Electronic Supplementary Information (ESI)

Contrasting ground- and excited-state intramolecular aggregation in choline chloride-based deep eutectic solvents *versus* a liquid polymer

Shreya Juneja, Himanshu, and Siddharth Pandey*

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi – 110016, India.

*To whom correspondence should be addressed.

E-mail: sipandey@chemistry.iitd.ac.in, Phone: +91-11-26596503, Fax: +91-11-26581102

Table of Contents

	Page No.
Table S1	S3
Table S2	S7
Table S3	S11
Fig. S1	S12
Fig. S2	S13
Fig. S3	S14
Fig. S4	S15
Fig. S5	S16

Table S1. Recovered excited-state intensity decay parameters for 1Py(3)1Py (10 μM; excitation with 340 nm NanoLED) dissolved in PDMS2000, DESs ChCl:Urea and ChCl:Gly, along with glycerol (Gly) at different temperatures obtained via global fitting strategy. Errors associated with decay times are ≤ ± 5%.

Temperature (K)	λ_{em} (nm)	τ_1 (ns) (α_1)	τ_2 (ns) (α_2)	χ^2
		PDMS2000		
293.15	377	9.1 (0.99_9)	20.7 (0.00_1)	0.95
	487	9.1 (–0.49)	20.7 (0.51)	1.61
303.15	377	6.9 (0.98)	19.1 (0.02)	1.22
	487	6.9 (–0.49)	19.1 (0.51)	1.71
313.15	377	5.6 (0.97)	16.8 (0.03)	0.89
	487	5.6 (–0.49)	16.8 (0.51)	1.43
323.15	377	4.4 (0.97)	15.6 (0.03)	0.95
	487	4.4 (–0.49)	15.6 (0.51)	1.40
333.15	377	3.6 (0.96)	14.0 (0.04)	0.94
	487	3.6 (–0.49)	14.0 (0.51)	1.05
343.15	377	2.8 (0.96)	12.7 (0.04)	0.89
	487	2.8 (–0.50)	12.7 (0.50)	1.60
353.15	377	2.4 (0.95)	11.7 (0.05)	0.86
	487	2.4 (–0.50)	11.7 (0.50)	1.38
363.15	377	2.0 (0.94)	10.6 (0.06)	0.76
	487	2.0 (–0.50)	10.6 (0.50)	1.47

		ChCl:Urea		
293.15	377	26.9 (0.95)	76.2 (0.05)	1.76
	487	26.9 (0.67)	76.2 (0.33)	2.94
303.15	377	14.2 (0.90)	58.0 (0.10)	2.05
	487	14.2 (0.56)	58.0 (0.44)	3.54
313.15	377	11.3 (0.93)	64.3 (0.07)	1.96
	487	11.3 (0.66)	64.3 (0.34)	3.81
323.15	377	23.7 (0.98)	151.5 (0.02)	3.02
	487	23.7 (0.90)	151.5 (0.10)	2.24
333.15	377	26.2 (0.97)	152.5 (0.03)	3.14
	487	26.2 (0.87)	152.5 (0.13)	2.33
343.15	377	32.5 (0.98)	194.9 (0.02)	3.22
	487	32.5 (0.90)	194.9 (0.10)	1.99
353.15	377	38.9 (0.98)	232.7 (0.02)	3.48
	487	38.9 (0.92)	232.7 (0.08)	1.68
363.15	377	39.9 (0.97)	240.3 (0.03)	3.46
	487	39.9 (0.92)	240.3 (0.08)	1.58
		ChCl:Gly		
293.15	377	17.6 (0.83)	68.2 (0.17)	1.49
	487	17.6 (0.09)	68.2 (0.91)	2.26
303.15	377	16.8 (0.85)	71.5 (0.15)	2.00

	487	16.8 (0.19)	71.5 (0.81)	2.17
313.15	377	28.4 (0.93)	81.7 (0.07)	2.17
	487	28.4 (0.25)	81.7 (0.75)	1.86
323.15	377	29.8 (0.96)	84.6 (0.04)	1.78
	487	29.8 (0.16)	84.6 (0.84)	2.02
333.15	377	26.2 (0.97)	80.9 (0.03)	1.56
	487	26.2 (–0.05)	80.9 (0.95)	2.40
343.15	377	21.9 (0.97)	77.0 (0.03)	1.34
	487	21.9 (–0.15)	77.0 (0.85)	3.14
353.15	377	17.1 (0.97)	72.7 (0.03)	1.13
	487	17.1 (–0.21)	72.7 (0.79)	3.74
363.15	377	13.9 (0.97)	69.6 (0.03)	1.08
	487	13.9 (–0.20)	69.6 (0.80)	4.15
		Gly		
293.15	377	27.6 (0.40)	97.1 (0.60)	2.00
	487	27.6 (0.61)	97.1 (0.39)	1.66
303.15	377	62.6 (0.96)	162.8 (0.04)	2.08
	487	62.6 (0.86)	162.8 (0.14)	1.75
313.15	377	57.8 (1.00)	116.2 (0.00)	1.40
	487	57.8 (0.51)	116.2 (0.49)	1.29

323.15	377	44.0 (0.99)	92.0 (0.01)	1.16
	487	44.0 (–0.17)	92.0 (0.83)	1.73
333.15	377	29.7 (0.98)	81.5 (0.02)	0.93
	487	29.7 (–0.31)	81.5 (0.69)	2.55
343.15	377	20.6 (0.98)	75.6 (0.02)	0.88
	487	20.6 (–0.33)	75.6 (0.67)	3.37
353.15	377	14.6 (0.98)	69.6 (0.02)	0.85
	487	14.6 (–0.34)	69.6 (0.66)	4.20
363.15	377	10.0 (0.98)	66.8 (0.02)	0.82
	487	10.0 (–0.33)	66.8 (0.67)	4.71

Table S2. Recovered excited-state intensity decay parameters for 1Py(3)1Py (10 μM; excitation with 340 nm NanoLED) dissolved in PDMS2000, DESs ChCl:Urea and ChCl:Gly, along with glycerol (Gly) at different temperatures. Errors associated with decay times and pre-exponential factors are ≤ ±5%.

Temperature (K)	λ_{em} (nm)	τ_1 (ns) (α_1)	τ_2 (ns) (α_2)	τ_3 (ns) (α_3)	χ^2
		PDMS2000			
293.15	377	2.0 (0.22)	9.4 (0.78)		1.15
	487	17.4 (–0.49)	17.6 (0.50)	8.1 (–0.01)	1.33
303.15	377	4.5 (0.58)	9.4 (0.42)		1.23
	487	16.6 (–0.49)	16.7 (0.50)	6.7 (–0.01)	1.27
313.15	377	4.5 (0.85)	10.7 (0.15)		1.06
	487	13.6 (–0.47)	14.0 (0.50)	4.9 (–0.03)	1.21
323.15	377	3.7 (0.91)	11.6 (0.09)		1.08
	487	12.8 (–0.48)	13.0 (0.50)	4.0 (–0.02)	1.86
333.15	377	2.8 (0.88)	8.8 (0.12)		1.12
	487	12.1 (–0.43)	12.5 (0.50)	3.5 (–0.07)	1.53
343.15	377	2.3 (0.88)	7.7 (0.12)		1.15
	487	2.8 (–0.50)	13.0 (0.50)	6.9 (0.00)	1.37
353.15	377	2.1 (0.91)	8.9 (0.09)		1.03
	487	2.5 (–0.51)	12.5 (0.38)	7.2 (0.11)	1.21
363.15	377	1.7 (0.91)	8.7 (0.09)		0.98
	487	2.0 (–0.50)	10.9 (0.48)	5.4 (0.02)	1.25

		ChCl:Urea			
293.15	377	4.3 (0.48)	33.5 (0.52)		1.25
	487	1.3 (0.63)	46.6 (0.33)	19.8 (–0.04)	1.22
303.15	377	5.8 (0.68)	30.4 (0.32)		1.33
	487	1.1 (0.61)	38.1 (0.38)	129.8 (0.01)	1.10
313.15	377	4.5 (0.81)	30.5 (0.19)		1.37
	487	0.9 (0.64)	30.6 (0.31)	80.5 (0.05)	1.14
323.15	377	2.5 (0.84)	26.6 (0.16)		1.32
	487	1.0 (0.63)	28.5 (0.30)	85.2 (0.07)	1.11
333.15	377	1.8 (0.87)	25.4 (0.13)		1.35
	487	1.2 (0.60)	33.7 (0.33)	98.4 (0.07)	1.16
343.15	377	1.2 (0.89)	22.6 (0.11)		1.49
	487	1.0 (0.62)	39.7 (0.33)	125.6 (0.05)	1.11
353.15	377	0.7 (0.91)	19.1 (0.09)		1.42
	487	34.9 (–0.49)	35.0 (0.50)	137.7 (0.00)	1.37
363.15	377	0.6 (0.92)	17.6 (0.08)		1.46
	487	67.5 (–0.50)	68.4 (0.42)	62.3 (0.08)	1.31
		ChCl:Gly			
293.15	377	8.3 (0.66)	46.9 (0.34)		1.09
	487	41.9 (–0.48)	43.05 (0.51)	105.3 (0.01)	1.19
303.15	377	5.6 (0.71)	45.3 (0.29)		1.10

	487	1.2 (0.30)	60.1 (0.66)	148.5 (0.04)	1.10
313.15	377	3.6 (0.71)	41.3 (0.29)		1.08
	487	45.2 (–0.50)	45.3 (0.50)	113.9 (0.00)	1.16
323.15	377	2.5 (0.71)	36.9 (0.29)		1.06
	487	44.3 (–0.50)	44.6 (0.50)	118.1 (0.00)	1.15
333.15	377	1.9 (0.70)	32.0 (0.30)		1.02
	487	41.1 (–0.50)	41.3 (0.50)	143.9 (0.00)	1.18
343.15	377	1.3 (0.71)	27.1 (0.29)		1.07
	487	34.6 (–0.50)	34.6 (0.50)	129.6 (0.00)	1.12
353.15	377	1.1 (0.70)	22.1 (0.30)		1.08
	487	28.3 (–0.50)	28.1 (0.50)	114.0 (0.00)	1.12
363.15	377	1.0 (0.67)	18.4 (0.33)		1.15
	487	22.9 (–0.50)	22.8 (0.50)	107.5 (0.00)	1.07
			Gly		
293.15	377	3.7 (0.55)	87.6 (0.45)		1.10
	487	39.0 (0.61)	1.7 (0.18)	116.4 (0.20)	1.13
303.15	377	2.6 (0.57)	74.3 (0.43)		1.08
	487	31.0 (0.54)	73.6 (0.09)	110.7 (0.37)	1.14
313.15	377	2.1 (0.54)	60.2 (0.46)		1.07
	487	41.5 (–0.08)	94.2 (0.70)	21.9 (0.22)	1.13

323.15	377	1.8 (0.49)	46.3 (0.51)		1.09
	487	55.8 (–0.50)	56.2 (0.50)	136.6 (0.00)	1.12
333.15	377	1.4 (0.47)	33.4 (0.53)		1.06
	487	41.5 (–0.50)	41.9 (0.50)	135.0 (0.00)	1.20
343.15	377	1.1 (0.47)	24.0 (0.53)		1.07
	487	31.6 (–0.50)	31.7 (0.50)	120.8 (0.00)	1.18
353.15	377	0.8 (0.48)	17.3 (0.52)		1.15
	487	24.8 (–0.50)	25.4 (0.50)	114.2 (0.00)	1.15
363.15	377	9.0 (0.81)	19.4 (0.19)		1.23
	487	13.5 (–0.46)	28.2 (0.47)	111.4 (0.07)	1.12

Table S3. Fluorescence Lifetimes ($\tau_{1\text{-MePy}}$) and Excited-State Intensity Decay Rates ($k_M = 1/\tau_{1\text{-MePy}}$) recovered from Excited-State Intensity Decay Fit to a Single Exponential Decay Function for 1-MePy dissolved in PDMS2000 at different temperatures. Errors associated with decay times are ≤ ±5% ($\lambda_{emission}^{monomer} = 377\ nm$).

T/ K	$\tau_{1\text{-MePy}}$ /ns	k_M (10^6, s^{-1})	χ^2
293.15	26.4	37.9	1.14
303.15	23.0	43.5	1.13
313.15	20.6	48.6	1.06
323.15	18.3	54.7	1.26
333.15	16.3	61.3	1.39
343.15	15.0	66.8	1.13
353.15	13.9	71.9	1.12
363.15	12.6	79.2	1.19

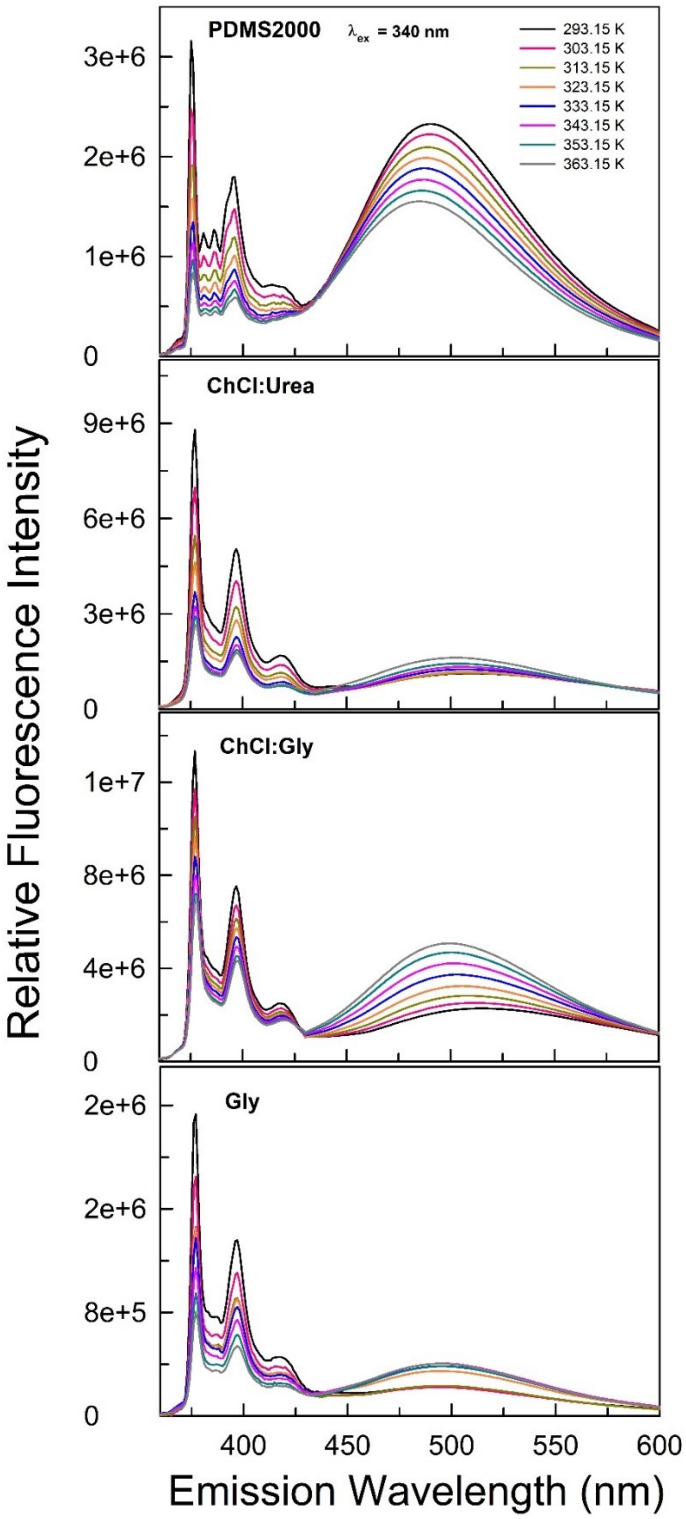

Fig. S1. Relative steady-state fluorescence emission spectra [λ_{ex} = 340 nm (Xe arc lamp); excitation and emission slits are 1.5 and 1.5 nm, respectively] of 1Py(3)1Py (10 μM) dissolved in PDMS2000, DESs ChCl:Urea and ChCl:Gly, along with glycerol (Gly) at different temperatures.

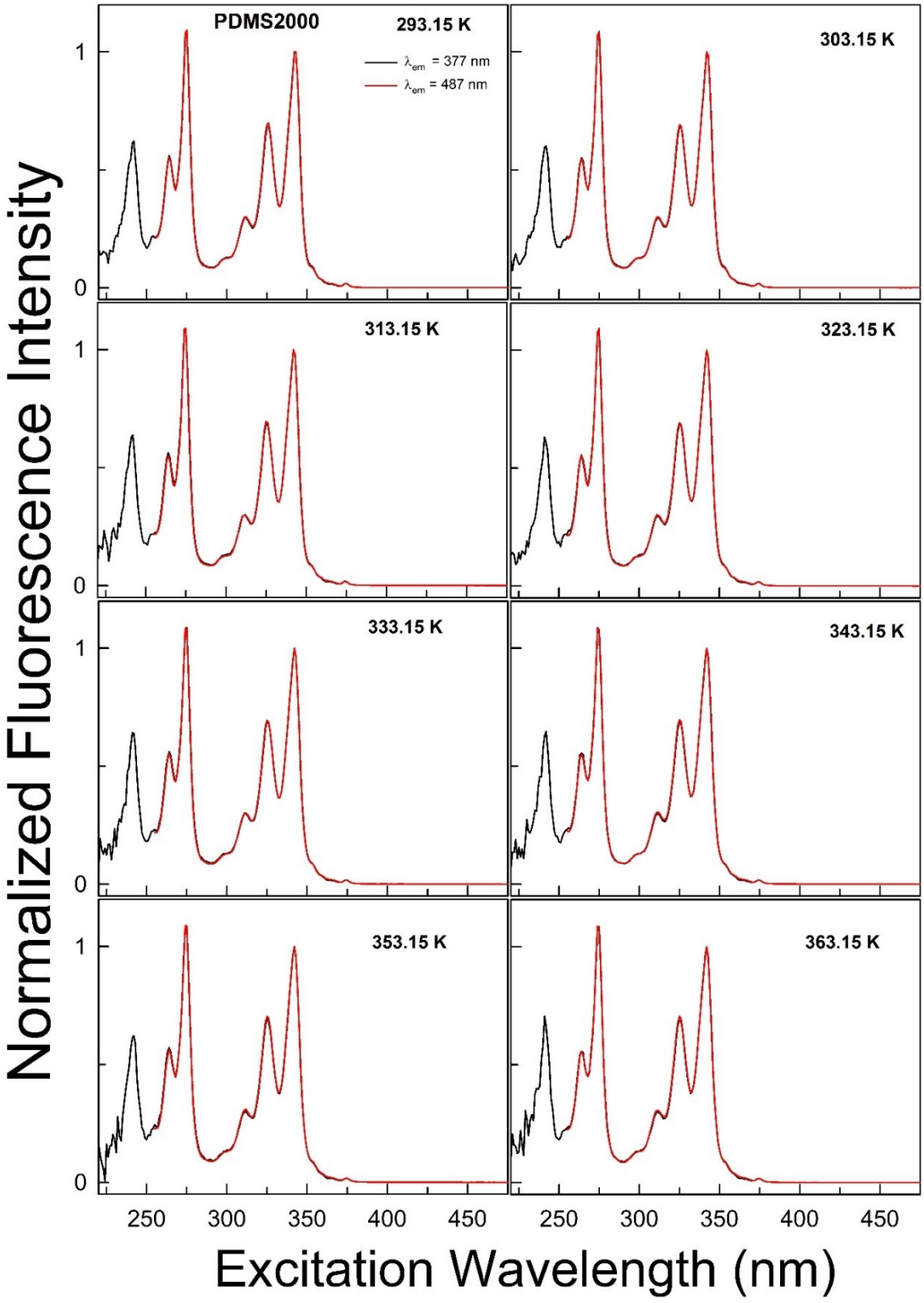

Fig. S2. Normalized emission wavelength-dependent fluorescence excitation spectra of 1Py(3)1Py (10 μM) dissolved in PDMS2000 recorded while monitoring the emission at 377 nm and 487 nm [emission and excitation slits are 2 and 2 nm, respectively] at different temperatures.

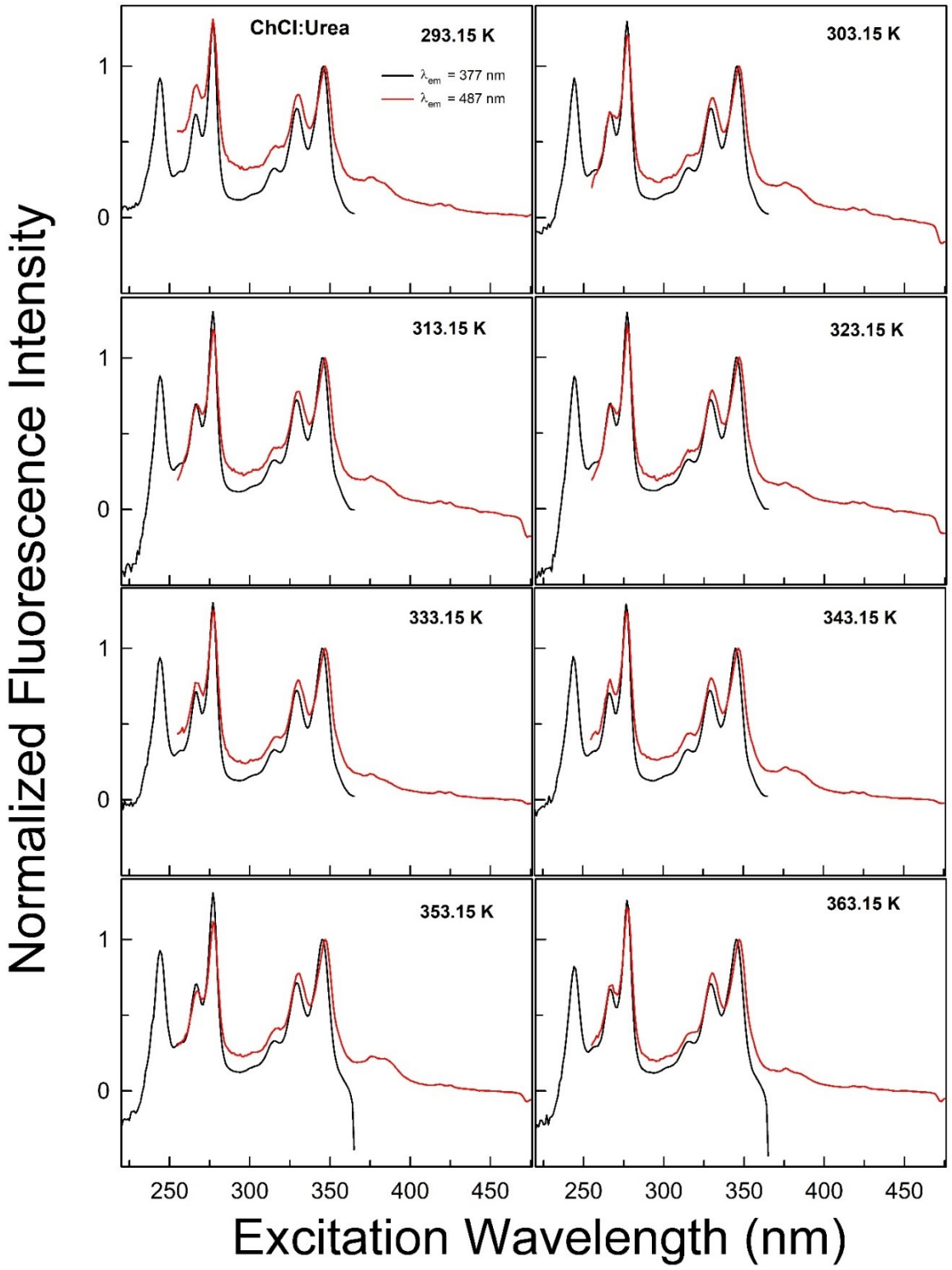

Fig. S3. Normalized emission wavelength-dependent fluorescence excitation spectra of 1Py(3)1Py (10 μM) dissolved in DES ChCl:Urea recorded while monitoring the emission at 377 nm and 487 nm [emission and excitation slits are 2 and 2 nm, respectively] at different temperatures.

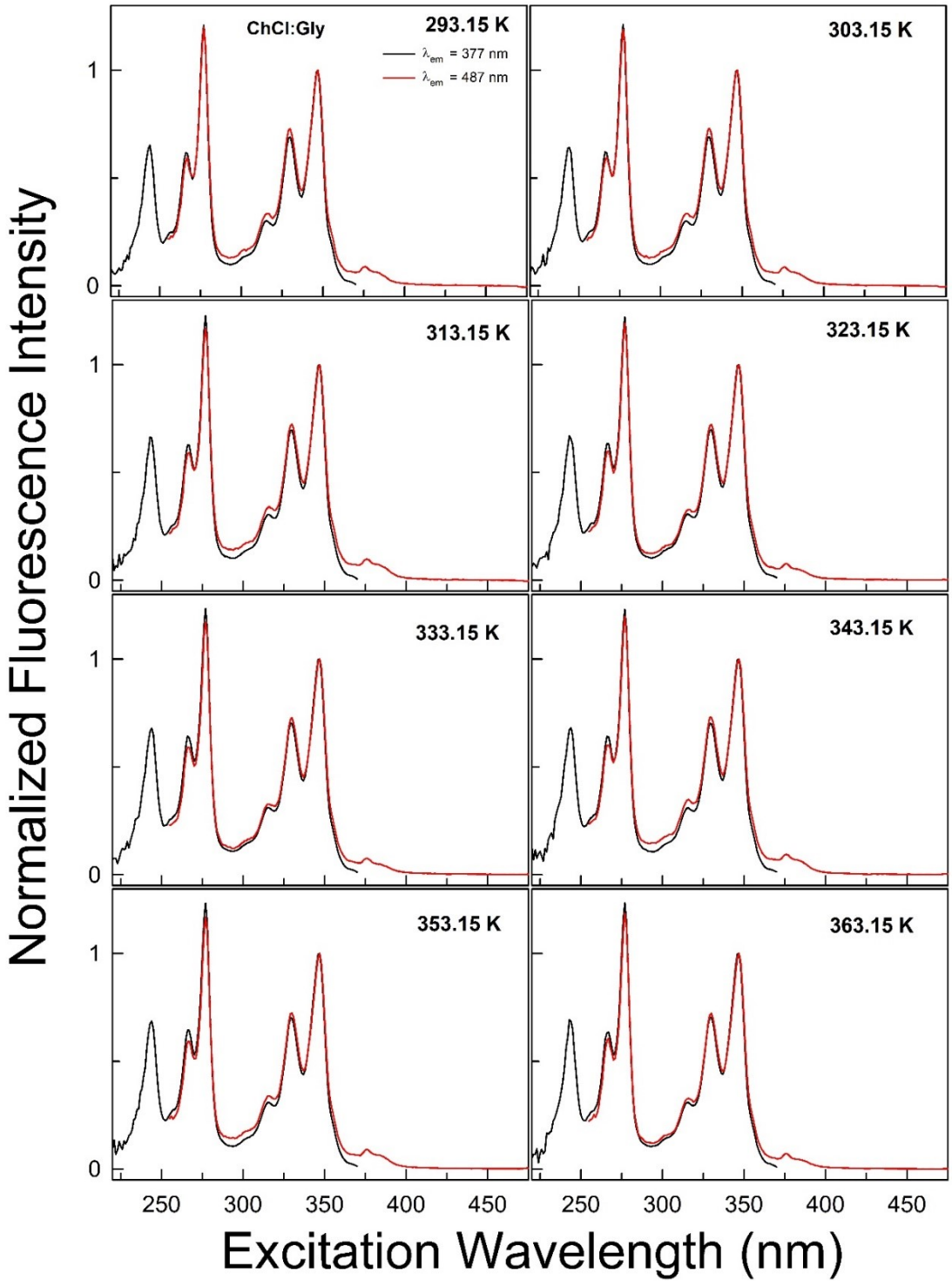

Fig. S4. Normalized emission wavelength-dependent fluorescence excitation spectra of 1Py(3)1Py (10 μM) dissolved in DES ChCl:Gly recorded while monitoring the emission at 377 nm and 487 nm [emission and excitation slits are 2 and 2 nm, respectively] at different temperatures.

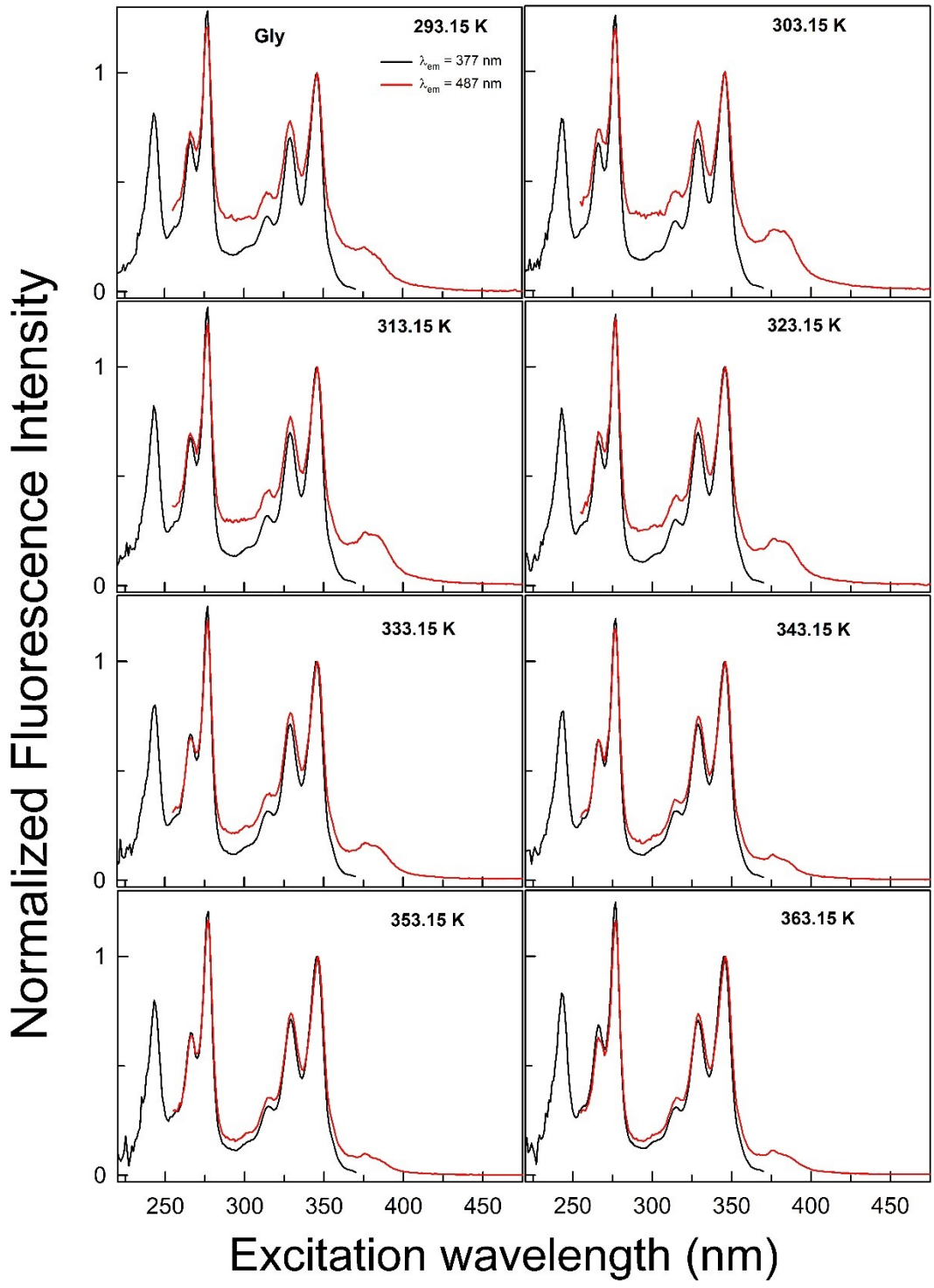

Fig. S5. Normalized emission wavelength-dependent fluorescence excitation spectra of 1Py(3)1Py (10 μM) dissolved in glycerol (Gly) recorded while monitoring the emission at 377 nm and 487 nm [emission and excitation slits are 2 and 2 nm, respectively] at different temperatures.