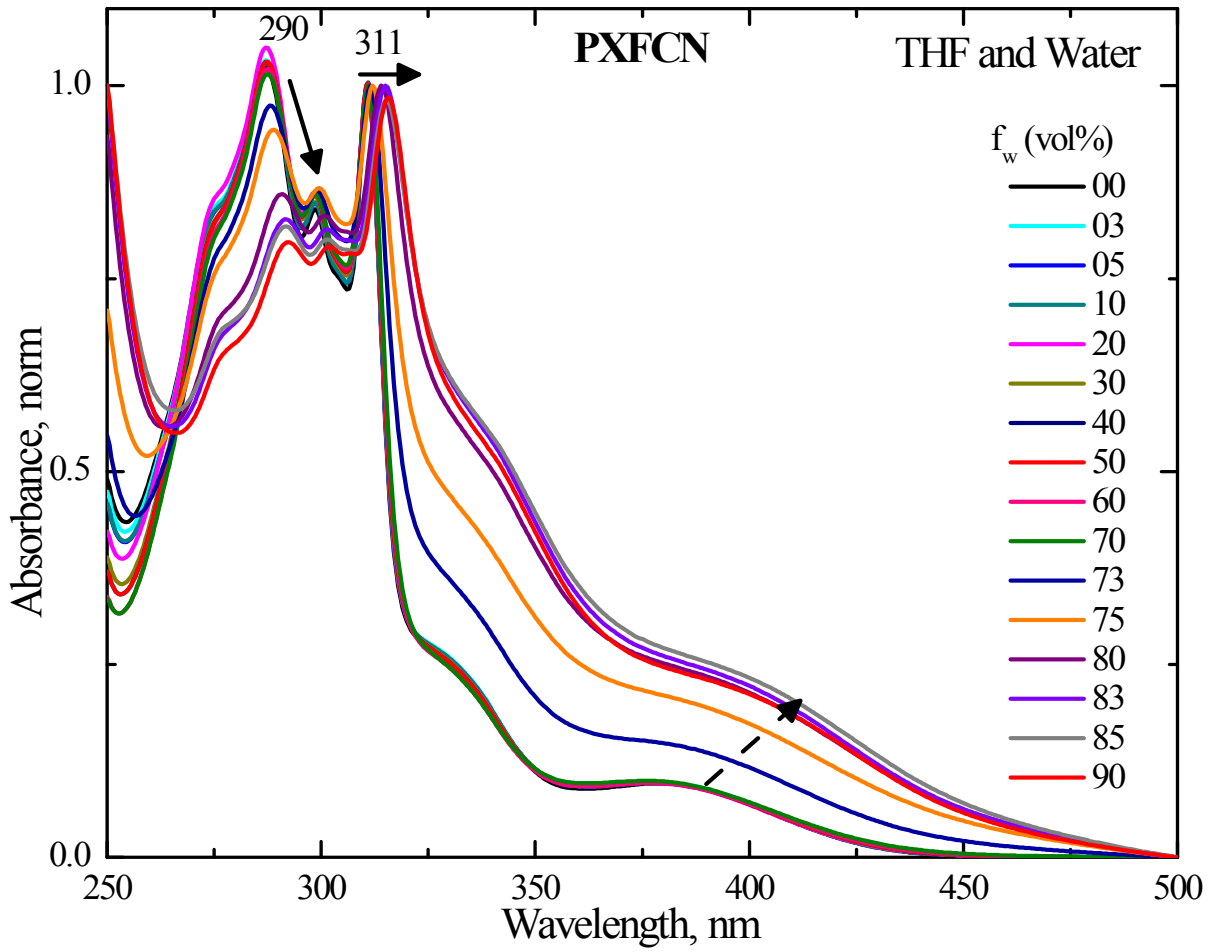

Figure S7 Absorption spectra of **PXFCN** in THF and water mixtures with increase of water fractions (f_w).

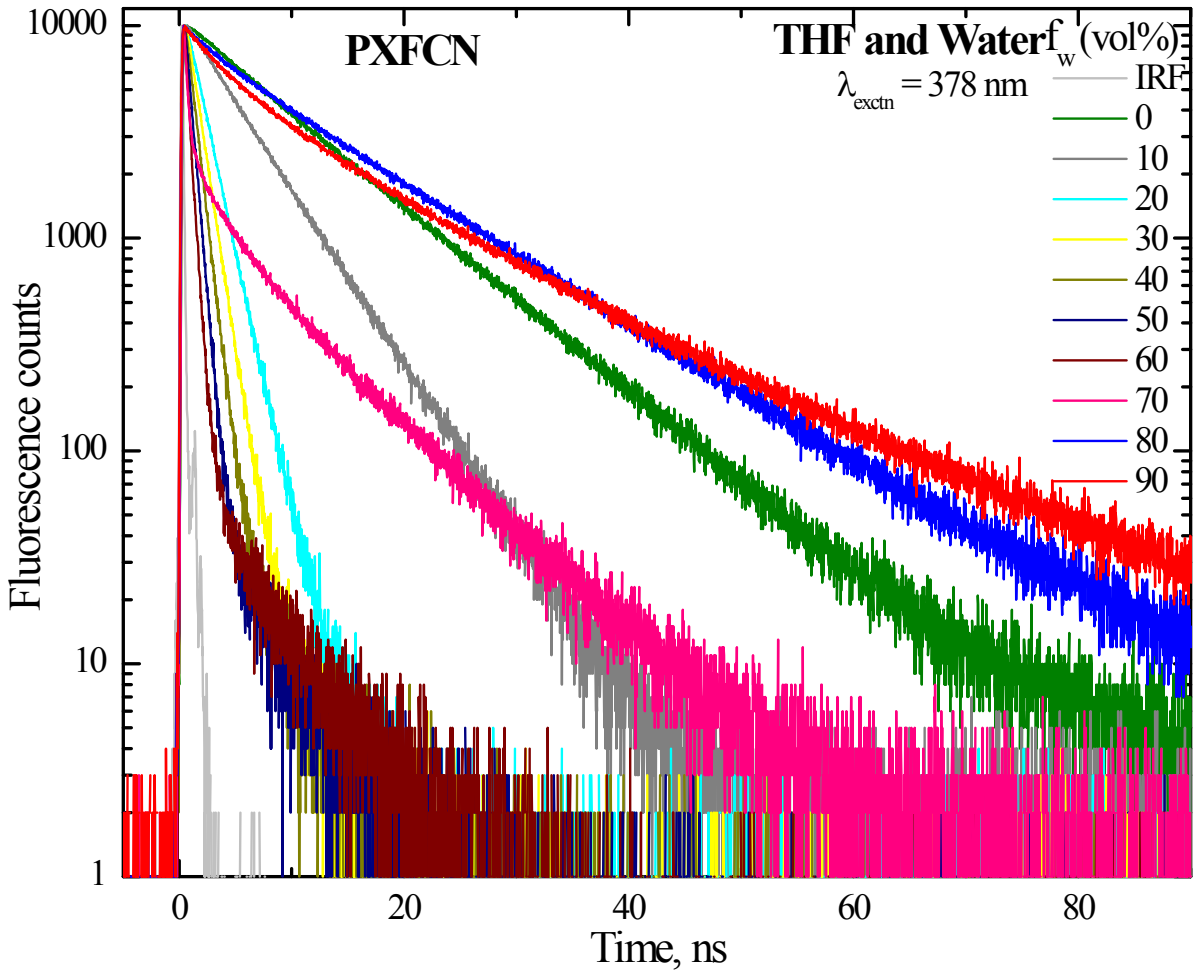

Figure S8 Fluorescence decay profiles of **PXFCN** in THF and water mixtures with different water fractions, f_w (vol%) obtained by exciting at 378 nm.

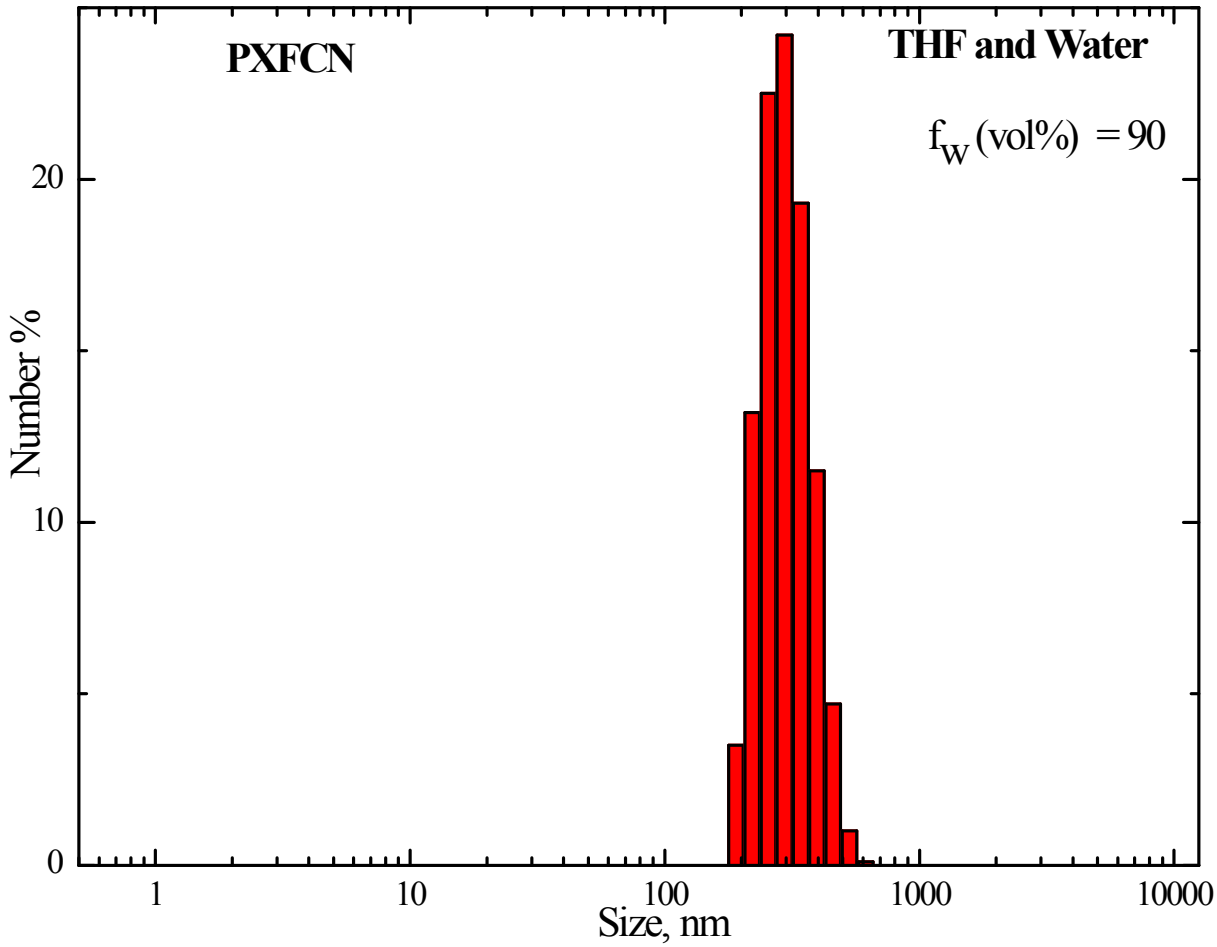

Figure S9 Dynamic light scattering of **PXFCN** in THF and water mixture at f_w 90%.

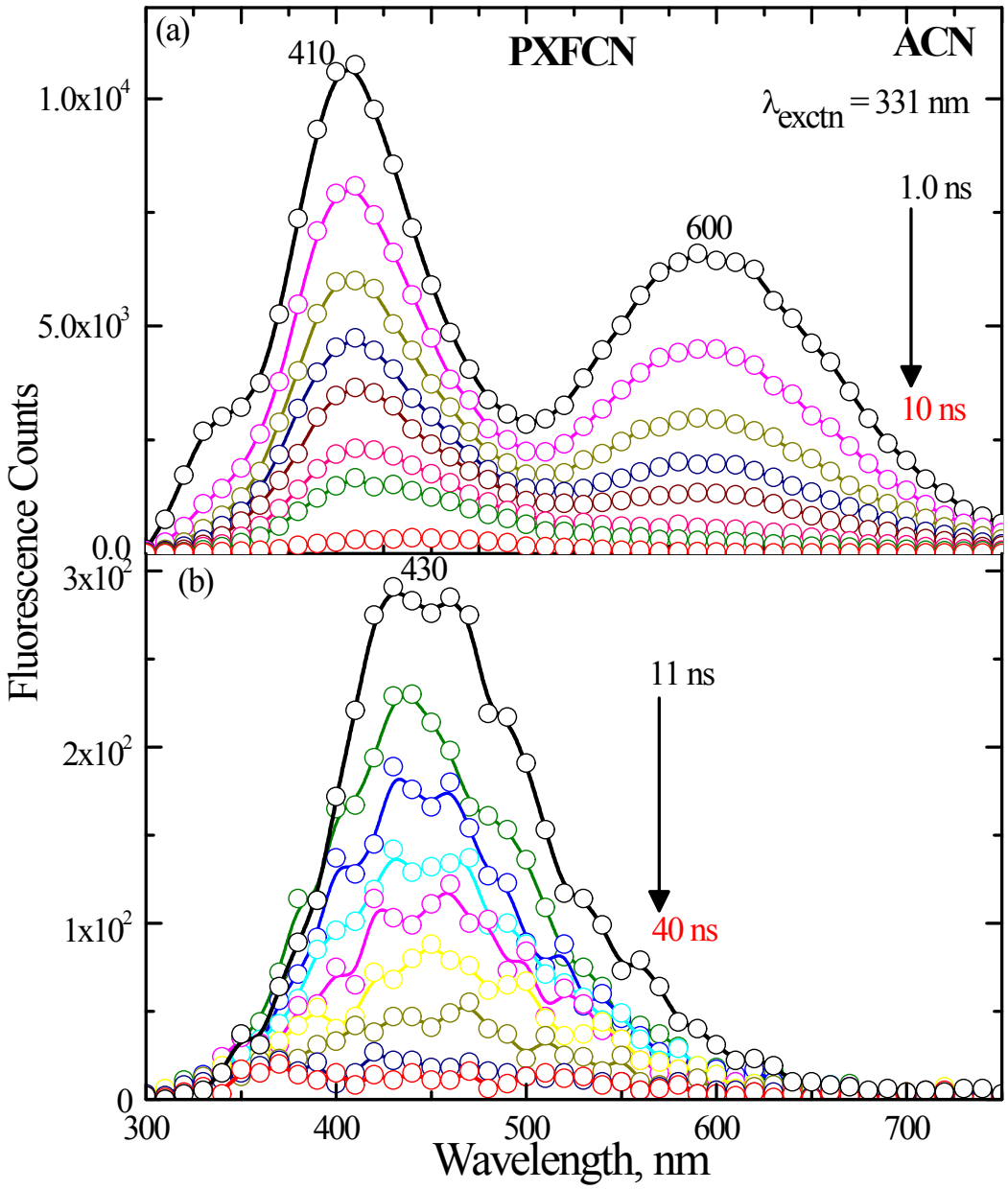

Figure S10 Time-resolved emission spectra of **PXFCN** in ACN obtained by exciting at 331 nm shown for spectral delay time from 1 to 10 (a) and 11 to 40 ns (b). Spline function is used along with the experimental data.

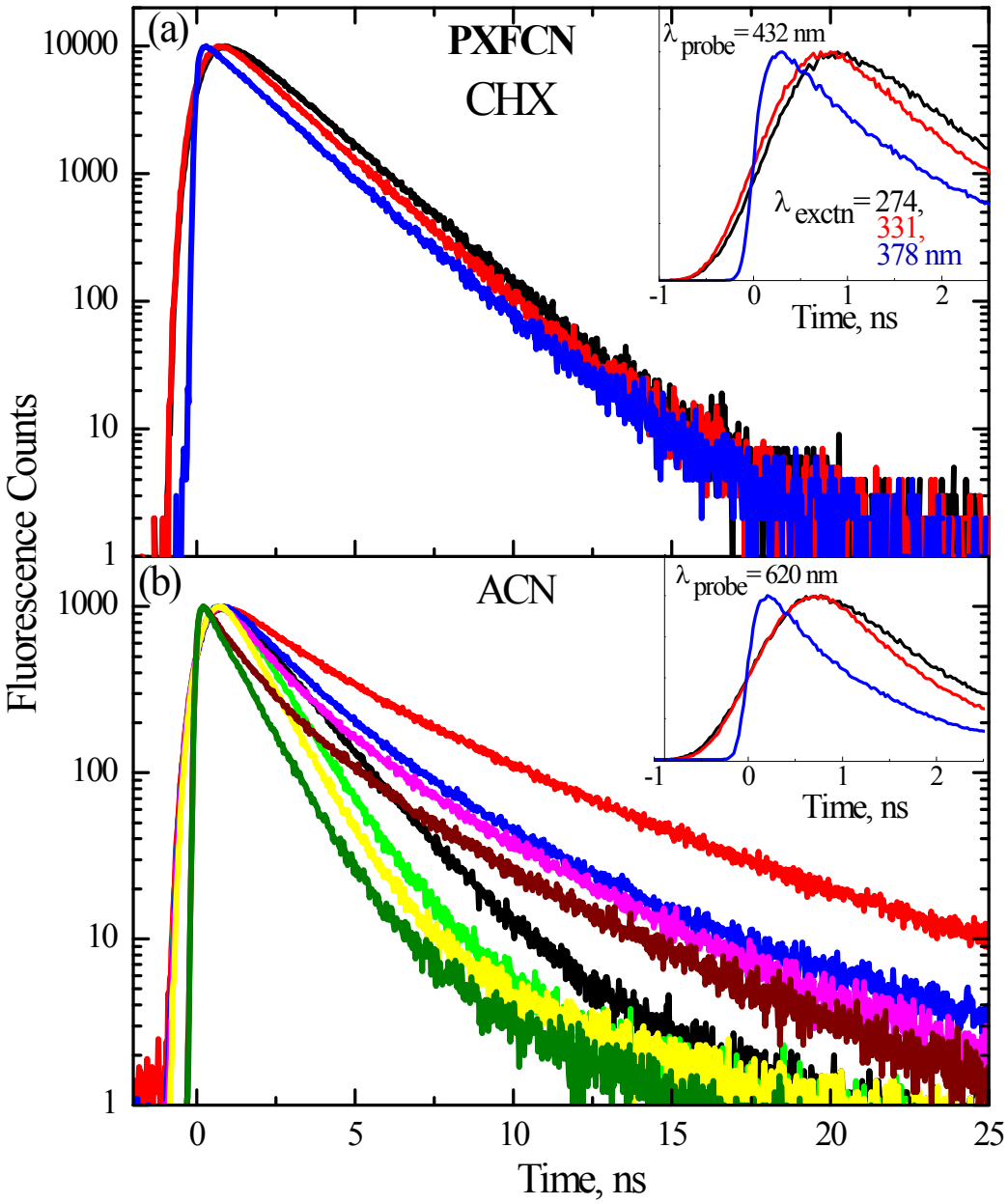

Figure S11 Fluorescence dynamics of **PXFCN** in CHX (a) probed at 432 nm and ACN (b) probed at 330, 405, 450 and 620 nm obtained by exciting at 274, 331 and 378 nm. The insets show the kinetics starting from −1.0 ns to 2.5 ns to explicitly represent the growth of the signal obtained by 274 and 331 nm the excitation wavelengths.

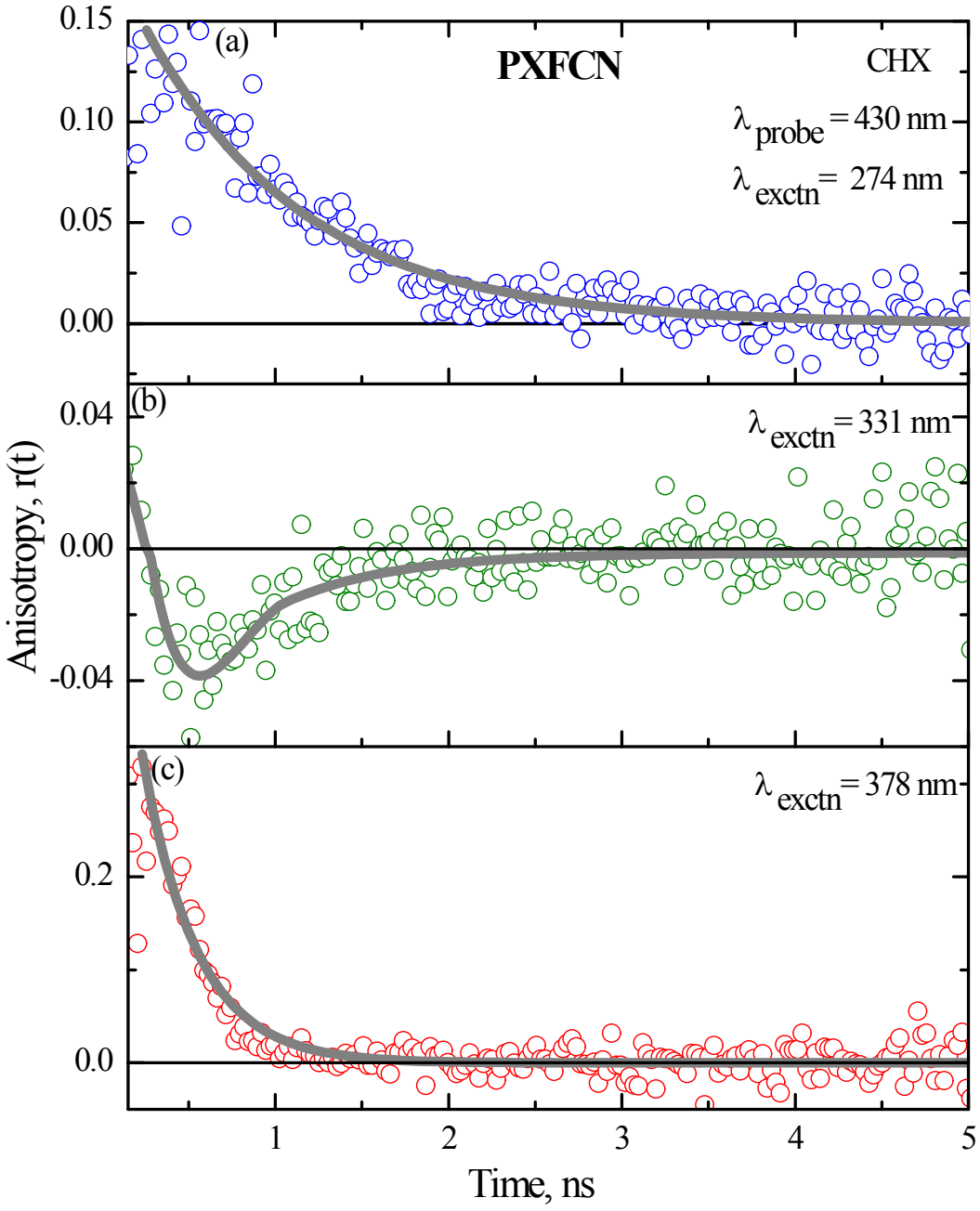

Figure S12 Fluorescence anisotropy decay of **PXFCN** in CHX probed at 430 nm by exciting at 274 (a), 330 (b) and 378 (c) nm.

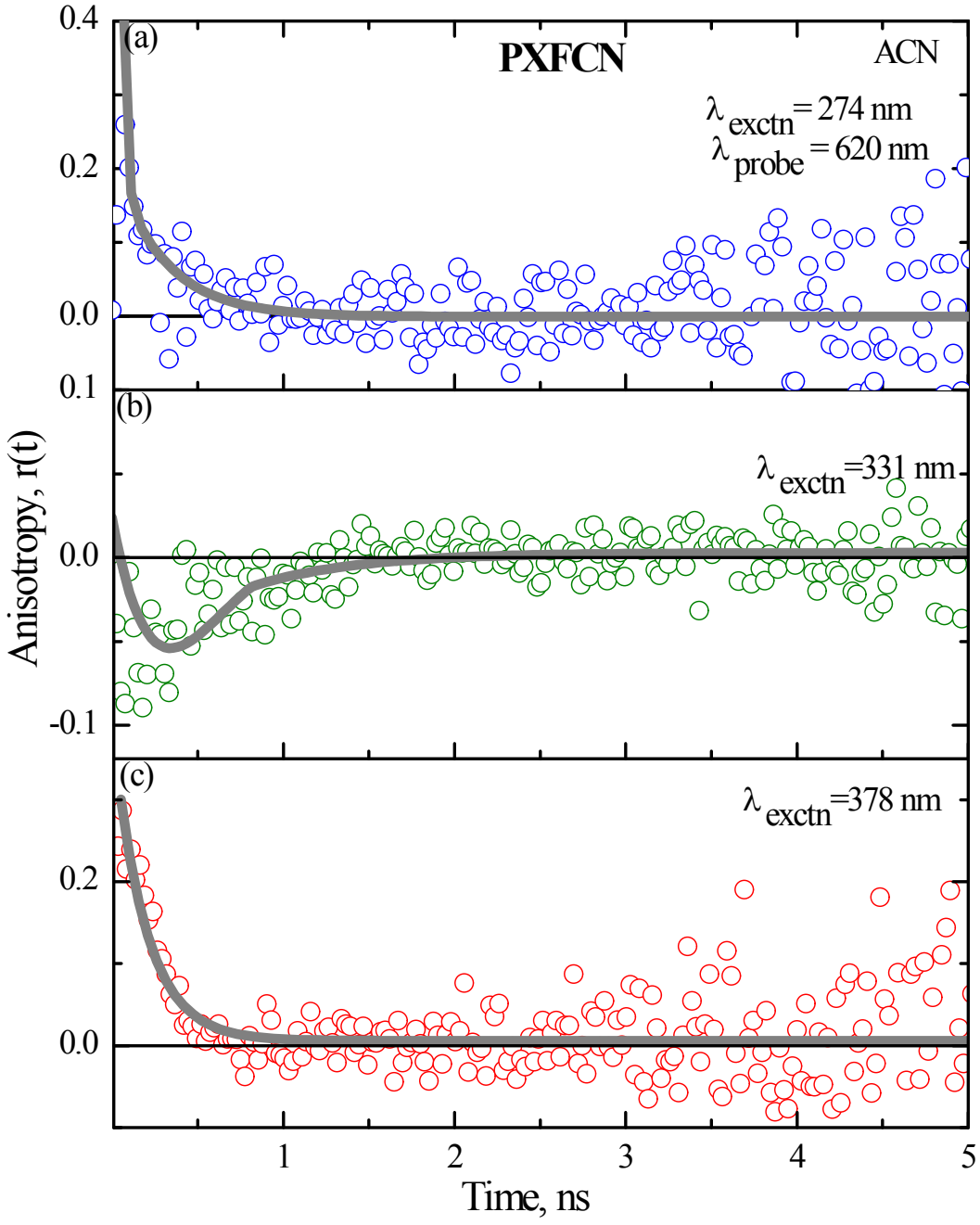

Figure S13 Fluorescence anisotropy decay of **PXFCN** in ACN probed at 620 nm by exciting at 274 (a), 330 (b) and 378 (c) nm.

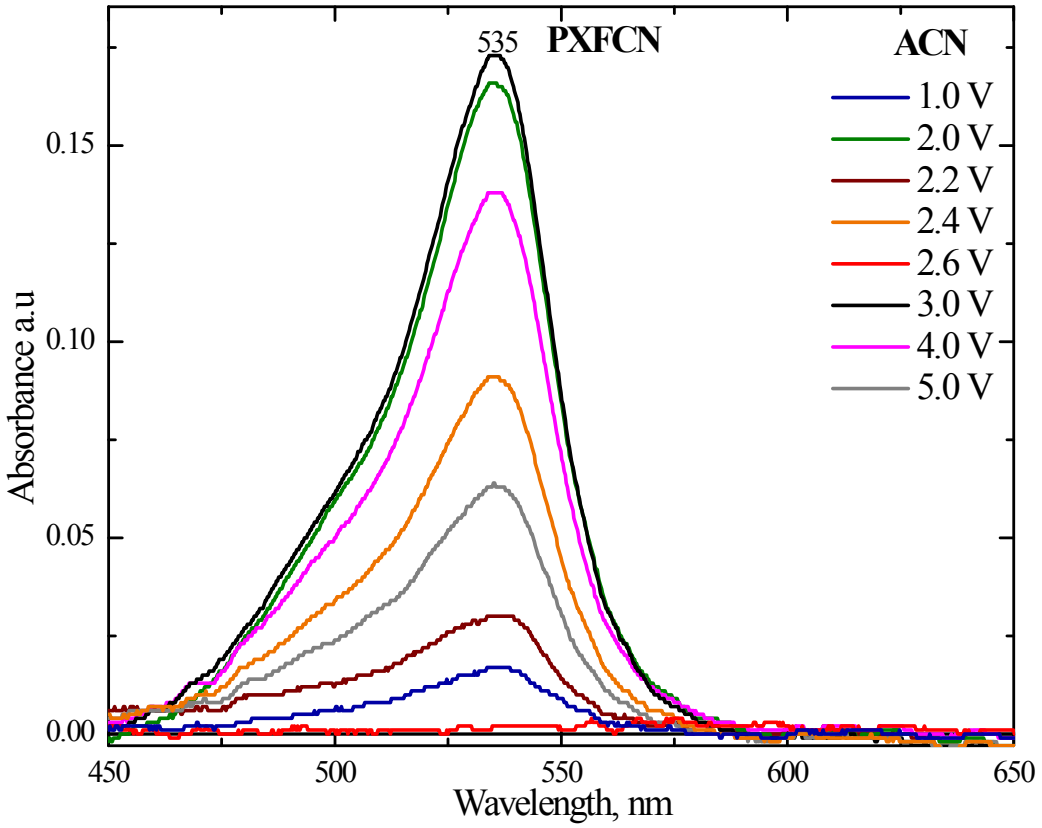

Figure S14 Spectroelectrochemical spectra of **PXFCN** in ACN upon stepwise increase of the potential from 1.0 to 5.0 volts.

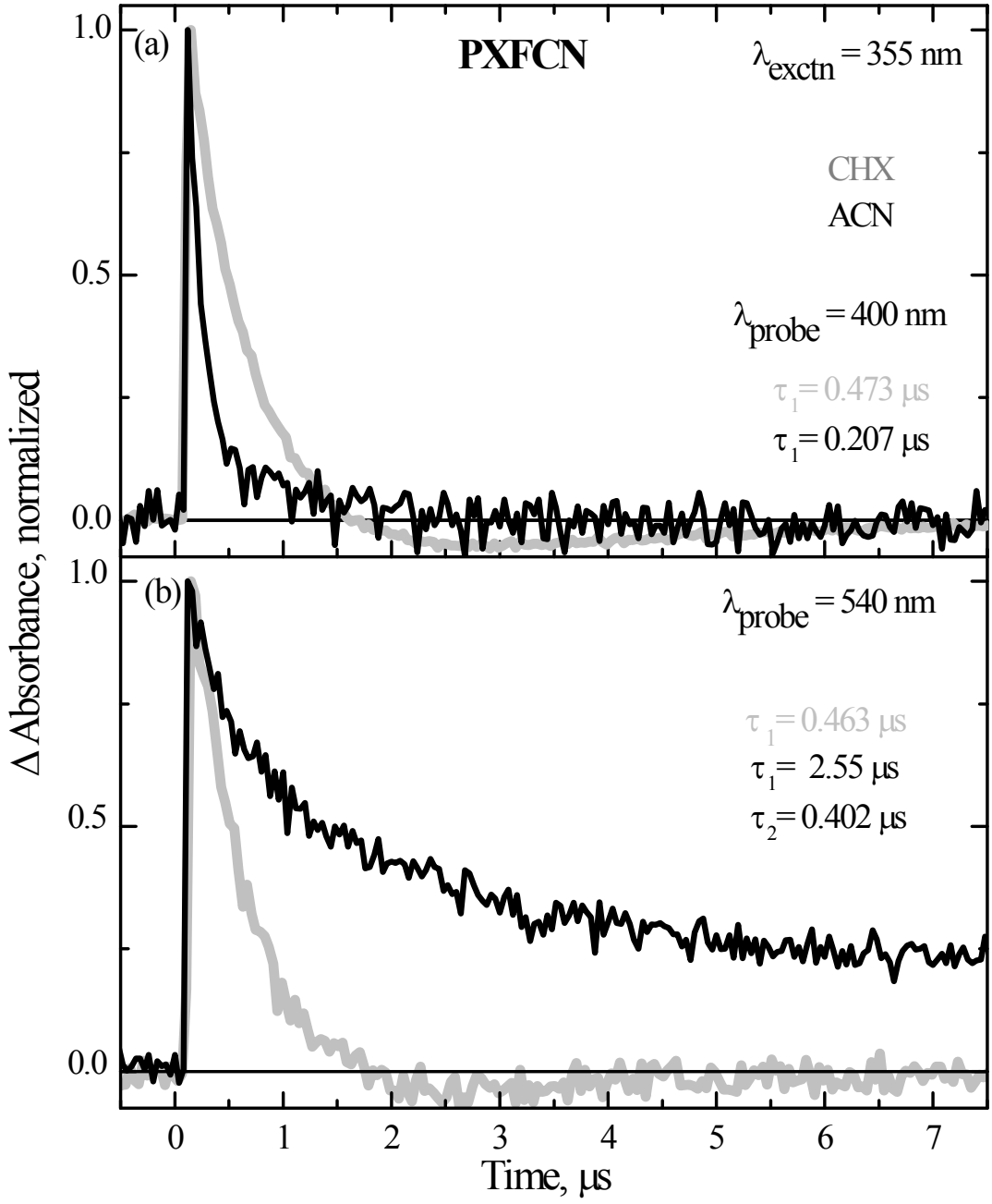

Figure S15. Transient kinetic decays of **PXFCN** at 400 (a) and 540 (b) nm obtained by exciting at 355 nm using laser flash photolysis in argon saturated CHX (grey) and ACN (black).

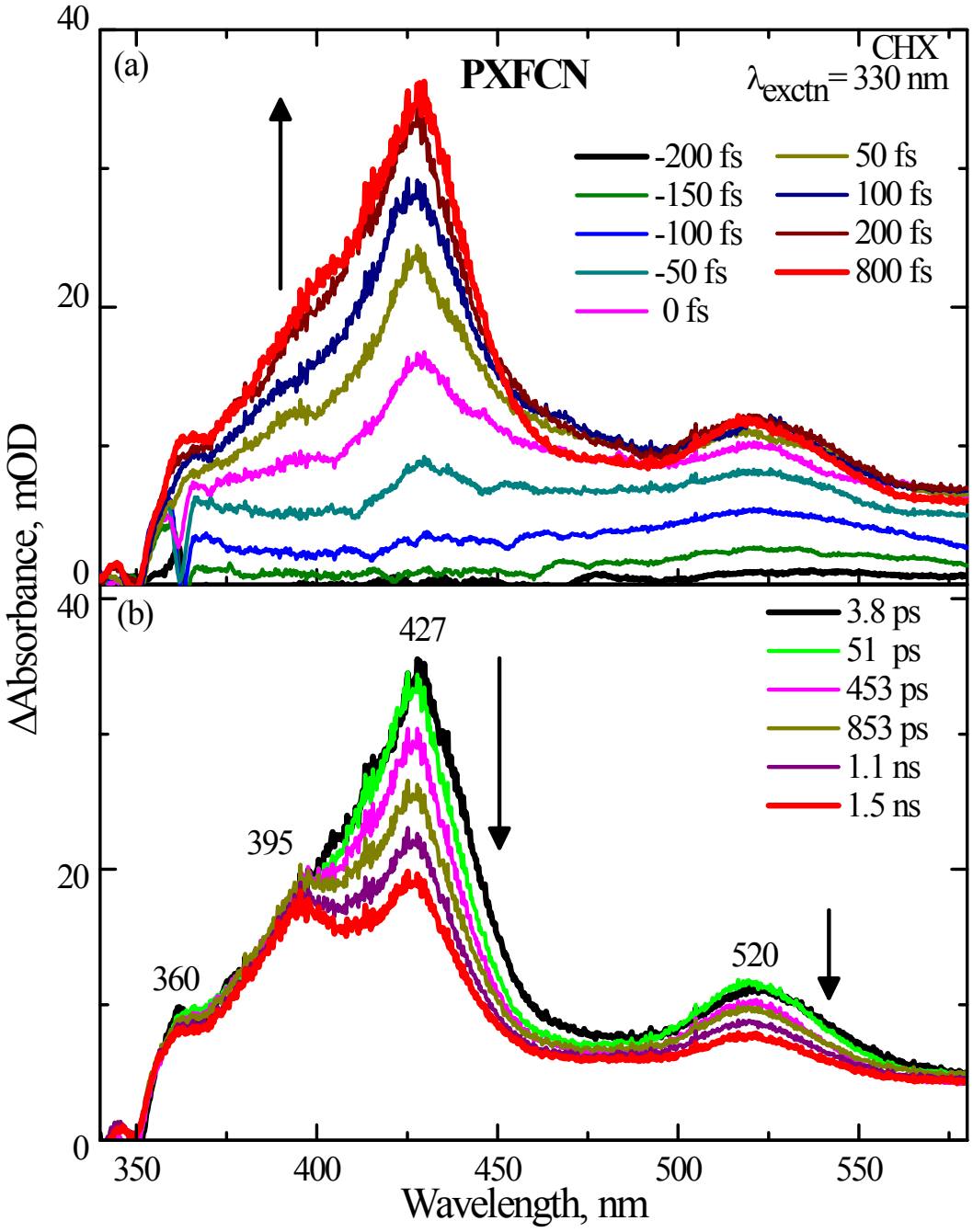

Figure S16 Femtosecond time-resolved transient absorption spectra of **PXFCN** in CHX upon excitation at 330 nm shown at different time delays. The arrows show the direction of the spectral evolution.

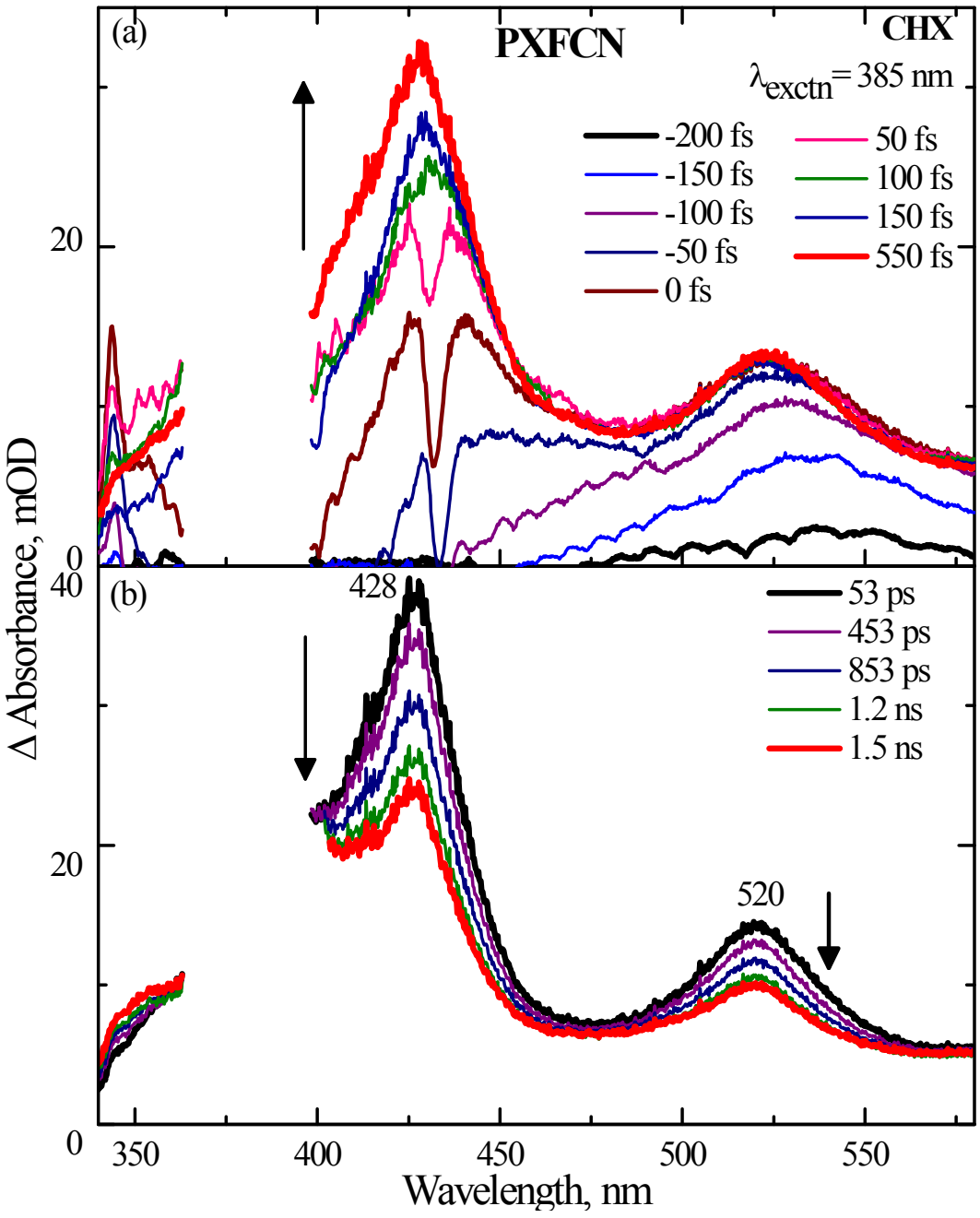

Figure S17 Femtosecond time-resolved transient absorption spectra of **PXFCN** in CHX upon excitation at 385 nm shown at different time delays. The arrows show the direction of the spectral evolution.

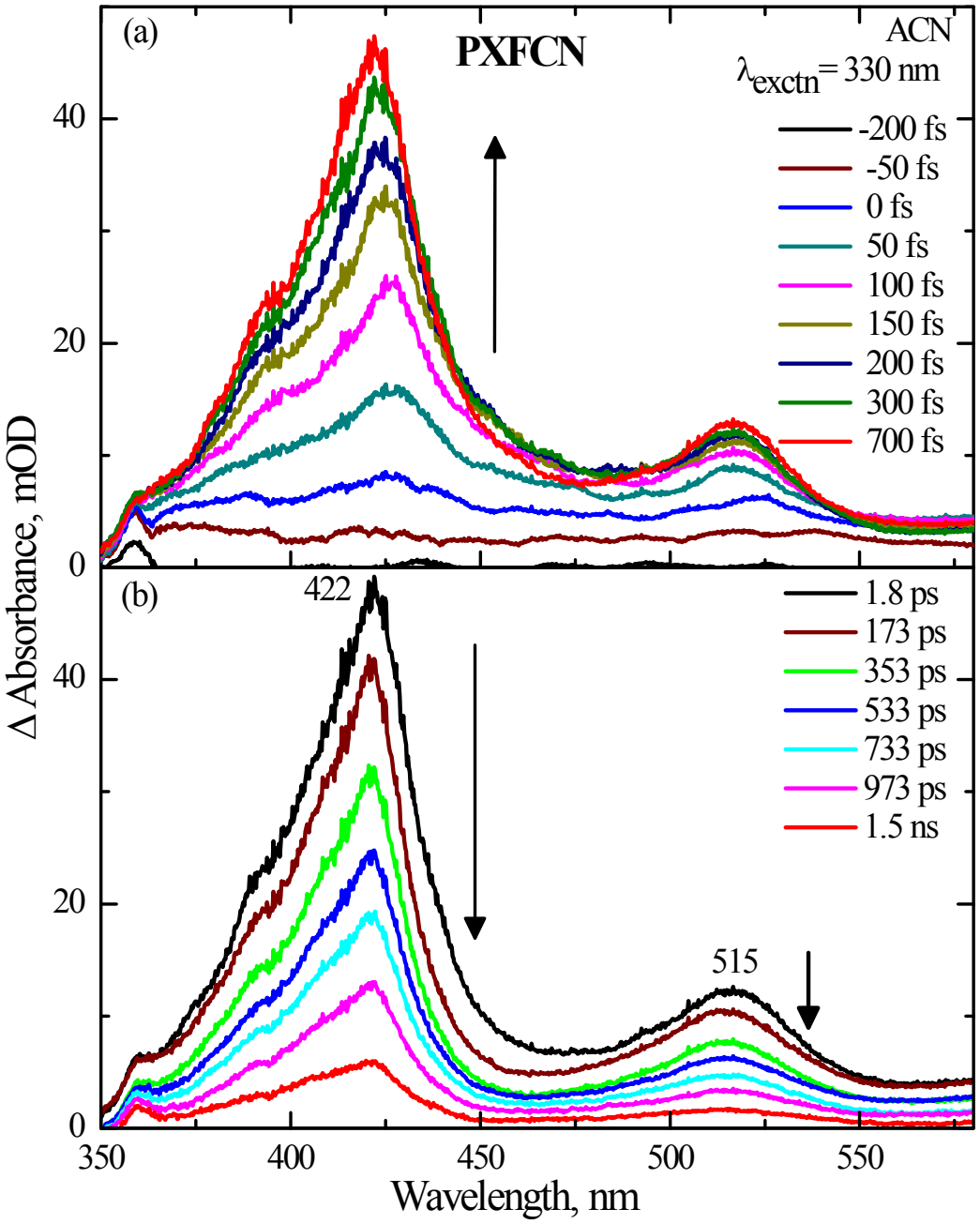

Figure S18 Femtosecond time-resolved transient absorption spectra of **PXFCN** in ACN upon excitation at 330 nm shown at different time delays. The arrows show the direction of the spectral evolution.

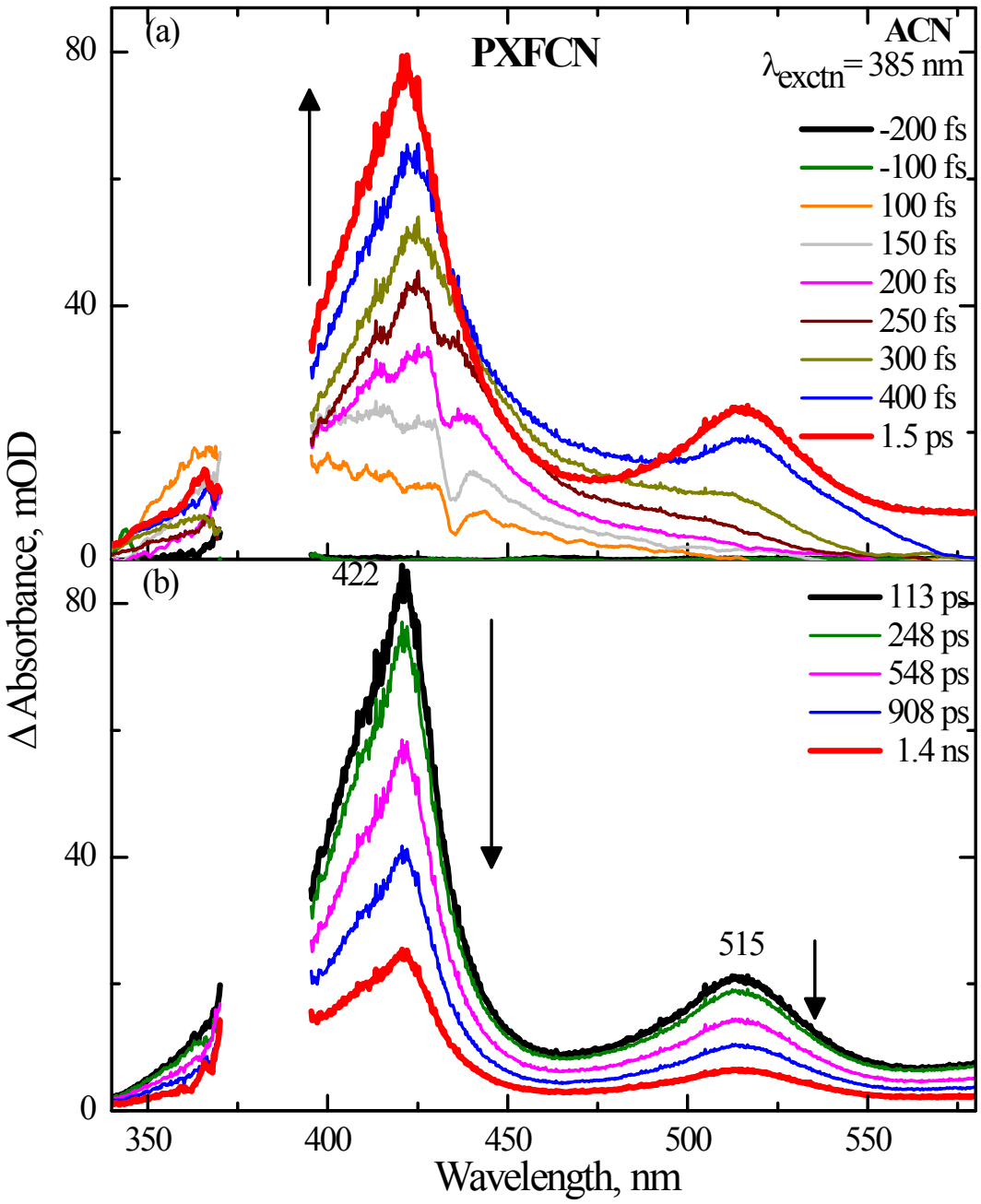

Figure S19 Femtosecond time-resolved transient absorption spectra of **PXFCN** in ACN upon excitation at 385 nm shown at different time delays. The arrows show the direction of the spectral evolution.

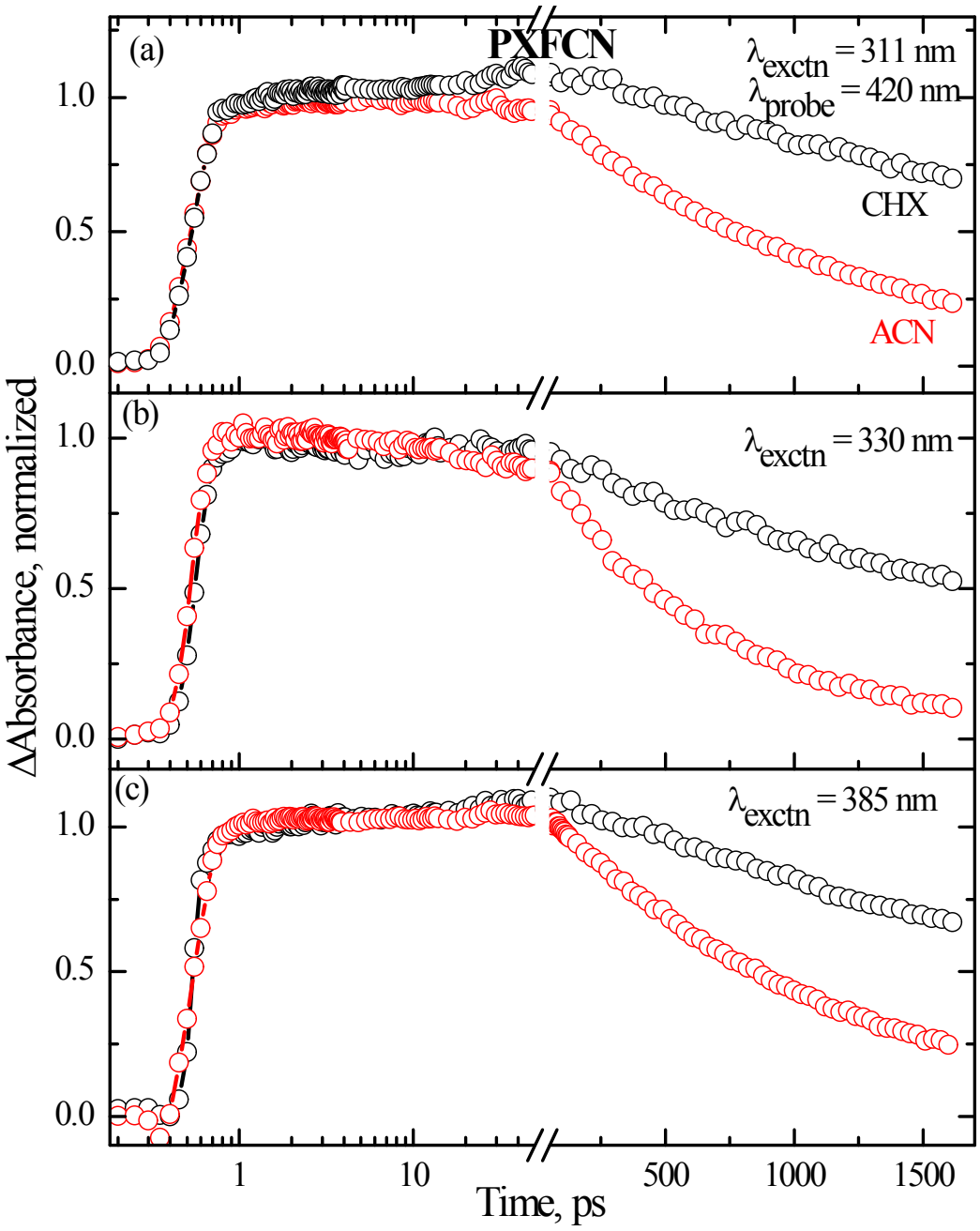

Figure S20 Femtosecond time resolved decay profiles of **PXFCN** probing at 420 nm in CHX (black) and ACN (red) obtained by various excitation 311(a), 330 (b) and 385 (c) nm

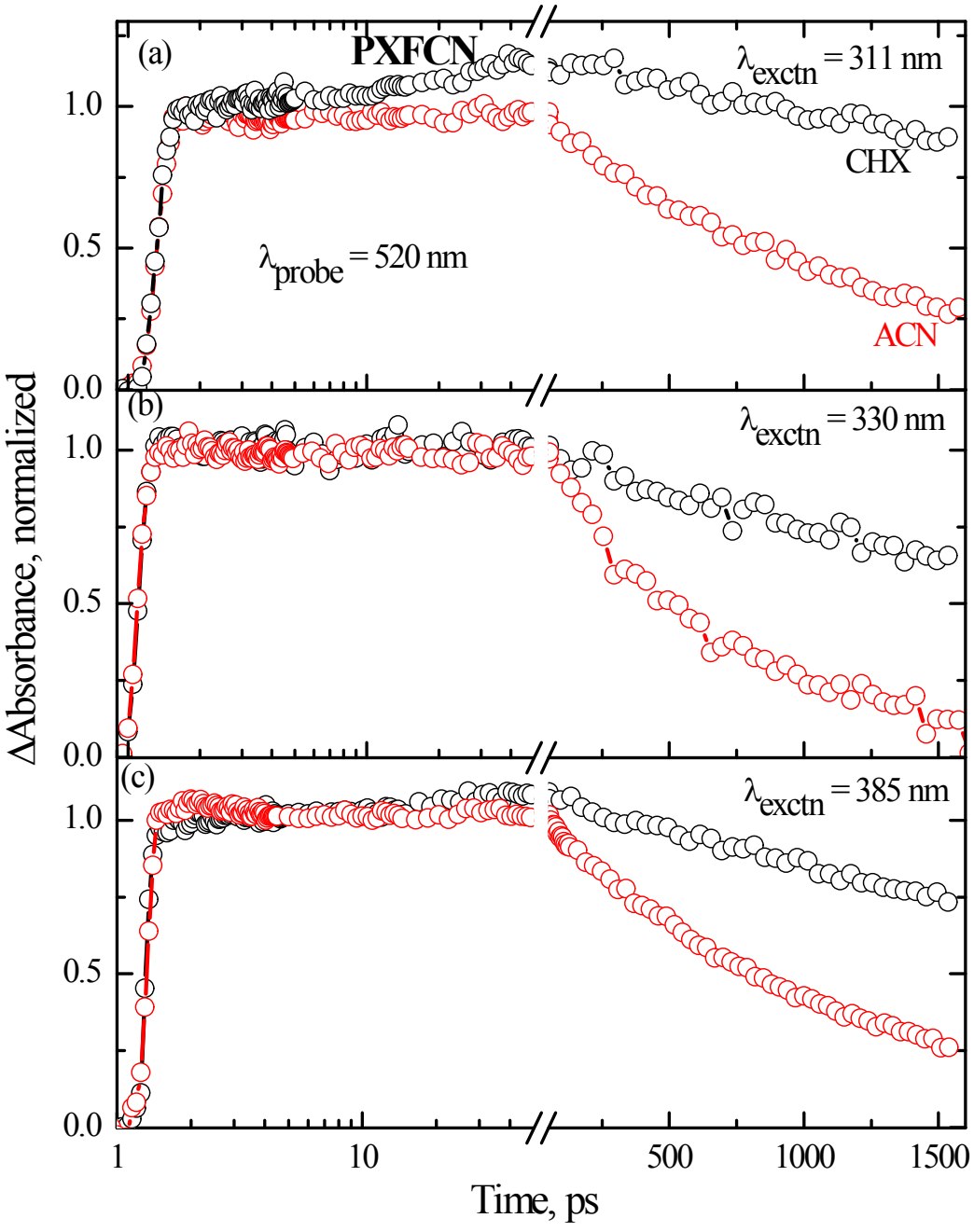

Figure S21 Femtosecond time resolved decay profiles of **PXFCN** probing at 520 nm in CHX (black) and ACN (red) obtained by various excitation 311(a), 330 (b) and 385 (c) nm

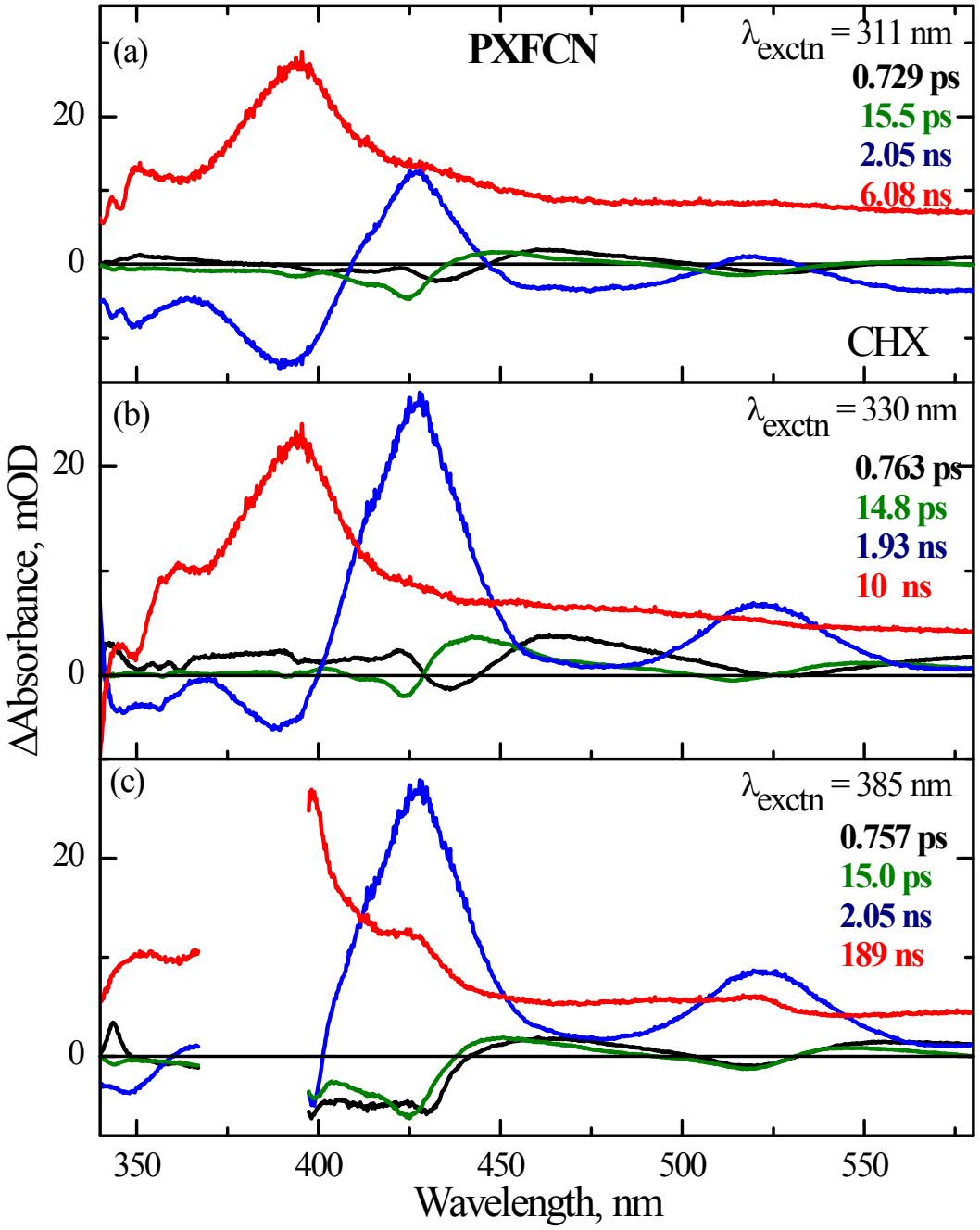

Figure S22 Decay associated spectra of **PXFCN** in CHX obtained by using global analysis for different excitation wavelengths.

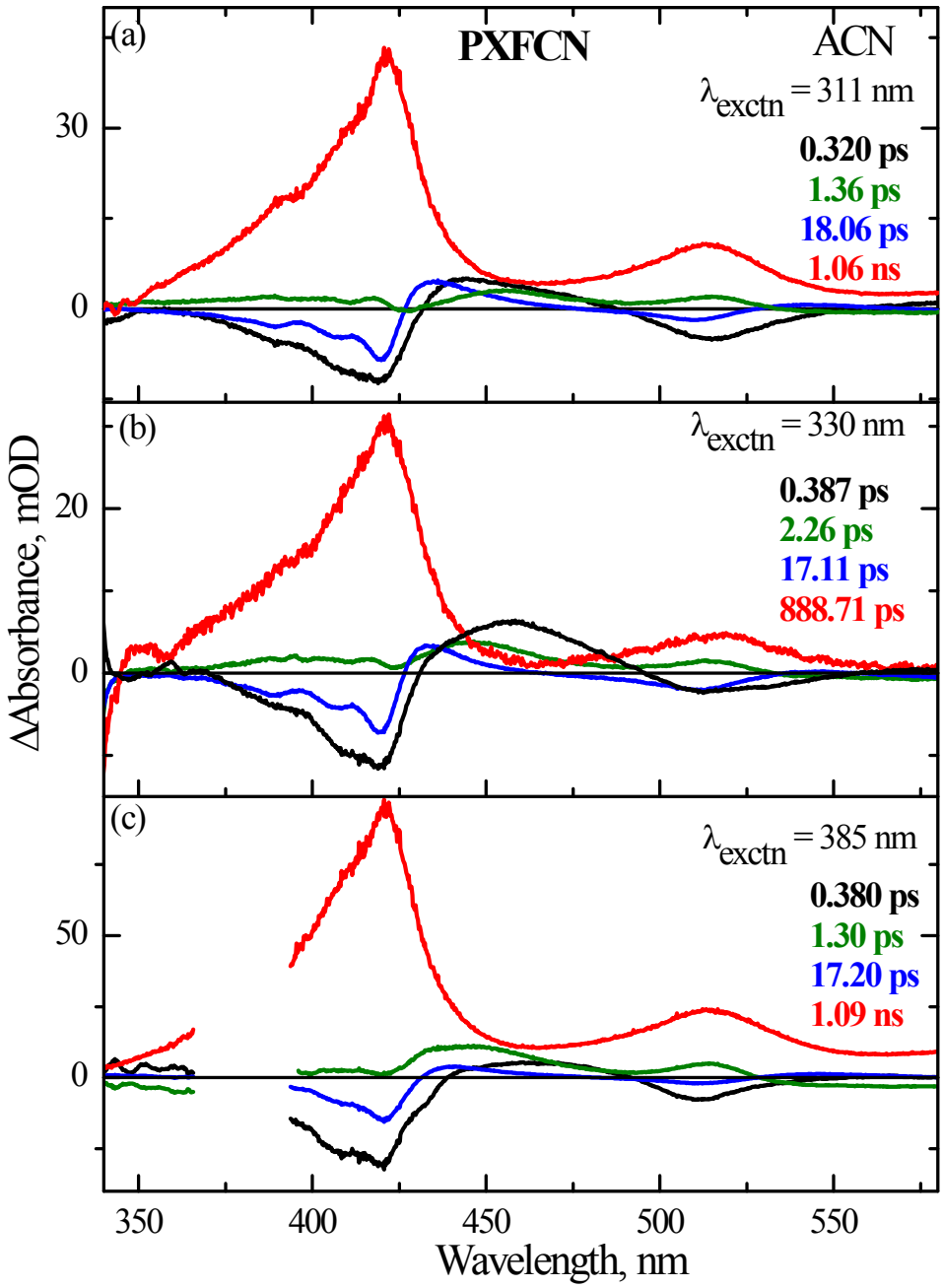

Figure S23 Decay associated spectra of **PXFCN** in ACN obtained by using global analysis for different excitation wavelengths.

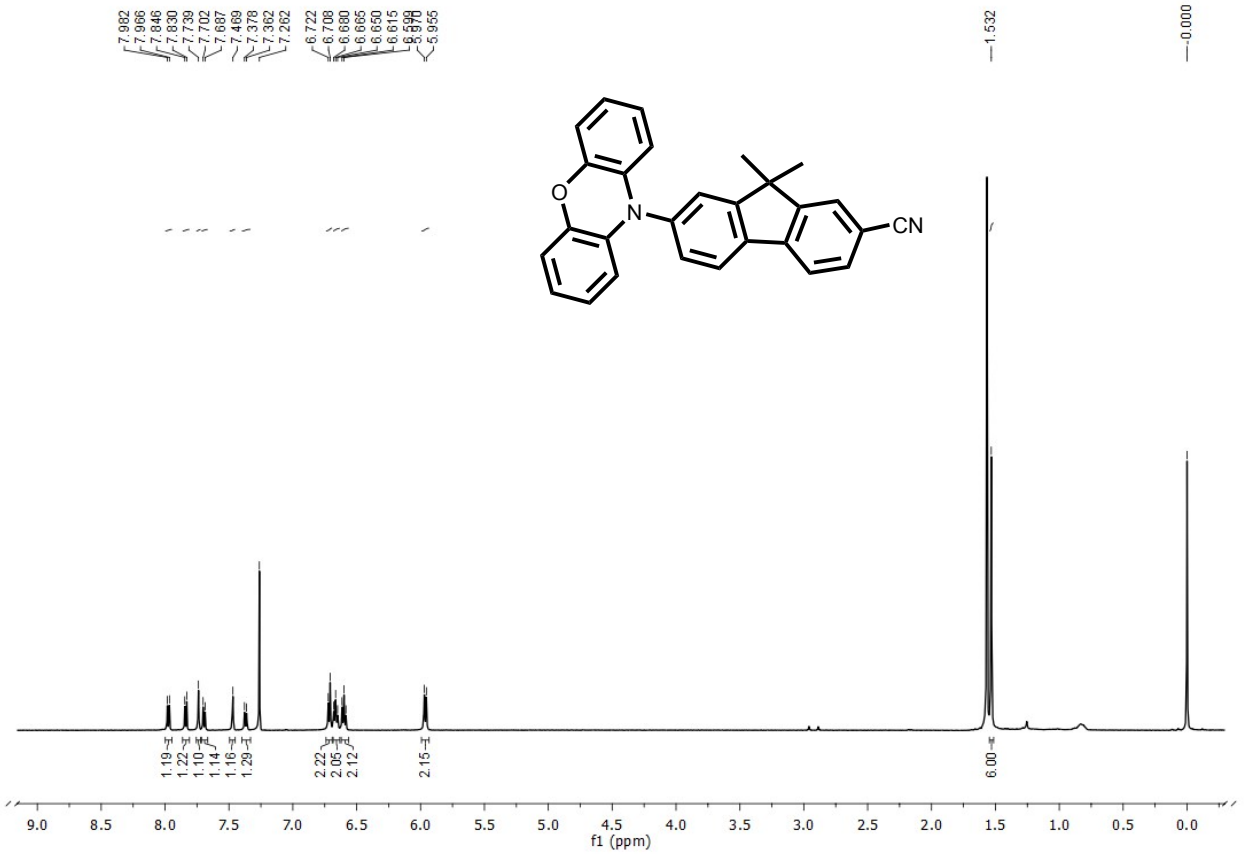

Figure S24 ^{1}H NMR spectra of 2-cyano-7-phenoxazine -9,9-dimethyl-9*H*-fluorene (**PXFCN**) in $CDCl_3$.

Table S1 Results of CAM B3LYP/6-31G(d) calculations for **PXFCN** in gaseous medium.

Medium	**Energy (eV)**	**λ_{max}[a] (nm)**	**f_{os}**	**Main transitions (weight)**	**μ_g (Debye)**	**μ_e (Debye)**
Gaseous	3.2	208.71	0.88	HOMO-1 → LUMO+3 (0.41) HOMO-1 → LUMO+2 (0.36)	2.69	22.80
		274.13	0.80	HOMO-2 → LUMO (0.65)		
		309.84	0.01	HOMO → LUMO+2 (0.43) HOMO → LUMO+3 (0.43)		
		354.96	0.00	HOMO → LUMO (0.65)		

[a]λ_{max} value obtained from the simulated absorption spectrum.

Table S2 Electrochemical data of DMF, PHO and **PXFCN** from Cyclic Voltammetry in acetonitrile.

Compound	**E_{oxd} (V)**	**E_{red} (V)**	**E_{HOMO} (eV)**	**E_{LUMO}(eV)**
DMF	1.20	-0.75	-5.56	-1.76
PHO	0.68	-0.54	-5.04	-1.65
PXFCN	0.70	-1.16	-5.08	-2.07

Table S3 Fluorescence lifetime obtained for **PXFCN** in different THF water mixtures obtained by excitation 378 nm (pulse duration < 100 ps).

Water fraction f_w (vol%)	λ_{max}, nm	Time constants τ_1, ns	A_1, %	τ_2, ns	A_2, %	χ^2
0	550	9.84	100	-	-	1.17
3	565	7.04	100	-	-	1.16
5	575	5.22	100	-	-	1.09
10	585	3.14	100	-	-	0.81
20	587	1.77	100	-	-	1.09
30	595	1.25	100	-	-	1.01
40	599	0.86	96.44	3.22	3.56	1.03
50	602	0.65	96.76	4.12	3.24	1.09
60	614	0.42	93.67	4.29	6.33	1.08
70	614	2.13	26.94	8.31	73.06	0.99
73	557	4.33	9.92	10.28	90.08	1.08
75	554	4.22	6.41	11.09	93.59	1.11
80	549	3.01	5.62	13.03	94.38	1.06
83	542	3.59	9.65	14.94	90.35	1.06
85	538	3.56	11.07	15.14	88.93	1.09
90	520	4.07	18.61	14.84	81.39	1.11

Table S4 Fluorescence lifetime of **DMF** and **PHO** in ACN and CHX

Sample	Solvent	λ_{exctn} /$\lambda_{ems,}$ nm	$\tau_{1,}$ ns	$A_{1,}$ %	$\tau_{2,}$ ns	$A_{2,}$ %
DMF	CHX	270/317	0.96	95.4	2.19	4.60
	ACN	270/333	0.68	88.6	2.39	11.40
PHO	CHX	270/373	0.97	69.49	1.58	30.51
	ACN	270/390	6.80	68.64	2.85	31.36

Table S5 Absolute and relative fluorescence quantum yield and standards used for **PXFCN** in different solvents.

Solvent	**Relative QY**	**Fluorescence Standards**	**Absolute QY**
CHX	0.100	C153 CHX(0.90)	0.0436
Toluene	0.169	C153 CHX(0.90)	0.0885
$CHCl_3$	0.178	C153 EtOAc(0.88)	0.1096
THF	0.128	C153 EtOAc (0.88)	0.0800
ACN	0.0073	C153 ACN (0.43)	0.001

Table S6 Bond parameters of **PXFCN** optimized geometry in S_0 state obtained from DFT calculation. [#p b3lyp/6-31g(d) opt freq=noraman scf=(maxcycle=800)]

C	-0.940486000	0.000075000	-2.039674000
C	-1.816998000	0.000019000	-0.951940000
C	-1.324660000	-0.000050000	0.368736000
C	0.044627000	-0.000068000	0.605152000
C	0.926499000	-0.000004000	-0.485594000
C	0.433370000	0.000069000	-1.798132000
H	-1.313864000	0.000121000	-3.060180000
H	0.451422000	-0.000131000	1.612692000
H	1.140141000	0.000111000	-2.622263000
C	-2.467981000	-0.000092000	1.382636000
C	-4.232164000	0.000120000	-1.924847000
C	-3.282292000	0.000018000	-0.899991000
C	-5.584421000	0.000104000	-1.594675000
C	-3.681069000	-0.000068000	0.453288000
C	-5.985697000	-0.000003000	-0.245349000
C	-5.026063000	-0.000082000	0.786915000
H	-6.340520000	0.000157000	-2.373017000
H	-5.356090000	-0.000152000	1.821609000
H	-3.929183000	0.000175000	-2.968116000
C	-2.436582000	1.266290000	2.268391000
H	-2.461242000	2.176015000	1.660210000
H	-3.296720000	1.284032000	2.947121000
H	-1.526977000	1.286368000	2.878951000

C	-2.436517000	-1.266425000	2.268413000
H	-1.526871000	-1.286481000	2.878913000
H	-3.296597000	-1.284167000	2.947221000
H	-2.461212000	-2.176183000	1.660279000
C	-7.381127000	-0.000017000	0.081266000
N	-8.513690000	-0.000030000	0.349047000
C	2.413152000	-2.465177000	-0.206256000
C	3.040155000	-1.217060000	-0.127479000
N	2.339899000	-0.000002000	-0.258967000
C	4.430605000	-1.186703000	0.090799000
O	5.132416000	0.000024000	0.175523000
C	4.430576000	1.186738000	0.090839000
C	3.040125000	1.217069000	-0.127437000
C	3.149481000	-3.646783000	-0.071897000
C	5.161185000	-2.358131000	0.226174000
C	5.161130000	2.358178000	0.226255000
C	2.413090000	2.465172000	-0.206159000
C	3.149391000	3.646790000	-0.071756000
C	4.522606000	3.599776000	0.144752000
H	6.230655000	2.277136000	0.393578000
H	1.343228000	2.511441000	-0.374978000
H	2.634843000	4.601001000	-0.138825000
H	5.100683000	4.512678000	0.250245000
C	4.522693000	-3.599743000	0.144622000

H	1.343291000	-2.511461000	-0.375080000
H	2.634957000	-4.601004000	-0.139007000
H	6.230709000	-2.277072000	0.393504000
H	5.100794000	-4.512633000	0.250079000

Table S7 Bond parameters of **PXFCN** optimized geometry in S_1 state obtained from TD-DFT calculation. [#pCAM-b3lyp/6-31g(d) td=(nstates=30, singlets) geom=connectivity Density=Current]

C	-0.940486000	0.000075000	-2.039674000
C	-1.816998000	0.000019000	-0.951940000
C	-1.324660000	-0.000050000	0.368736000
C	0.044627000	-0.000068000	0.605152000
6	0.926499000	-0.000004000	-0.485594000
6	0.433370000	0.000069000	-1.798132000
1	-1.313864000	0.000121000	-3.060180000
1	0.451422000	-0.000131000	1.612692000
1	1.140141000	0.000111000	-2.622263000
6	-2.467981000	-0.000092000	1.382636000
6	-4.232164000	0.000120000	-1.924847000
6	-3.282292000	0.000018000	-0.899991000
6	-5.584421000	0.000104000	-1.594675000
6	-3.681069000	-0.000068000	0.453288000
6	-5.985697000	-0.000003000	-0.245349000
6	-5.026063000	-0.000082000	0.786915000
1	-6.340520000	0.000157000	-2.373017000
1	-5.356090000	-0.000152000	1.821609000
1	-3.929183000	0.000175000	-2.968116000
6	-2.436582000	1.266290000	2.268391000

1	-2.461242000	2.176015000	1.660210000
1	-3.296720000	1.284032000	2.947121000
1	-1.526977000	1.286368000	2.878951000
6	-2.436517000	-1.266425000	2.268413000
1	-1.526871000	-1.286481000	2.878913000
1	-3.296597000	-1.284167000	2.947221000
1	-2.461212000	-2.176183000	1.660279000
6	-7.381127000	-0.000017000	0.081266000
7	-8.513690000	-0.000030000	0.349047000
6	2.413152000	-2.465177000	-0.206256000
6	3.040155000	-1.217060000	-0.127479000
7	2.339899000	-0.000002000	-0.258967000
6	4.430605000	-1.186703000	0.090799000
8	5.132416000	0.000024000	0.175523000
6	4.430576000	1.186738000	0.090839000
6	3.040125000	1.217069000	-0.127437000
6	3.149481000	-3.646783000	-0.071897000
6	5.161185000	-2.358131000	0.226174000
6	5.161130000	2.358178000	0.226255000
6	2.413090000	2.465172000	-0.206159000
6	3.149391000	3.646790000	-0.071756000
6	4.522606000	3.599776000	0.144752000
1	6.230655000	2.277136000	0.393578000
1	1.343228000	2.511441000	-0.374978000
1	2.634843000	4.601001000	-0.138825000
1	5.100683000	4.512678000	0.250245000
6	4.522693000	-3.599743000	0.144622000
1	1.343291000	-2.511461000	-0.375080000
1	2.634957000	-4.601004000	-0.139007000
1	6.230709000	-2.277072000	0.393504000
1	5.100794000	-4.512633000	0.250079000