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**Intramolecular dimer formation reveals anomalous
solvation within fluoruous solvent perfluorodecalin**

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Table S1. Recovered Excited-State Intensity Decay Parameters for BPP (20 μM ; excitation with 340 nm NanoLED) Dissolved in PFD and *n*-hexane added PFD at Different Mole Fraction Ratios and at Different Temperatures Obtained *via* Global Fitting Strategy. Errors Associated with Decay Times are $\leq \pm 5\%$.

T/K	$\lambda_{\text{em}}/\text{nm}$	$\tau_1/\text{ns} (\alpha_1)$	$\tau_2/\text{ns} (\alpha_2)$	χ^2
$x_{\text{PFD}} = 0.9 / x_{\text{Hex}} = 0.1$				
293.15	376	5.23 (0.89)	14.9 (0.11)	1.05
	480	5.23 (-0.48)	14.9 (0.52)	1.33
303.15	376	4.17 (0.89)	13.0 (0.11)	1.16
	480	4.17 (-0.49)	13.0 (0.51)	1.41
313.15	376	3.40 (0.89)	11.4 (0.11)	1.20
	480	3.40 (-0.48)	11.4 (0.52)	1.34
323.15	376	2.78 (0.90)	9.82 (0.10)	1.47
	480	2.78 (-0.49)	9.82 (0.51)	1.27
333.15	376	2.23 (0.90)	8.51 (0.10)	1.40
	480	2.23 (-0.49)	8.51 (0.51)	1.45
$x_{\text{PFD}} = 0.8 / x_{\text{Hex}} = 0.2$				
293.15	376	4.91 (0.94)	13.8 (0.06)	1.20
	480	4.91 (-0.49)	13.8 (0.51)	1.27
303.15	376	3.88 (0.94)	12.2 (0.06)	1.02
	480	3.88 (-0.49)	12.2 (0.51)	1.23
313.15	376	3.01 (0.93)	10.9 (0.07)	0.98
	480	3.01 (-0.49)	10.9 (0.51)	1.27
323.15	376	2.47 (0.93)	9.51 (0.07)	0.84
	480	2.47 (-0.50)	9.51 (0.50)	1.24
333.15	376	1.94 (0.90)	7.72 (0.10)	1.07
	480	1.94 (-0.48)	7.72 (0.52)	1.17
$x_{\text{PFD}} = 0.5 / x_{\text{Hex}} = 0.5$				
293.15	376	3.66 (0.97)	9.45 (0.03)	0.95
	480	3.66 (-0.49)	9.45 (0.51)	1.26

303.15	376	3.06 (0.97)	8.71 (0.03)	0.95
	480	3.06 (-0.50)	8.70 (0.50)	1.35
313.15	376	2.51 (0.95)	8.14 (0.05)	0.79
	480	2.51 (-0.50)	8.14 (0.50)	1.16
323.15	376	2.15 (0.95)	7.37 (0.05)	0.83
	480	2.15 (-0.50)	7.37 (0.50)	1.19
333.15	376	1.81 (0.94)	6.81 (0.06)	0.81
	480	1.81 (-0.50)	6.81 (0.50)	1.19
$x_{\text{PFD}} = 0.2 / x_{\text{Hex}} = 0.8$				
293.15	376	3.34 (0.97)	7.82 (0.03)	1.01
	480	3.34 (-0.50)	7.82 (0.50)	1.12
303.15	376	2.72 (0.97)	7.18 (0.03)	0.77
	480	2.72 (-0.50)	7.18 (0.50)	1.16
313.15	376	2.37 (0.95)	7.21 (0.05)	0.86
	480	2.37 (-0.50)	7.21 (0.50)	1.06
323.15	376	2.00 (0.94)	6.64 (0.06)	0.76
	480	2.00 (-0.51)	6.64 (0.49)	1.10
333.15	376	1.72 (0.94)	6.21 (0.06)	0.83
	480	1.72 (-0.51)	6.21 (0.49)	1.10
$x_{\text{PFD}} = 0.0 / x_{\text{Hex}} = 1.0$				
293.15	376	3.26 (0.96)	8.23 (0.04)	0.84
	480	3.26 (-0.49)	8.23 (0.51)	1.27
303.15	376	2.71 (0.96)	7.50 (0.04)	0.91
	480	2.71 (-0.50)	7.50 (0.50)	1.33
313.15	376	2.28 (0.95)	6.90 (0.05)	0.90
	480	2.28 (-0.50)	6.90 (0.50)	1.26
323.15	376	1.89 (0.95)	6.46 (0.05)	0.76
	480	1.89 (-0.50)	6.46 (0.50)	1.26
333.15	376	1.55 (0.93)	6.00 (0.07)	0.78
	480	1.55 (-0.50)	6.00 (0.50)	1.33

Table S2. Recovered Excited-State Intensity Decay Parameters for BPP (20 μM ; excitation with 340 nm NanoLED) Dissolved in $x_{\text{PFD}} = 0.95 / x_{\text{Hex}} = 0.05$ at Different Temperatures Obtained *via* Global Fitting Strategy. Errors Associated with Decay Times are $\leq \pm 5\%$.

T/K	$\lambda_{\text{em}}/\text{nm}$	$\tau_1/\text{ns} (\alpha_1)$	$\tau_2/\text{ns} (\alpha_2)$	χ^2
$x_{\text{PFD}} = 0.95 / x_{\text{Hex}} = 0.05$				
293.15	376	4.84 (0.88)	17.6 (0.12)	3.51
	480	4.84 (-0.35)	17.6 (0.65)	2.68
303.15	376	4.02 (0.91)	14.6 (0.09)	3.98
	480	4.02 (-0.40)	14.6 (0.60)	2.90
313.15	376	3.22 (0.91)	13.0 (0.09)	3.80
	480	3.22 (-0.41)	13.0 (0.59)	2.71
323.15	376	2.51 (0.91)	11.6 (0.09)	3.60
	480	2.51 (-0.44)	11.6 (0.56)	2.41
333.15	376	1.92 (0.92)	10.6 (0.08)	2.55
	480	1.92 (-0.47)	10.6 (0.53)	1.86

Table S3. Record of Various Rate Constants Associated with BPP (20 μM) Intramolecular Excimer Formation Using Birk's Scheme in PFD and *n*-hexane added PFD.

		k_a/ns^{-1}					
x_{PFD}		0.0	0.2	0.5	0.8	0.9	1.0
T/K							
293.15		0.173 ± 0.002	0.173 ± 0.002	0.158 ± 0.002	0.121 ± 0.002	0.115 ± 0.002	0.088 ± 0.004
303.15		0.231 ± 0.002	0.227 ± 0.002	0.204 ± 0.003	0.162 ± 0.002	0.148 ± 0.003	0.123 ± 0.005
313.15		0.288 ± 0.003	0.262 ± 0.003	0.259 ± 0.004	0.222 ± 0.003	0.185 ± 0.004	0.178 ± 0.006
323.15		0.371 ± 0.004	0.318 ± 0.003	0.307 ± 0.005	0.281 ± 0.004	0.236 ± 0.005	0.239 ± 0.007
333.15		0.466 ± 0.005	0.384 ± 0.004	0.373 ± 0.006	0.362 ± 0.005	0.304 ± 0.006	0.313 ± 0.009

		k_d/ns^{-1}					
x_{PFD}		0.0	0.2	0.5	0.8	0.9	1.0
T/K							
293.15		0.008 ± 0.003	0.005 ± 0.003	0.005 ± 0.004	0.008 ± 0.003	0.013 ± 0.003	0.006 ± 0.004
303.15		0.009 ± 0.003	0.007 ± 0.003	0.006 ± 0.004	0.011 ± 0.003	0.018 ± 0.004	0.009 ± 0.006
313.15		0.014 ± 0.004	0.015 ± 0.004	0.014 ± 0.005	0.017 ± 0.004	0.023 ± 0.005	0.016 ± 0.006
323.15		0.018 ± 0.005	0.022 ± 0.004	0.017 ± 0.006	0.021 ± 0.005	0.025 ± 0.007	0.019 ± 0.008
333.15		0.032 ± 0.006	0.026 ± 0.005	0.025 ± 0.007	0.037 ± 0.007	0.032 ± 0.007	0.025 ± 0.012

		k_E/ns^{-1}					
x_{PFD}		0.0	0.2	0.5	0.8	0.9	1.0
T/K							
293.15		0.121 ± 0.001	0.128 ± 0.001	0.106 ± 0.002	0.072 ± 0.001	0.067 ± 0.001	0.066 ± 0.002
303.15		0.134 ± 0.001	0.139 ± 0.001	0.115 ± 0.002	0.082 ± 0.002	0.077 ± 0.002	0.077 ± 0.002
313.15		0.145 ± 0.001	0.138 ± 0.001	0.123 ± 0.002	0.092 ± 0.002	0.088 ± 0.002	0.088 ± 0.003
323.15		0.156 ± 0.002	0.150 ± 0.001	0.135 ± 0.002	0.105 ± 0.002	0.102 ± 0.002	0.103 ± 0.003
333.15		0.168 ± 0.002	0.160 ± 0.001	0.146 ± 0.002	0.131 ± 0.003	0.118 ± 0.002	0.117 ± 0.004

		k_M/ns^{-1}					
x_{PFD}		0.0	0.2	0.5	0.8	0.9	1.0
T/K							
293.15		0.127 ± 0.001	0.122 ± 0.001	0.110 ± 0.002	0.075 ± 0.002	0.063 ± 0.001	0.057 ± 0.002
303.15		0.128 ± 0.001	0.134 ± 0.001	0.117 ± 0.002	0.085 ± 0.002	0.074 ± 0.002	0.066 ± 0.002
313.15		0.136 ± 0.001	0.146 ± 0.001	0.126 ± 0.002	0.093 ± 0.002	0.086 ± 0.002	0.077 ± 0.002
323.15		0.139 ± 0.001	0.161 ± 0.002	0.141 ± 0.002	0.103 ± 0.002	0.098 ± 0.002	0.091 ± 0.002
333.15		0.146 ± 0.001	0.172 ± 0.002	0.155 ± 0.002	0.115 ± 0.002	0.111 ± 0.002	0.105 ± 0.002

Table S4. Recovered Excited-State Intensity Decay Parameters for 1-Methylpyrene (20 μM ; excitation with 340 nm NanoLED) Dissolved in PFD and *n*-Hexane Added PFD at Different Mole Fraction Ratios and at Different Temperatures. Errors Associated with Decay Times are $\leq \pm 5\%$.

T/K	$\lambda_{\text{em}}/\text{nm}$	$\tau_1/\text{ns} (\alpha_1)$	$\tau_2/\text{ns} (\alpha_2)$	χ^2
$x_{\text{PFD}} = 1.0 / x_{\text{Hex}} = 0.0$				
293.15	376	17.6 (1.00)		1.40
		1.28 (0.01)	17.8 (0.99)	1.37
303.15	376	15.2 (1.00)		1.15
		2.50 (0.02)	15.4 (0.98)	1.12
313.15	376	12.9 (1.00)		1.22
		2.19 (0.02)	13.1 (0.98)	1.19
323.15	376	11.0 (1.00)		1.16
		3.54 (0.04)	11.3 (0.96)	1.12
333.15	376	9.48 (1.00)		1.37
		2.57 (0.04)	10.8 (0.96)	1.22
$x_{\text{PFD}} = 0.95 / x_{\text{Hex}} = 0.05$				
293.15	376	16.7 (1.00)		1.26
		2.51 (0.02)	17.0 (0.98)	1.19
303.15	376	14.4 (1.00)		1.40
		1.06 (0.01)	14.5 (0.99)	1.36
313.15	376	12.4 (1.00)		1.21
		3.77 (0.05)	12.9 (0.95)	1.12
323.15	376	10.8 (1.00)		1.31
		1.11 (0.03)	11.0 (0.97)	1.20
333.15	376	9.40 (1.00)		1.30
		1.77 (0.03)	9.60 (0.97)	1.22
$x_{\text{PFD}} = 0.9 / x_{\text{Hex}} = 0.1$				
293.15	376	15.3 (1.00)		1.36
		2.51 (0.04)	15.9 (0.96)	1.14

303.15	376	13.0 (1.00)		1.32
		2.49 (0.04)	13.6 (0.96)	1.13
313.15	376	11.2 (1.00)		1.41
		2.12 (0.04)	11.6 (0.96)	1.22
323.15	376	9.71 (1.00)		1.42
		2.44 (0.06)	10.2 (0.93)	1.18
333.15	376	8.59 (1.00)		1.43
		1.86 (0.06)	8.99 (0.94)	1.21
$x_{\text{PFD}} = 0.8 / x_{\text{Hex}} = 0.2$				
293.15	376	13.2 (1.00)		1.18
		1.11 (0.01)	13.3 (0.99)	1.14
303.15	376	11.7 (1.00)		1.26
		1.07 (0.01)	11.8 (0.99)	1.23
313.15	376	10.6 (1.00)		1.28
		1.23 (0.02)	10.7 (0.98)	1.21
323.15	376	9.55 (1.00)		1.29
		1.08 (0.02)	9.67 (0.98)	1.24
333.15	376	8.58 (1.00)		1.16
		1.05 (0.02)	8.68 (0.98)	1.13
$x_{\text{PFD}} = 0.5 / x_{\text{Hex}} = 0.5$				
293.15	376	8.93 (1.00)		1.81
		1.11 (0.02)	9.09 (0.98)	1.18
303.15	376	8.49 (1.00)		1.21
		1.62 (0.03)	8.55 (0.97)	1.17
313.15	376	7.74 (1.00)		1.11
		2.09 (0.03)	7.93 (0.97)	1.06
323.15	376	6.89 (1.00)		1.32
		1.65 (0.04)	7.08 (0.96)	1.24
333.15	376	6.29 (1.00)		1.27

		1.16 (0.04)	6.44 (0.96)	1.17
$x_{\text{PFD}} = 0.2 / x_{\text{Hex}} = 0.8$				
293.15	376	8.11 (1.00)		1.36
		0.11 (0.09)	8.23 (0.91)	1.13
303.15	376	7.36 (1.00)		1.26
		1.61 (0.03)	7.49 (0.97)	1.22
313.15	376	6.75 (1.00)		1.20
		0.66 (0.02)	6.85 (0.98)	1.14
323.15	376	6.18 (1.00)		1.13
		0.42 (0.02)	6.21 (0.98)	1.07
333.15	376	5.74 (1.00)		1.03
		0.37 (0.03)	5.80 (0.97)	0.98
$x_{\text{PFD}} = 0.0 / x_{\text{Hex}} = 1.0$				
293.15	376	7.14 (1.00)		2.39
		1.34 (0.13)	7.90 (0.87)	1.08
303.15	376	7.05 (1.00)		2.92
		1.29 (0.13)	7.79 (0.87)	1.32
313.15	376	6.68 (1.00)		2.63
		1.13 (0.13)	7.38 (0.87)	1.09
323.15	376	6.46 (1.00)		2.51
		1.19 (0.14)	7.18 (0.86)	1.14
333.15	376	6.16 (1.00)		2.52
		1.11 (0.14)	6.85 (0.86)	0.95

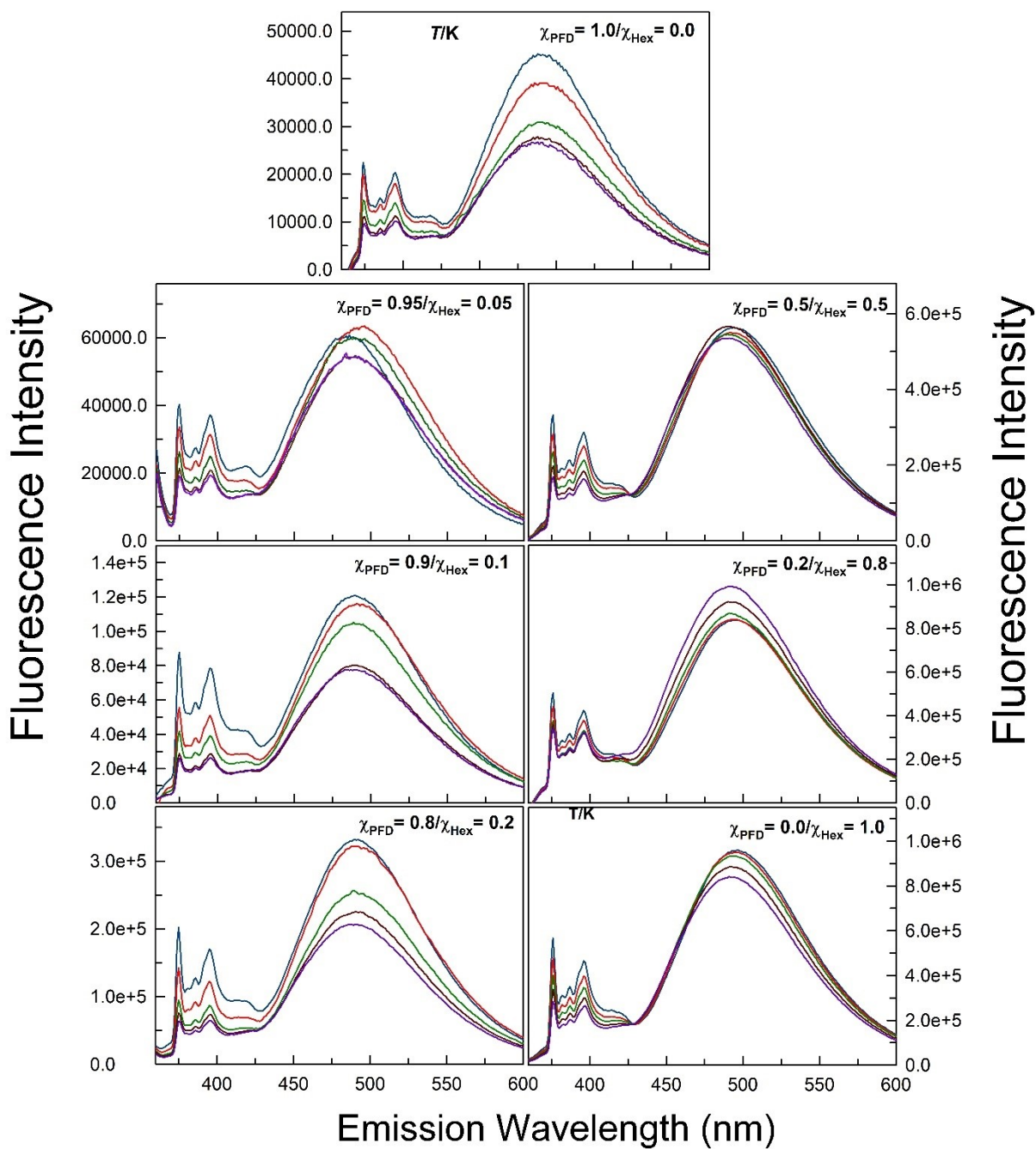


Figure S1: Steady-state fluorescence emission spectra [$\lambda_{\text{ex}} = 340$ nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μM) dissolved in PFD and *n*-hexane added PFD over the temperature range ($T = 293.15\text{--}333.15$ K).

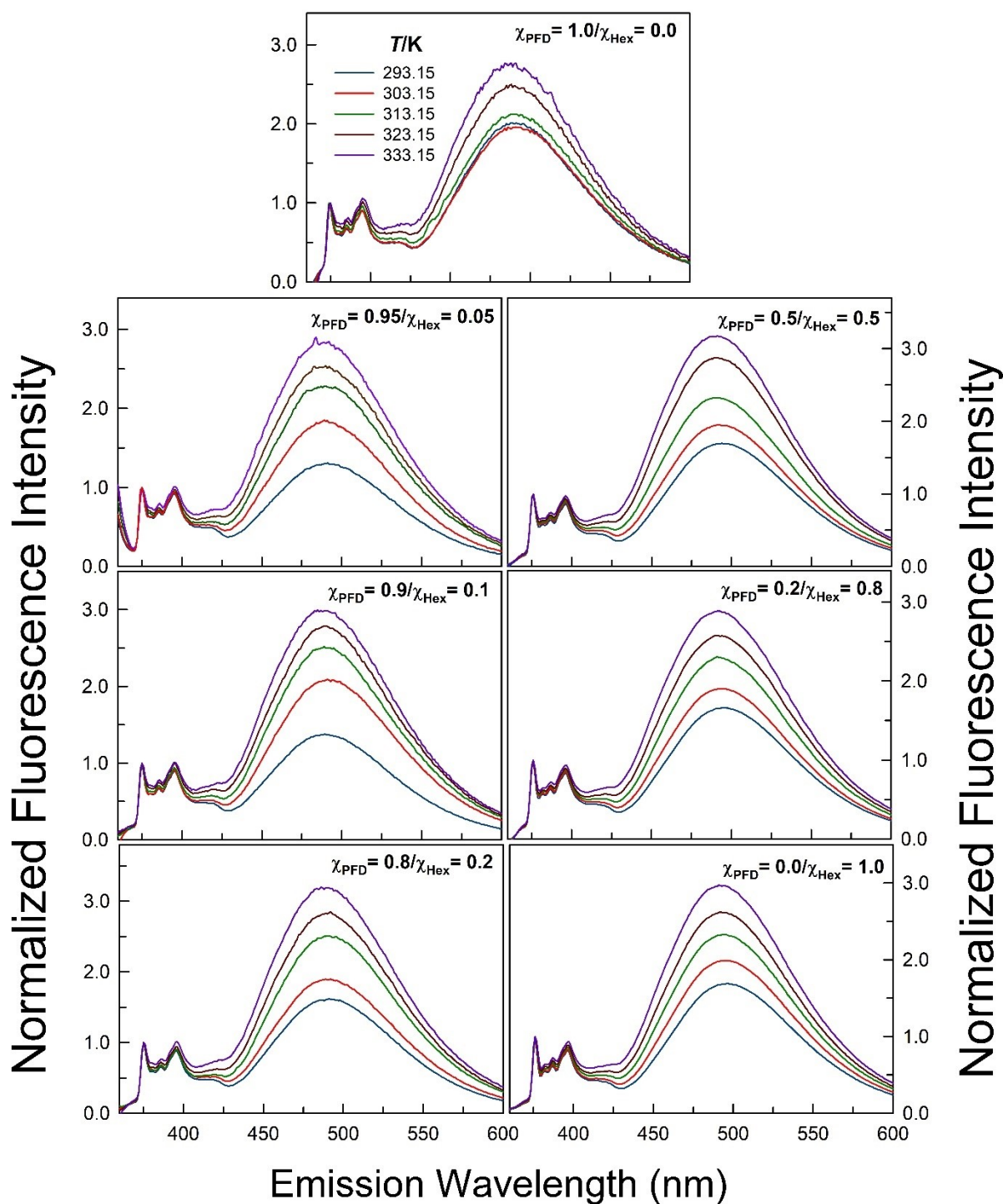


Figure S2: Normalized Steady-state fluorescence emission spectra [$\lambda_{\text{ex}} = 340$ nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μM) dissolved in PFD and *n*-hexane added PFD over the temperature range ($T = 293.15$ – 333.15 K).

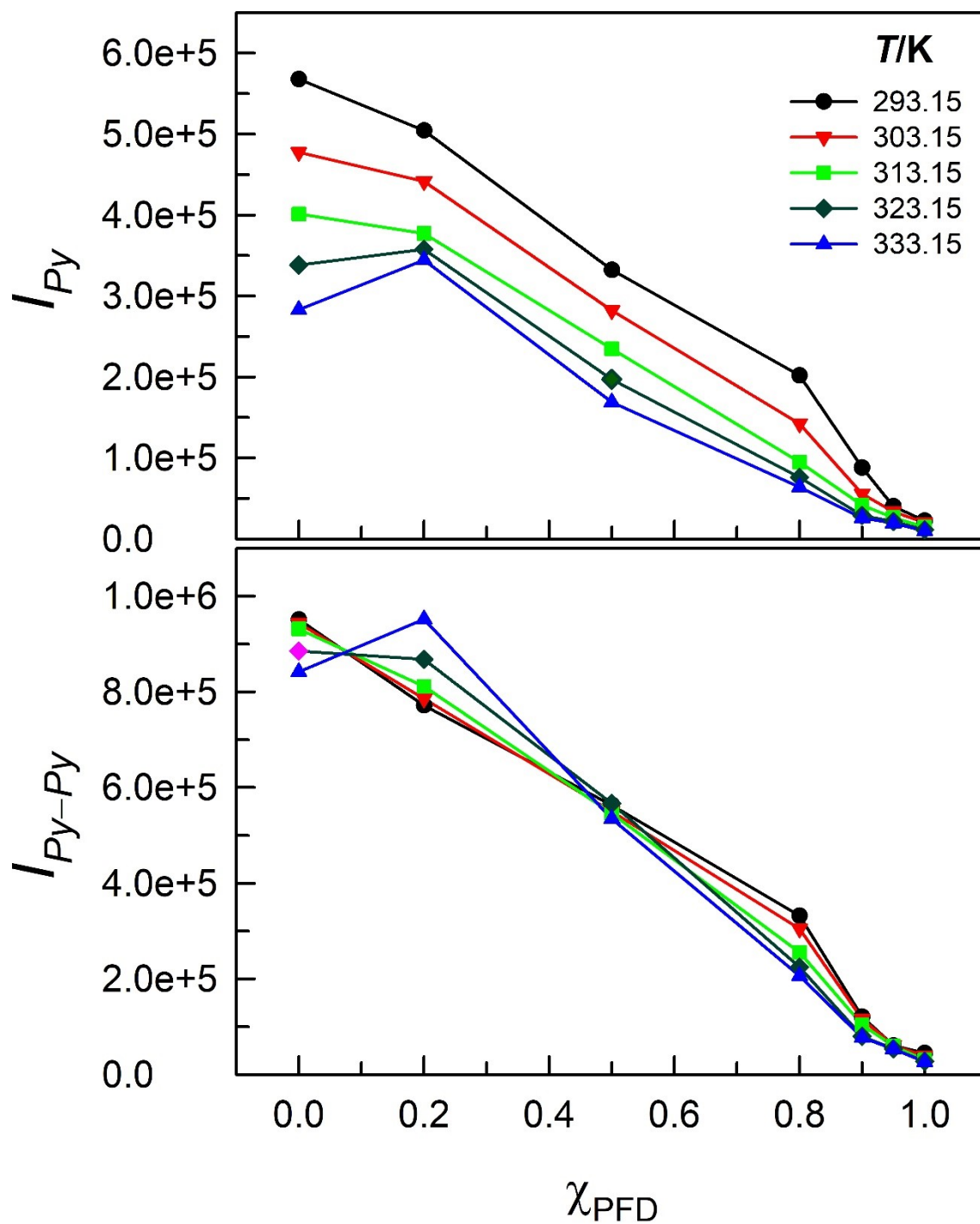


Figure S3: Variation of $I_{\text{Py-Py}}$ and I_{Py} with mole ratio for BPP (20 μM) dissolved in PFD and *n*-hexane added PFD at different temperatures.

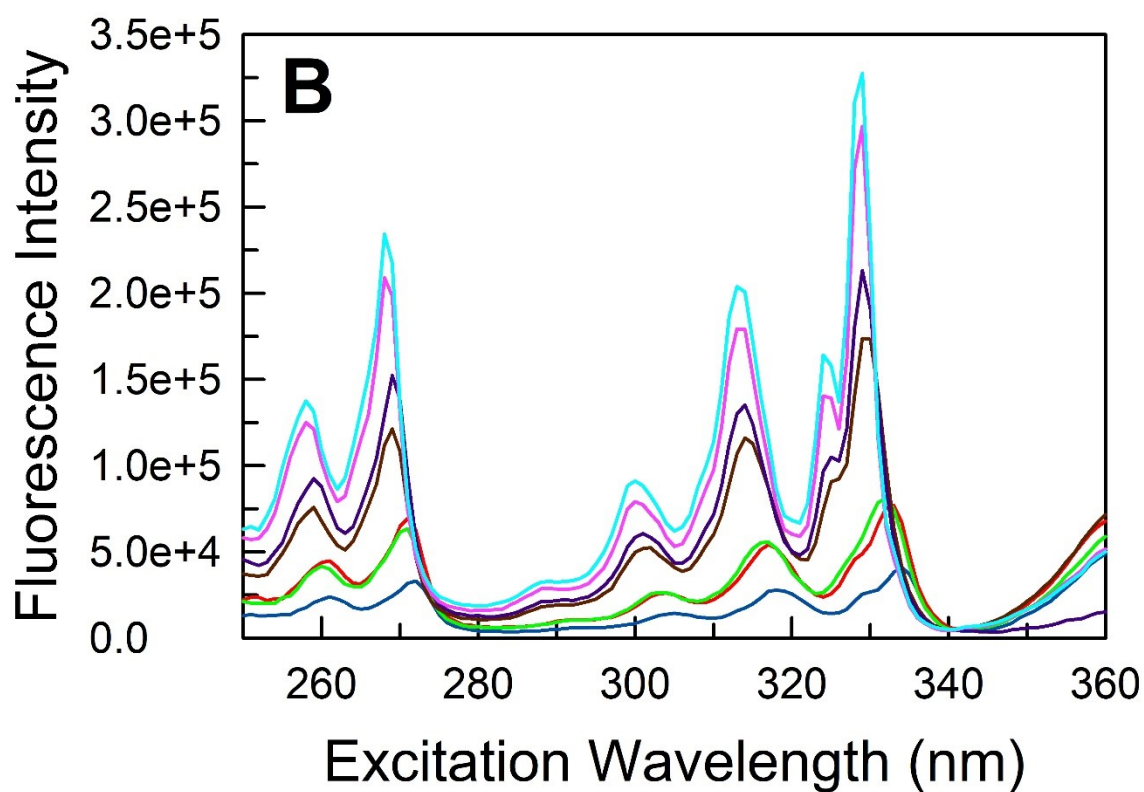
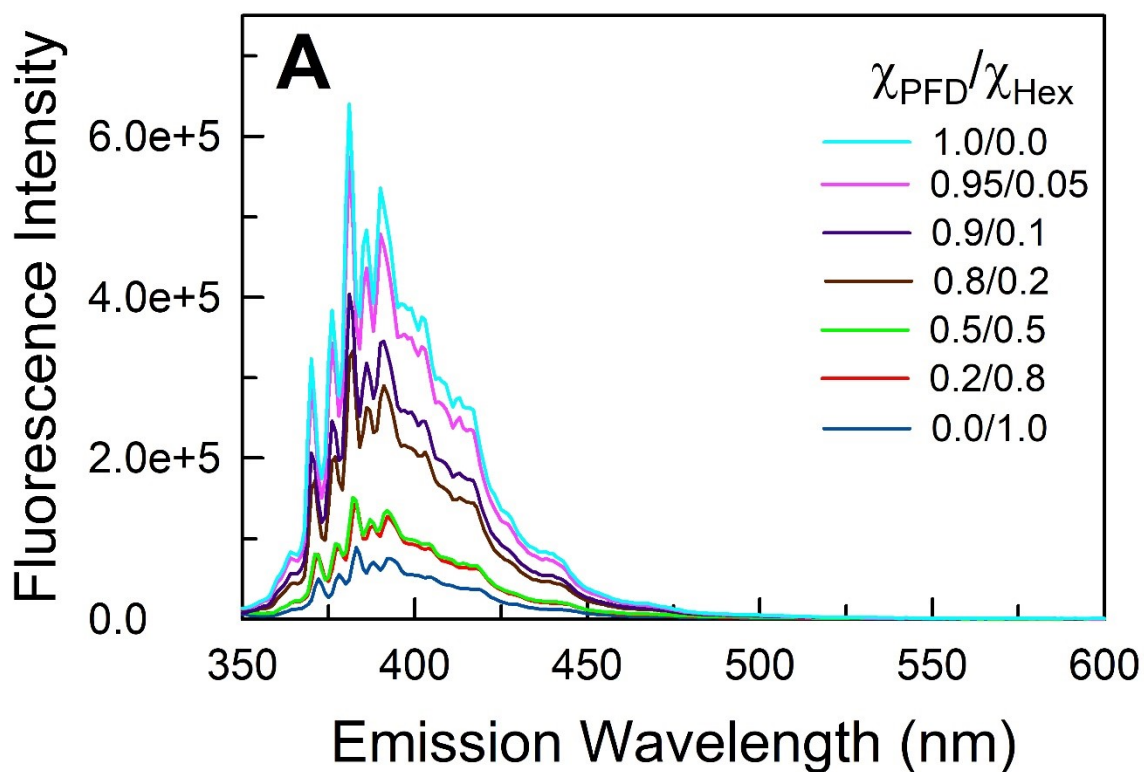


Figure S4: Steady-state fluorescence emission spectra [panel A; $\lambda_{\text{ex}} = 329$ nm] and excitation spectra [panel B; $\lambda_{\text{em}} = 370$ nm] of pyrene ($20 \mu\text{M}$) dissolved in PFD and *n*-hexane added PFD at $T = 298.15$ K (excitation and emission slits are 1.0 and 1.0 nm, respectively).

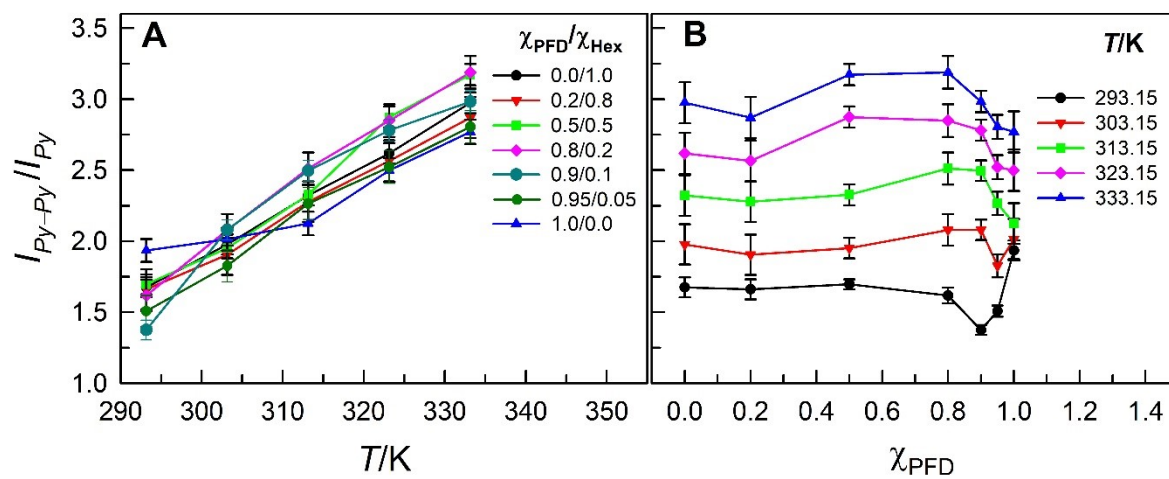


Figure S5: Variation of I_{Py-Py} / I_{Py} with temperature (panel A) and with mole ratio (panel B) for BPP (20 μ M) dissolved in PFD and *n*-hexane added PFD.

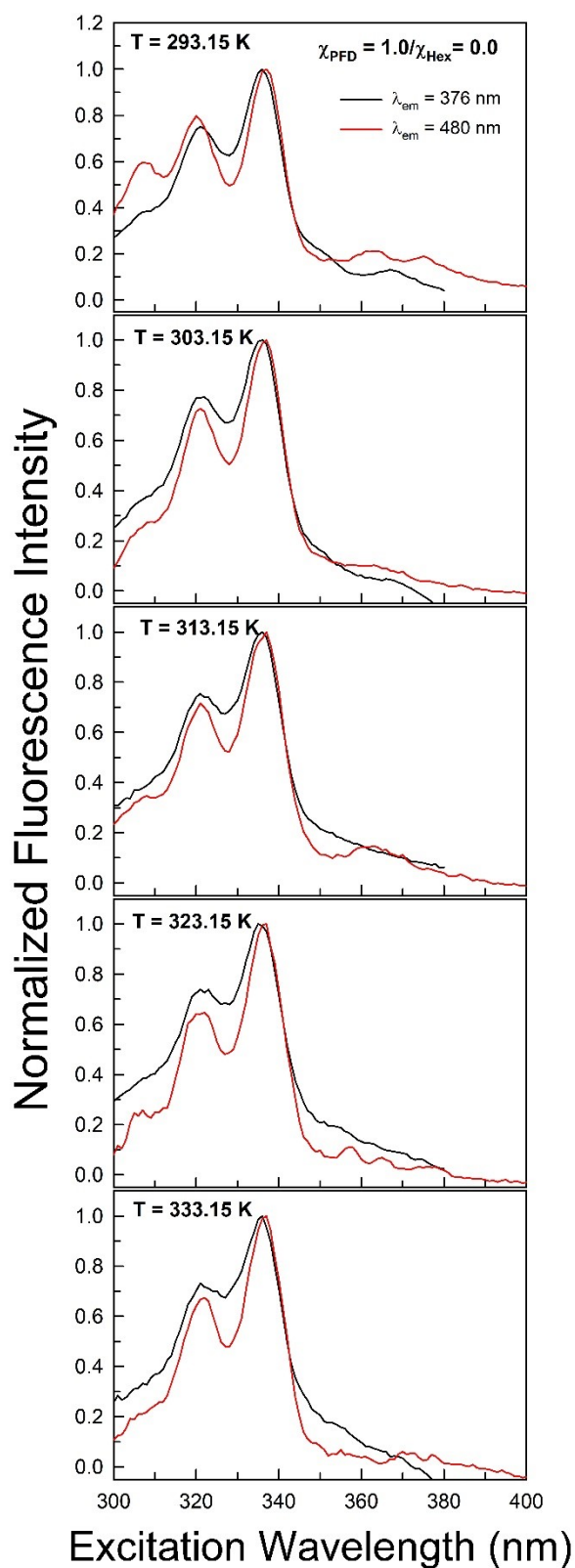


Figure S6: Fluorescence excitation spectra [$\lambda_{em} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μ M) dissolved in PFD over the temperature range ($T = 293.15$ – 333.15 K).

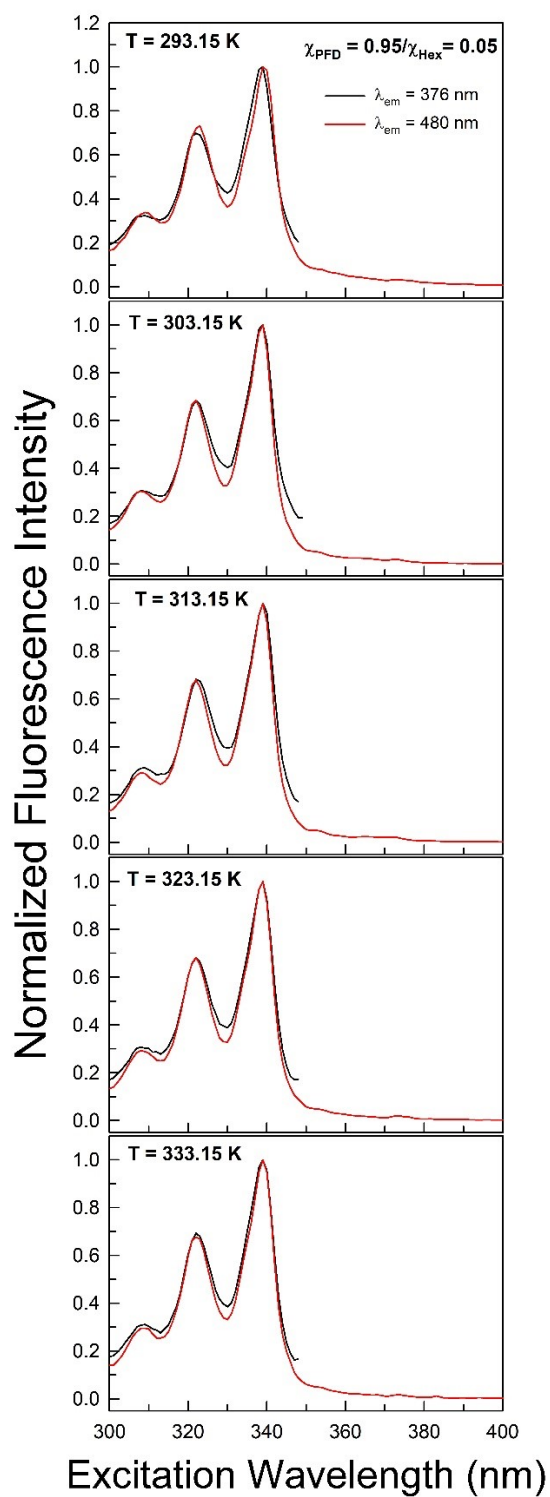


Figure S7: Fluorescence excitation spectra [$\lambda_{em} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μ M) dissolved in *n*-hexane added PFD ($x_{PFD} = 0.95/x_{Hex} = 0.05$) over the temperature range ($T = 293.15$ – 333.15 K).

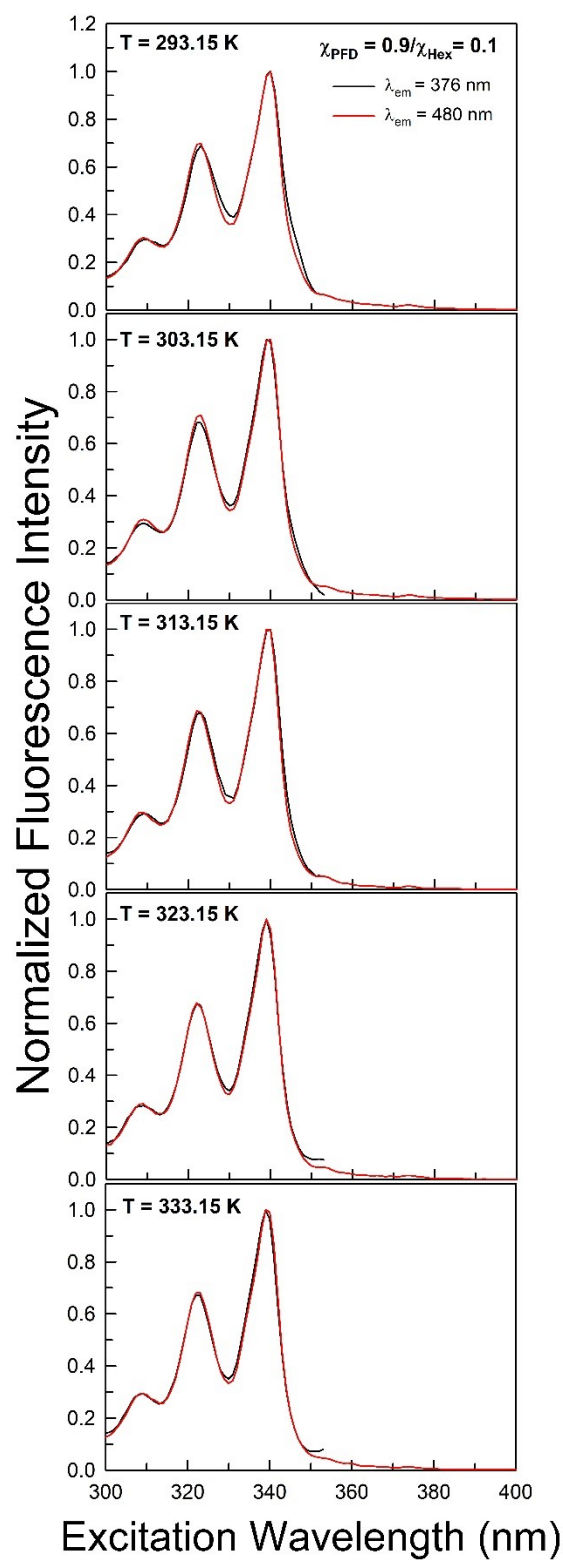


Figure S8: Fluorescence excitation spectra [$\lambda_{em} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μ M) dissolved in *n*-hexane added PFD ($x_{PFD} = 0.9/x_{Hex} = 0.1$) over the temperature range ($T = 293.15$ – 333.15 K).

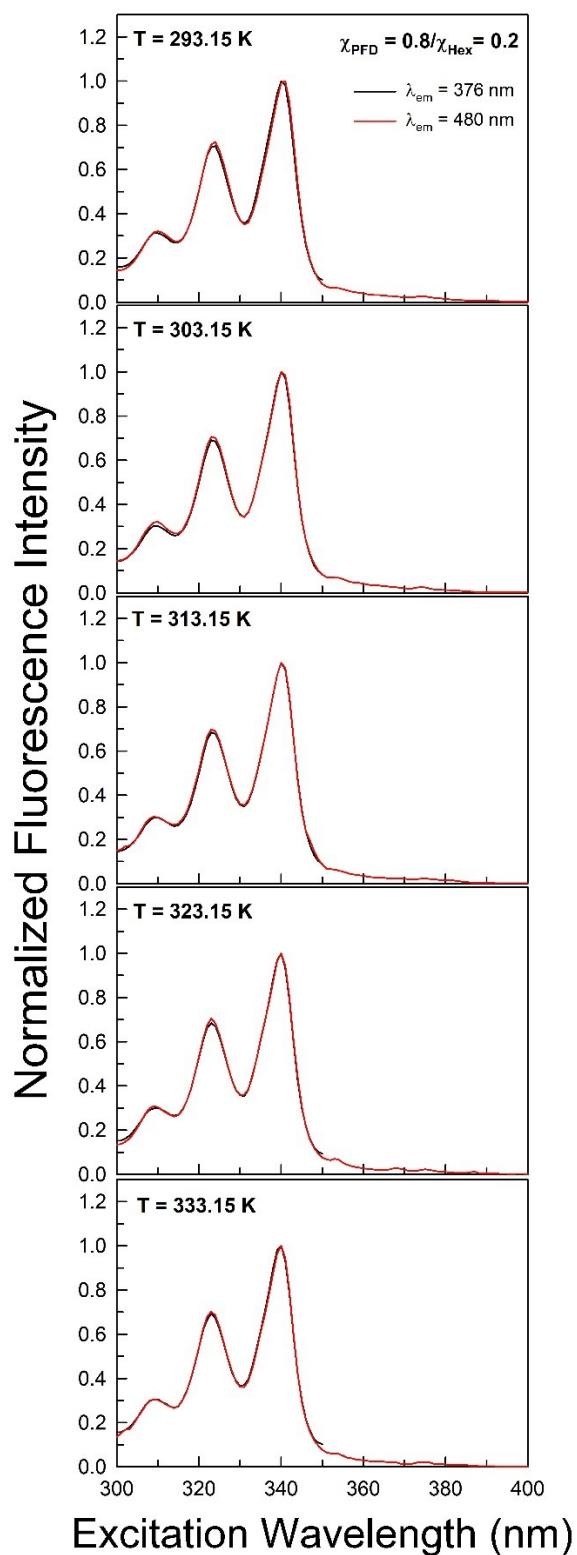


Figure S9: Fluorescence excitation spectra [$\lambda_{\text{em}} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μM) dissolved in *n*-hexane added PFD ($x_{\text{PFD}} = 0.8/x_{\text{Hex}} = 0.2$) over the temperature range ($T = 293.15\text{--}333.15$ K).

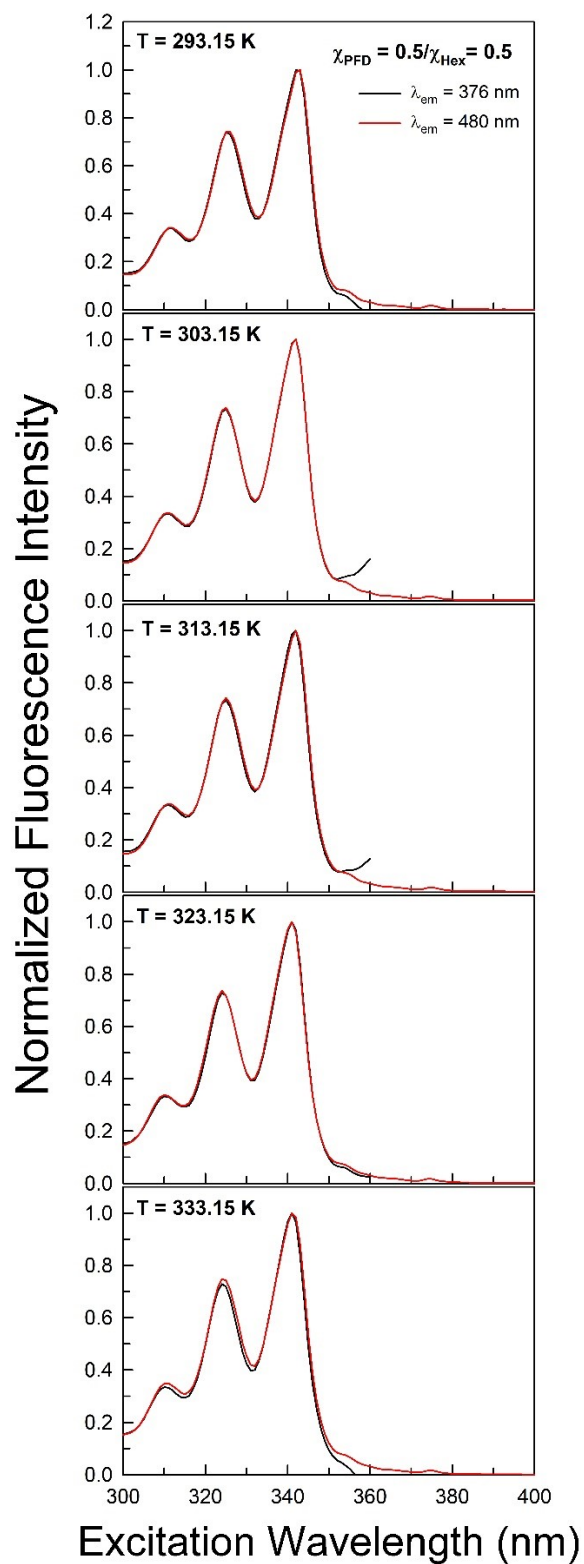


Figure S10: Fluorescence excitation spectra [$\lambda_{\text{em}} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μM) dissolved in *n*-hexane added PFD ($x_{\text{PFD}} = 0.5/x_{\text{Hex}} = 0.5$) over the temperature range ($T = 293.15\text{--}333.15$ K).

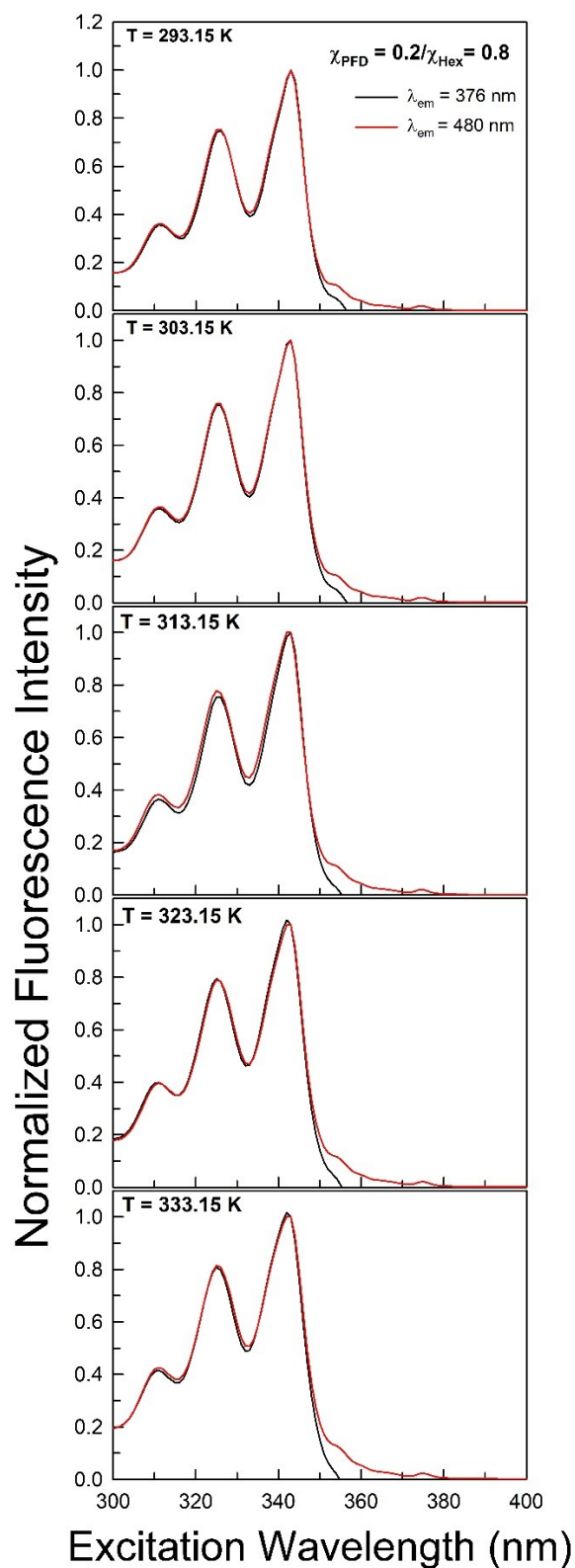


Figure S11: Fluorescence excitation spectra [$\lambda_{\text{em}} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μM) dissolved in *n*-hexane added PFD ($x_{\text{PFD}} = 0.2/x_{\text{Hex}} = 0.8$) over the temperature range ($T = 293.15\text{--}333.15$ K).

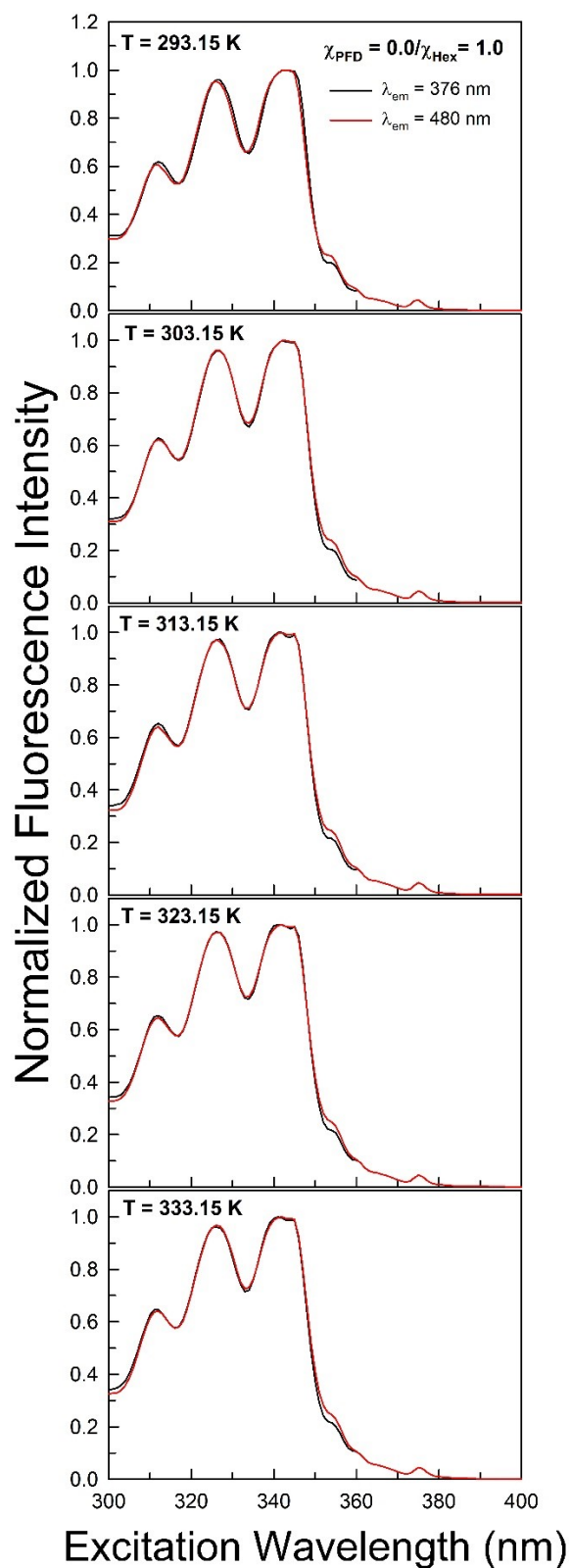


Figure S12: Fluorescence excitation spectra [$\lambda_{\text{em}} = 376$ nm, and 480 nm; excitation and emission slits are 2.0 and 2.0 nm, respectively] of BPP (20 μM) dissolved in *n*-hexane added PFD ($x_{\text{PFD}} = 0.0/x_{\text{Hex}} = 1.0$) over the temperature range ($T = 293.15\text{--}333.15$ K).

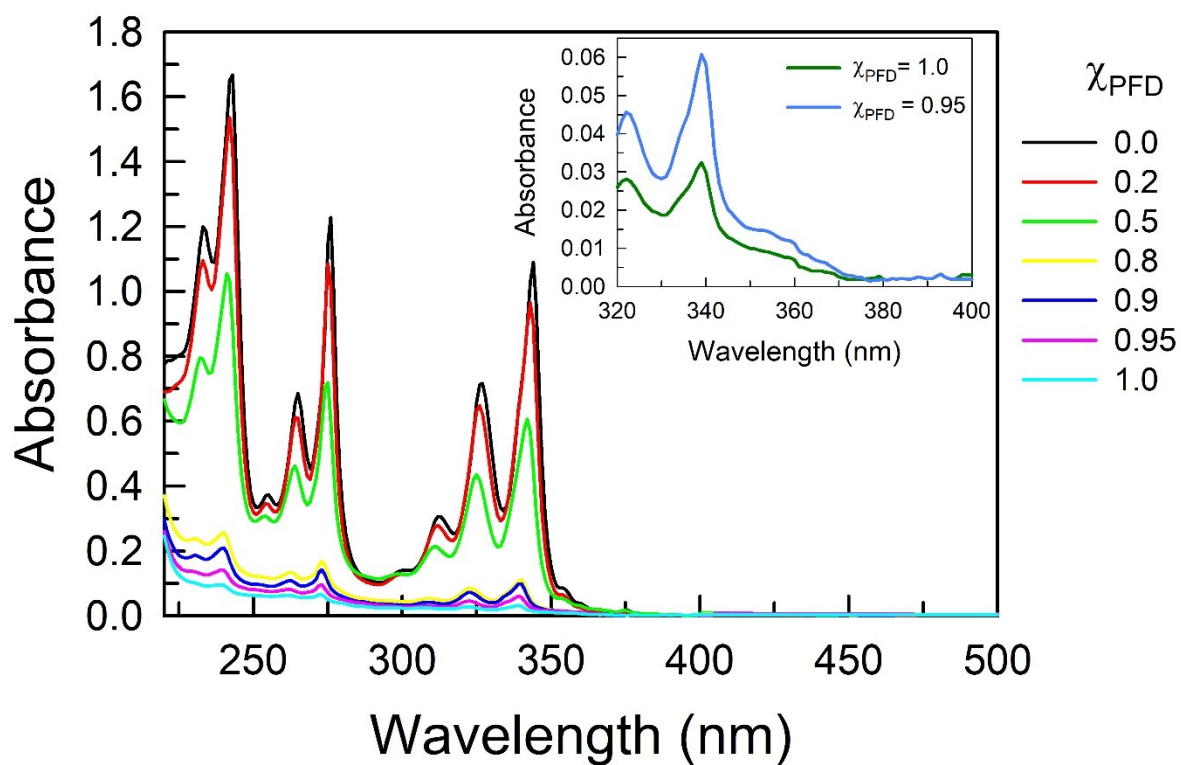


Figure S13: UV-vis absorbance spectra of BPP (20 μ M) dissolved in PFD, *n*-hexane, and *n*-hexane added PFD mixtures under ambient conditions. Inset shows magnified absorbance intensity in $\chi_{PFD} = 0.95$ and 1.0, respectively.

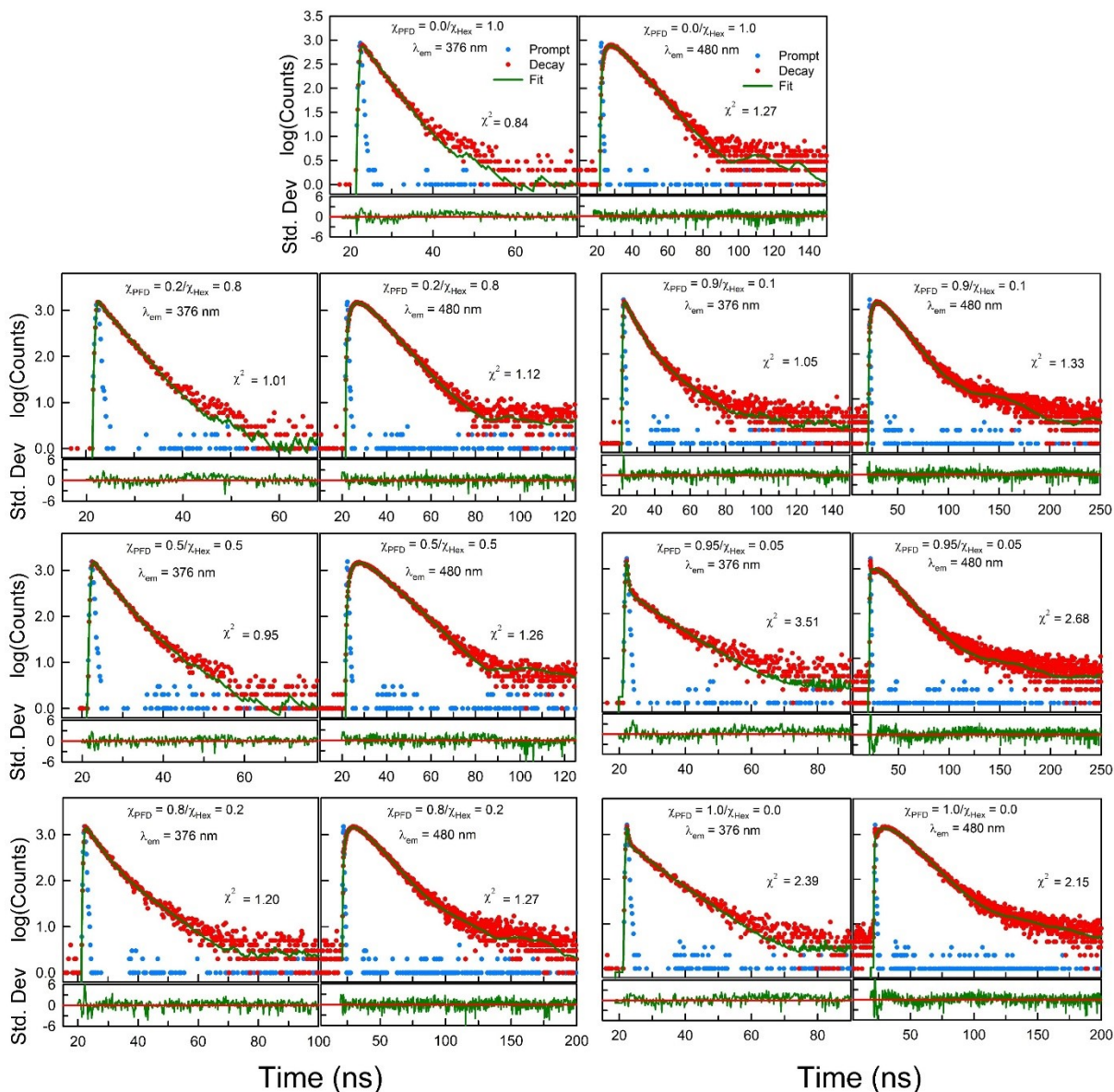


Figure S14: Fits to double exponential decay function of the excited-state intensity decay of BPP (20 μM ; excitation with 340 nm NanoLED) dissolved in PFD and *n*-hexane added PFD at 376 nm (left panel) and 480 nm (right panel) at 293.15 K via global fitting strategy. Residuals are provided below each panel.