ELECTRONIC SUPPORTING INFORMATION (ESI)

Fluorescence of pyrene and its derivatives to reveal constituent and composition dependent solvation within hydrophobic deep eutectic solvents

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Table S1. Comparison of the Ratio of Band I-to-Band III Emission Intensities of Pyrene (Py I_1/I_3) Dissolved in DESs Investigated in this Work (λ_{ex} = 337 nm; slit: excitation/emission = 1.0/1.0 nm) with Solvent Systems Reported in Literature at 298.15 K (unless stated otherwise)

DES	**Py I_1/I_3**[a]	**solvent**	**Py I_1/I_3**[b]
Thy : Men		Ethaline	2.14
1 : 1	0.96	Glyceline	2.21
1 : 2	0.89	Reline	2.51
DA : Men			
1 : 1	0.78	[bmim][BF_4]	2.01
1 : 2	0.78	[bmim][PF_6]	1.92
Thy : DA		[$N_{1,4,4,4}$][Tf_2N]	1.92
2 : 1	0.93	[bmpyrr][Tf_2N]	2.10
1 : 1	0.87		
1 : 2	0.85	*n*-Butanol	1.05
		Cyclohexane	0.56

[a]Py I_1/I_3 at 293.15 K. (Present Work)
[b]ref 42

Table S2. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the Investigated DESs at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) are ≤±5%.

T (K) \ DES		Thy : Men		DA : Men		Thy : DA		
		1 : 1	1 : 2	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2
293.15	τ	66.0	77.1	77.2	85.6	78.8	77.9	76.9
	χ^2	1.24	1.20	1.33	1.02	1.14	1.23	1.30
303.15	τ	49.6	56.9	60.4	66.4	63.6	63.0	62.9
	χ^2	1.38	1.10	1.42	1.31	1.25	1.28	1.27
313.15	τ	39.6	45.1	47.3	54.9	52.3	52.0	51.8
	χ^2	1.29	1.22	1.16	1.07	1.17	1.23	1.34
323.15	τ	32.2	36.4	41.7	44.9	44.5	42.9	43.3
	χ^2	1.59	1.53	1.42	1.30	1.23	1.26	1.45
333.15	τ	27.3	30.5	36.1	38.2	36.7	36.8	35.9
	χ^2	1.46	1.31	1.29	1.10	1.21	1.37	1.35
343.15	τ	23.7	26.0	30.1	31.8	31.6	32.1	30.0
	χ^2	1.74	1.64	1.14	1.35	1.38	1.57	1.52
353.15	τ	21.3	22.9	26.0	28.9	26.4	24.6	26.2
	χ^2	1.57	1.52	1.18	1.10	1.29	1.54	1.53
363.15	τ	18.2	19.7	22.2	23.6	22.6	21.5	22.2
	χ^2	1.40	1.54	1.11	1.25	1.26	1.49	1.61

Table S3. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**Thy : Men (1 : 1)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		293.15	313.15	333.15	353.15	363.15
0.000	τ_0 (α_1)	66.0 (1.00)	39.6 (1.00)	27.3 (1.00)	21.3 (1.00)	18.2 (1.00)
	χ^2	1.24	1.29	1.46	1.57	1.40
0.005	τ_1 (α_1)	–	0.25 (0.02)	0.16 (0.04)	0.28 (0.03)	0.17 (0.04)
	τ_2 (α_2)	44.2 (1.00)	17.8 (0.98)	13.0 (0.96)	11.0 (0.97)	9.81 (0.96)
	χ^2	1.18	1.37	1.26	1.16	1.15
0.009	τ_1 (α_1)	–	0.31 (0.03)	0.56 (0.04)	0.08 (0.17)	0.01 (1.00)
	τ_2 (α_2)	30.4 (1.00)	12.6 (0.97)	8.96 (0.96)	6.90 (0.83)	6.20 (0.00)
	χ^2	1.19	1.28	1.27	0.97	1.13
0.014	τ_1 (α_1)	0.42 (0.02)	0.36 (0.05)	0.14 (0.11)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	23.4 (0.98)	9.93 (0.95)	6.59 (0.89)	5.10 (0.00)	4.53 (0.00)
	χ^2	1.43	1.15	1.13	1.32	1.00
0.019	τ_1 (α_1)	0.56 (0.03)	0.34 (0.06)	0.14 (0.13)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	19.3 (0.97)	8.20 (0.94)	5.30 (0.87)	4.07 (0.00)	3.66 (0.00)
	χ^2	1.39	1.25	0.96	1.03	1.05
0.023	τ_1 (α_1)	1.44 (0.04)	0.15 (0.12)	0.14 (0.15)	0.01 (1.00)	0.24 (1.00)
	τ_2 (α_2)	16.3 (0.96)	6.52 (0.88)	4.49 (0.85)	3.42 (0.00)	3.12 (0.00)
	χ^2	1.40	1.02	0.93	0.93	0.84
0.028	τ_1 (α_1)	0.52 (0.04)	0.15 (0.15)	0.37 (0.17)	0.01 (1.00)	0.01 (0.16)
	τ_2 (α_2)	13.7 (0.96)	5.57 (0.85)	3.91 (0.83)	2.97 (0.00)	2.67 (0.84)
	χ^2	1.26	1.07	0.89	1.06	0.94

0.033	τ_1 (α_1)	0.69 (0.06)	0.14 (0.16)	0.11 (1.00)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	12.3 (0.94)	5.03 (0.84)	3.34 (0.00)	0.00 (1.00)	2.25 (0.00)
	χ^2	1.25	1.03	0.96	1.17	1.12
0.037	τ_1 (α_1)	0.90 (0.07)	0.11 (0.24)	0.10 (0.31)	0.01 (1.00)	0.25 (0.22)
	τ_2 (α_2)	11.4 (0.93)	4.49 (0.76)	3.05 (0.69)	2.27 (0.00)	2.07 (0.78)
	χ^2	1.20	1.09	1.09	1.04	1.07
0.042	τ_1 (α_1)	0.53 (0.07)	0.14 (0.28)	0.14 (1.00)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	9.93 (0.93)	4.14 (0.72)	2.82 (0.00)	2.04 (0.00)	1.84 (0.00)
	χ^2	1.13	1.07	1.08	0.95	1.52

Table S4. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**Thy : Men (1 : 2)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		**293.15**	**313.15**	**333.15**	**353.15**	**363.15**
0.000	τ_o (α_1)	77.1 (1.00)	45.1 (1.00)	30.5 (1.00)	22.9 (1.00)	19.7 (1.00)
	χ^2	1.20	1.22	1.31	1.52	1.54
0.005	τ_1 (α_1)	0.23 (0.01)	0.14 (0.01)	0.20 (0.03)	0.25 (0.03)	0.52 (0.02)
	τ_2 (α_2)	49.5 (0.99)	25.9 (0.99)	16.0 (0.97)	11.8 (0.97)	10.7 (0.98)
	χ^2	1.10	1.20	1.34	1.21	1.18
0.009	τ_1 (α_1)	0.49 (0.01)	0.12 (0.01)	0.68 (0.04)	0.19 (0.06)	0.36 (0.04)
	τ_2 (α_2)	36.1 (0.99)	18.0 (0.99)	11.2 (0.96)	7.97 (0.94)	7.05 (0.96)
	χ^2	1.20	1.14	1.30	1.13	1.15
0.014	τ_1 (α_1)	0.68 (0.01)	0.18 (0.03)	0.37 (0.05)	0.21 (0.10)	0.23 (0.07)
	τ_2 (α_2)	28.3 (0.99)	14.0 (0.97)	8.27 (0.95)	5.87 (0.90)	5.02 (0.93)
	χ^2	1.11	1.24	1.20	0.96	1.19
0.019	τ_1 (α_1)	1.10 (0.02)	0.15 (0.08)	0.49 (0.06)	0.16 (0.14)	0.20 (0.11)
	τ_2 (α_2)	23.6 (0.98)	11.4 (0.92)	6.57 (0.94)	4.62 (0.86)	4.02 (0.89)
	χ^2	1.11	1.17	1.21	1.06	0.97
0.023	τ_1 (α_1)	0.77 (0.02)	0.62 (0.05)	0.17 (0.12)	0.13 (0.17)	0.18 (0.15)
	τ_2 (α_2)	20.2 (0.98)	9.86 (0.95)	5.36 (0.88)	3.82 (0.83)	3.35 (0.85)
	χ^2	1.14	1.27	0.88	0.92	1.13
0.028	τ_1 (α_1)	0.95 (0.03)	0.25 (0.07)	0.32 (0.10)	0.21 (0.12)	0.15 (0.20)
	τ_2 (α_2)	17.8 (0.97)	8.23 (0.93)	4.66 (0.90)	3.28 (0.88)	2.93 (0.80)
	χ^2	1.12	1.14	0.86	1.19	1.14

0.033	τ_1 (α_1)	0.41 (0.04)	0.22 (0.09)	0.26 (0.12)	0.15 (0.17)	0.12 (0.26)
	τ_2 (α_2)	15.5 (0.96)	7.24 (0.91)	4.14 (0.88)	2.90 (0.83)	2.55 (0.74)
	χ^2	1.22	0.99	0.98	1.13	1.32
0.037	τ_1 (α_1)	1.00 (0.05)	0.27 (0.12)	0.15 (0.13)	0.22 (0.22)	0.10 (0.30)
	τ_2 (α_2)	14.1 (0.95)	6.51 (0.88)	3.67 (0.87)	2.62 (0.78)	2.25 (0.70)
	χ^2	1.13	1.12	1.12	0.93	1.01
0.042	τ_1 (α_1)	0.85 (0.05)	0.32 (0.15)	0.25 (0.13)	0.12 (0.30)	0.32 (0.36)
	τ_2 (α_2)	12.6 (0.95)	5.75 (0.85)	3.27 (0.87)	2.36 (0.70)	2.02 (0.64)
	χ^2	1.35	0.97	1.04	1.09	1.02

Table S5. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**DA : Men (1 : 1)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		293.15	313.15	333.15	353.15	363.15
0.000	τ_o (α_1)	77.2 (1.00)	47.3 (1.00)	36.1 (1.00)	26.0 (1.00)	22.2 (1.00)
	χ^2	1.33	1.16	1.29	1.18	1.11
0.005	τ_1 (α_1)	0.79 (0.06)	1.51 (0.05)	0.40 (0.09)	0.48 (0.08)	0.38 (0.09)
	τ_2 (α_2)	44.0 (0.94)	27.4 (0.95)	21.4 (0.91)	15.1 (0.92)	11.1 (0.91)
	χ^2	1.16	1.21	1.00	1.12	1.05
0.009	τ_1 (α_1)	0.80 (0.08)	0.91 (0.06)	0.35 (0.12)	0.31 (0.11)	0.32 (0.13)
	τ_2 (α_2)	31.0 (0.92)	18.6 (0.94)	14.8 (0.88)	9.84 (0.89)	7.11 (0.87)
	χ^2	1.17	1.17	1.05	1.20	1.15
0.014	τ_1 (α_1)	0.78 (0.10)	0.82 (0.07)	0.41 (0.14)	0.40 (0.14)	0.31 (0.15)
	τ_2 (α_2)	24.1 (0.90)	14.5 (0.93)	11.6 (0.86)	7.54 (0.86)	5.50 (0.85)
	χ^2	1.26	1.07	1.01	1.24	1.03
0.019	τ_1 (α_1)	0.70 (0.12)	1.12 (0.10)	0.34 (0.18)	0.30 (0.18)	0.34 (0.18)
	τ_2 (α_2)	19.4 (0.88)	11.7 (0.90)	9.31 (0.82)	5.98 (0.82)	4.68 (0.82)
	χ^2	1.18	1.11	1.03	1.06	1.10
0.023	τ_1 (α_1)	0.60 (0.14)	0.89 (0.11)	0.35 (0.19)	0.34 (0.20)	0.28 (0.22)
	τ_2 (α_2)	16.2 (0.86)	9.94 (0.89)	7.65 (0.81)	5.11 (0.80)	4.00 (0.78)
	χ^2	1.29	1.16	1.11	0.92	1.00
0.028	τ_1 (α_1)	0.74 (0.16)	0.93 (0.12)	0.40 (0.23)	0.37 (0.22)	0.37 (0.21)
	τ_2 (α_2)	14.0 (0.84)	8.82 (0.88)	6.32 (0.77)	4.39 (0.78)	3.58 (0.79)
	χ^2	1.15	1.21	1.10	0.94	1.00

0.033	τ_1 (α_1)	0.65 (0.18)	0.67 (0.13)	0.31 (0.25)	0.30 (0.24)	0.27 (0.24)
	τ_2 (α_2)	12.0 (0.82)	7.62 (0.87)	5.59 (0.75)	3.79 (0.76)	3.18 (0.76)
	χ^2	1.17	1.14	0.95	1.10	1.02
0.037	τ_1 (α_1)	0.64 (0.19)	0.56 (0.14)	0.36 (0.26)	0.32 (0.27)	0.22 (0.28)
	τ_2 (α_2)	10.9 (0.81)	6.82 (0.86)	4.86 (0.74)	3.42 (0.73)	2.84 (0.72)
	χ^2	1.10	1.10	1.13	0.86	1.01
0.042	τ_1 (α_1)	0.55 (0.21)	0.86 (0.16)	0.30 (0.29)	0.25 (0.29)	0.21 (0.29)
	τ_2 (α_2)	9.52 (0.79)	6.22 (0.84)	4.40 (0.71)	3.08 (0.71)	2.58 (0.71)
	χ^2	1.11	1.09	1.04	1.05	1.16

Table S6. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**DA : Men (1 : 2)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		**293.15**	**313.15**	**333.15**	**353.15**	**363.15**
0.000	τ_o (α_1)	85.6 (1.00)	54.9 (1.00)	38.2 (1.00)	28.9 (1.00)	23.6 (1.00)
	χ^2	1.02	1.07	1.10	1.10	1.25
0.005	τ_1 (α_1)	0.86 (0.05)	0.63 (0.05)	0.43 (0.05)	0.45 (0.07)	0.44 (0.08)
	τ_2 (α_2)	53.1 (0.95)	29.8 (0.95)	19.5 (0.95)	15.4 (0.93)	11.9 (0.92)
	χ^2	1.17	1.23	1.23	1.21	1.29
0.009	τ_1 (α_1)	0.83 (0.07)	0.59 (0.08)	0.56 (0.09)	0.41 (0.11)	0.35 (0.12)
	τ_2 (α_2)	35.7 (0.93)	20.3 (0.92)	12.5 (0.91)	10.0 (0.89)	8.07 (0.88)
	χ^2	1.15	1.28	1.10	1.28	1.09
0.014	τ_1 (α_1)	0.80 (0.09)	0.54 (0.10)	0.48 (0.11)	0.42 (0.12)	0.30 (0.15)
	τ_2 (α_2)	27.7 (0.91)	15.2 (0.90)	9.72 (0.89)	7.42 (0.88)	6.05 (0.85)
	χ^2	1.03	1.26	1.17	1.13	1.12
0.019	τ_1 (α_1)	0.70 (0.10)	0.55 (0.13)	0.52 (0.14)	0.46 (0.16)	0.31 (0.18)
	τ_2 (α_2)	22.4 (0.90)	12.0 (0.87)	7.73 (0.86)	6.03 (0.84)	4.86 (0.82)
	χ^2	1.21	1.21	1.16	1.08	1.00
0.023	τ_1 (α_1)	0.70 (0.12)	0.56 (0.15)	0.49 (0.16)	0.37 (0.18)	0.31 (0.19)
	τ_2 (α_2)	19.1 (0.88)	10.2 (0.85)	6.53 (0.84)	4.96 (0.82)	4.07 (0.81)
	χ^2	1.26	1.20	1.15	1.04	1.10
0.028	τ_1 (α_1)	0.67 (0.13)	0.52 (0.17)	0.49 (0.17)	0.33 (0.19)	0.32 (0.21)
	τ_2 (α_2)	16.4 (0.87)	8.50 (0.83)	5.69 (0.83)	4.18 (0.81)	3.47 (0.79)
	χ^2	1.02	1.23	0.89	1.01	1.13

0.033	τ_1 (α_1)	0.66 (0.15)	0.37 (0.19)	0.42 (0.18)	0.30 (0.22)	0.27 (0.23)
	τ_2 (α_2)	14.3 (0.85)	7.31 (0.81)	4.87 (0.82)	3.68 (0.78)	2.98 (0.77)
	χ^2	1.20	1.06	1.10	1.01	1.10
0.037	τ_1 (α_1)	0.64 (0.17)	0.44 (0.20)	0.36 (0.21)	0.30 (0.24)	0.26 (0.29)
	τ_2 (α_2)	12.6 (0.83)	6.46 (0.80)	4.34 (0.79)	3.27 (0.76)	2.78 (0.71)
	χ^2	1.25	1.21	1.04	0.82	1.04
0.042	τ_1 (α_1)	0.60 (0.19)	0.42 (0.21)	0.36 (0.22)	0.40 (0.25)	0.27 (0.30)
	τ_2 (α_2)	11.1 (0.81)	5.78 (0.79)	3.88 (0.78)	2.95 (0.75)	2.58 (0.70)
	χ^2	1.20	1.07	0.93	1.03	1.02

Table S7. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**Thy : DA (2 : 1)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		**293.15**	**313.15**	**333.15**	**353.15**	**363.15**
0.000	τ_o (α_1)	78.8 (1.00)	52.3 (1.00)	36.7 (1.00)	26.4 (1.00)	22.6 (1.00)
	χ^2	1.14	1.17	1.21	1.29	1.26
0.005	τ_1 (α_1)	0.37 (0.02)	0.32 (0.02)	0.34 (0.03)	0.21 (0.04)	0.01 (1.00)
	τ_2 (α_2)	38.1 (0.98)	22.4 (0.98)	14.7 (0.97)	10.9 (0.96)	7.92 (0.00)
	χ^2	1.05	1.29	1.20	1.19	1.14
0.009	τ_1 (α_1)	0.26 (0.03)	0.45 (0.03)	0.28 (0.05)	0.31 (0.06)	0.01 (1.00)
	τ_2 (α_2)	25.7 (0.97)	14.4 (0.97)	9.26 (0.95)	6.07 (0.94)	5.02 (0.00)
	χ^2	1.11	1.12	1.07	1.11	1.03
0.014	τ_1 (α_1)	0.54 (0.03)	0.42 (0.04)	0.13 (1.00)	0.28 (0.09)	0.01 (1.00)
	τ_2 (α_2)	19.9 (0.97)	10.8 (0.96)	6.93 (0.00)	4.38 (0.91)	3.79 (0.00)
	χ^2	1.24	1.22	1.09	0.97	0.91
0.019	τ_1 (α_1)	0.42 (0.04)	0.46 (0.05)	0.01 (1.00)	0.38 (0.12)	0.26 (0.16)
	τ_2 (α_2)	15.9 (0.96)	8.65 (0.95)	5.35 (0.00)	3.58 (0.88)	3.03 (0.84)
	χ^2	1.16	1.29	1.03	1.15	0.94
0.023	τ_1 (α_1)	0.43 (0.06)	0.25 (0.09)	0.01 (1.00)	0.27 (0.16)	0.01 (1.00)
	τ_2 (α_2)	13.0 (0.94)	7.14 (0.91)	4.40 (0.00)	2.88 (0.84)	2.53 (0.00)
	χ^2	1.16	1.07	1.07	1.26	1.14
0.028	τ_1 (α_1)	0.42 (0.08)	0.31 (0.09)	0.02 (1.00)	0.30 (0.20)	0.01 (1.00)
	τ_2 (α_2)	10.8 (0.92)	6.04 (0.91)	3.90 (0.00)	2.36 (0.80)	2.24 (0.00)
	χ^2	1.26	1.01	0.89	1.08	1.14

0.033	τ_1 (α_1)	0.37 (0.10)	0.20 (0.14)	0.13 (0.26)	0.21 (0.24)	0.21 (0.29)
	τ_2 (α_2)	9.53 (0.90)	5.29 (0.86)	3.36 (0.74)	2.07 (0.76)	1.97 (0.71)
	χ^2	1.08	1.00	1.26	1.06	1.09
0.037	τ_1 (α_1)	0.19 (0.15)	0.24 (0.14)	0.08 (0.30)	0.35 (0.30)	0.01 (1.00)
	τ_2 (α_2)	8.23 (0.85)	4.63 (0.86)	2.99 (0.70)	1.89 (0.70)	1.65 (0.00)
	χ^2	1.27	1.08	1.15	1.15	1.04
0.042	τ_1 (α_1)	0.30 (0.15)	0.19 (0.20)	0.01 (1.00)	0.20 (0.33)	0.17 (0.33)
	τ_2 (α_2)	7.32 (0.85)	4.27 (0.80)	2.73 (0.00)	1.73 (0.67)	1.57 (0.67)
	χ^2	1.04	1.19	1.26	1.09	1.06

Table S8. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**Thy : DA (1 : 1)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		**293.15**	**313.15**	**333.15**	**353.15**	**363.15**
0.000	τ_o (α_1)	77.9 (1.00)	52.0 (1.00)	36.8 (1.00)	24.6 (1.00)	21.5 (1.00)
	χ^2	1.23	1.23	1.37	1.54	1.49
0.005	τ_1 (α_1)	0.24 (0.02)	0.22 (0.02)	0.08 (0.04)	0.06 (0.28)	0.01 (1.00)
	τ_2 (α_2)	42.5 (0.98)	24.8 (0.98)	18.0 (0.96)	11.4 (0.72)	7.74 (0.00)
	χ^2	1.17	1.12	1.32	1.10	1.27
0.009	τ_1 (α_1)	0.32 (0.03)	0.37 (0.04)	0.26 (0.06)	0.07 (0.31)	0.04 (0.80)
	τ_2 (α_2)	27.1 (0.97)	16.0 (0.96)	11.0 (0.94)	7.02 (0.69)	5.22 (0.20)
	χ^2	1.17	1.06	1.18	1.21	1.04
0.014	τ_1 (α_1)	0.46 (0.04)	0.23 (0.06)	0.33 (0.08)	0.05 (0.61)	0.01 (1.00)
	τ_2 (α_2)	22.4 (0.96)	11.7 (0.94)	8.06 (0.92)	5.22 (0.39)	4.01 (0.00)
	χ^2	1.12	1.02	1.30	1.04	0.79
0.019	τ_1 (α_1)	0.26 (0.06)	0.41 (0.07)	0.10 (0.24)	0.01 (1.00)	0.02 (1.00)
	τ_2 (α_2)	18.2 (0.94)	9.22 (0.93)	6.29 (0.76)	4.14 (0.00)	3.24 (0.00)
	χ^2	1.13	1.17	1.11	0.99	1.07
0.023	τ_1 (α_1)	0.31 (0.07)	0.20 (0.10)	0.11 (0.23)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	15.3 (0.93)	7.59 (0.90)	5.10 (0.77)	3.47 (0.00)	2.78 (0.00)
	χ^2	1.19	1.15	1.11	1.05	0.89
0.028	τ_1 (α_1)	0.24 (0.08)	0.21 (0.13)	0.12 (0.28)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	12.9 (0.92)	6.48 (0.87)	4.36 (0.72)	2.98 (0.00)	2.35 (0.00)
	χ^2	1.24	1.19	1.21	1.08	1.17

0.033	τ_1 (α_1)	0.26 (0.09)	0.20 (0.14)	0.12 (0.31)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	11.6 (0.91)	5.50 (0.86)	3.84 (0.69)	2.54 (0.00)	2.13 (0.00)
	χ^2	1.24	1.18	1.02	1.13	1.24
0.037	τ_1 (α_1)	0.25 (0.11)	0.17 (0.21)	0.20 (0.24)	0.05 (0.83)	0.01 (1.00)
	τ_2 (α_2)	10.1 (0.89)	4.88 (0.79)	3.34 (0.76)	2.26 (0.17)	1.93 (0.00)
	χ^2	1.29	0.96	1.15	1.20	1.16
0.042	τ_1 (α_1)	0.26 (0.13)	0.19 (0.21)	0.10 (0.47)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	9.18 (0.87)	4.45 (0.79)	3.11 (0.53)	2.02 (0.00)	1.80 (0.00)
	χ^2	1.17	1.11	0.84	0.97	1.08

Table S9. Recovered Excited-State Intensity Decay Parameters for Pyrene (10 μM; λ_{em} = 373 nm; excitation with a 340 nm nano-LED) Dissolved in the DES [**Thy : DA (1 : 2)**] at Varying Nitromethane Concentrations at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. The Errors Associated with Decay Times (τ/ns) and Pre-Exponential Factor (α) are ≤±5%.

$[CH_3NO_2]$/M \ *T* (K)		**293.15**	**313.15**	**333.15**	**353.15**	**363.15**
0.000	τ_o (α_1)	76.9 (1.00)	51.8 (1.00)	35.9 (1.00)	26.2 (1.00)	22.2 (1.00)
	χ^2	1.30	1.34	1.35	1.53	1.61
0.005	τ_1 (α_1)	0.35 (0.03)	0.32 (0.03)	0.12 (0.14)	0.24 (0.06)	0.24 (0.08)
	τ_2 (α_2)	39.2 (0.97)	27.4 (0.97)	16.3 (0.86)	12.3 (0.94)	10.8 (0.92)
	χ^2	1.09	1.09	1.05	1.05	1.21
0.009	τ_1 (α_1)	0.43 (0.04)	0.30 (0.06)	0.25 (0.11)	0.18 (0.13)	0.21 (0.10)
	τ_2 (α_2)	25.5 (0.96)	16.8 (0.94)	10.2 (0.89)	7.66 (0.87)	7.00 (0.90)
	χ^2	1.15	1.11	1.22	1.25	1.06
0.014	τ_1 (α_1)	0.42 (0.05)	0.40 (0.07)	0.14 (0.22)	0.09 (0.32)	0.01 (1.00)
	τ_2 (α_2)	18.7 (0.95)	12.3 (0.93)	7.51 (0.78)	5.51 (0.68)	5.15 (0.00)
	χ^2	1.17	1.15	1.04	0.98	0.89
0.019	τ_1 (α_1)	0.33 (0.09)	0.33 (0.10)	0.01 (1.00)	0.11 (0.30)	0.01 (1.00)
	τ_2 (α_2)	14.9 (0.91)	9.48 (0.90)	6.16 (0.00)	4.33 (0.70)	4.03 (0.00)
	χ^2	1.13	1.17	1.05	1.03	0.99
0.023	τ_1 (α_1)	0.27 (0.09)	0.36 (0.11)	0.02 (1.00)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	12.3 (0.91)	7.71 (0.89)	5.26 (0.00)	3.56 (0.00)	3.36 (0.00)
	χ^2	1.25	1.07	1.02	1.17	1.12
0.028	τ_1 (α_1)	0.33 (0.10)	0.29 (0.15)	0.05 (0.80)	0.01 (1.00)	0.01 (1.00)
	τ_2 (α_2)	10.5 (0.90)	6.57 (0.85)	4.50 (0.20)	3.09 (0.00)	2.88 (0.00)
	χ^2	1.10	1.12	1.10	1.18	1.11

0.033	τ_1 (α_1)	0.25 (0.13)	0.21 (0.20)	0.01 (1.00)	0.09 (0.48)	0.05 (0.79)
	τ_2 (α_2)	9.20 (0.87)	5.76 (0.80)	3.91 (0.00)	2.68 (0.52)	2.54 (0.21)
	χ^2	1.19	0.88	0.97	1.16	1.20
0.037	τ_1 (α_1)	0.32 (0.14)	0.35 (0.20)	0.01 (1.00)	0.09 (0.51)	0.05 (0.86)
	τ_2 (α_2)	8.38 (0.86)	5.11 (0.80)	3.45 (0.00)	2.42 (0.49)	2.31 (0.14)
	χ^2	1.26	1.14	1.19	1.20	0.90
0.042	τ_1 (α_1)	0.20 (0.18)	0.22 (0.24)	0.01 (1.00)	0.01 (1.00)	0.07 (0.98)
	τ_2 (α_2)	7.45 (0.82)	4.50 (0.76)	3.04 (0.00)	2.13 (0.00)	2.08 (0.02)
	χ^2	1.27	0.89	0.98	1.12	1.13

Table S10. Recovered Intensity Decay Parameters and Microviscosity (η_μ/ns) for Py-PDMS-Py (10 μM; λ_{em} = 480 nm; excitation with a 340 nm nano-LED) Dissolved in the Investigated DESs at Different Temperatures in the Range 293.15 K ≤ *T* ≤ 363.15 K. Excimer Decay Time (τ_E/ns) is Associated with an Error of ≤ ±5%.

T (K) \ DES		Thy : Men		DA : Men		Thy : DA		
		1 : 1	1 : 2	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2
293.15	τ_E	32.7	55.8	51.8	43.4	52.2	37.1	48.8
	χ^2	1.44	1.43	1.58	1.63	1.47	1.51	2.27
	η_μ	535 ± 16	1929 ± 35	1034 ± 20	526 ± 12	1036 ± 21	796 ± 18	872 ± 20
303.15	τ_E	30.3	35.5	42.7	35.5	44.0	36.2	42.3
	χ^2	1.21	1.34	1.48	1.41	1.47	1.45	2.12
	η_μ	299 ± 10	822 ± 23	639 ± 15	332 ± 9	653 ± 16	572 ± 14	604 ± 15
313.15	τ_E	29.5	31.0	36.2	24.3	36.9	31.5	36.0
	χ^2	1.12	1.23	1.44	1.43	1.38	1.46	2.00
	η_μ	181 ± 6	532 ± 17	411 ± 11	176 ± 7	396 ± 10	396 ± 11	392 ± 11
323.15	τ_E	24.2	30.7	31.7	19.0	31.5	28.6	30.7
	χ^2	1.12	1.21	1.42	1.42	1.25	1.23	1.96
	η_μ	105 ± 4	375 ± 12	296 ± 9	114 ± 6	267 ± 9	289 ± 9	272 ± 9
333.15	τ_E	18.5	26.7	27.9	17.6	25.9	25.2	26.6
	χ^2	1.14	1.33	1.34	1.27	1.17	1.27	1.86
	η_μ	65 ± 4	286 ± 10	246 ± 9	93 ± 6	188 ± 8	218 ± 8	198 ± 7
343.15	τ_E	12.2	23.2	24.5	16.4	22.6	22.1	22.8
	χ^2	1.23	1.43	1.22	1.37	1.13	1.33	1.84
	η_μ	37 ± 3	222 ± 9	201 ± 8	78 ± 5	148 ± 8	166 ± 8	154 ± 6
353.15	τ_E	9.18	19.5	20.9	10.2	19.8	19.1	19.8
	χ^2	1.15	1.20	1.67	1.33	1.03	1.46	1.81
	η_μ	26 ± 3	147 ± 8	138 ± 7	46 ± 5	120 ± 7	136 ± 7	122 ± 6
363.15	τ_E	6.85	15.6	14.9	7.91	17.0	16.7	17.0
	χ^2	1.22	1.24	1.44	1.47	1.05	1.67	1.83
	η_μ	19 ± 2	108 ± 7	96 ± 6	36 ± 4	102 ± 6	113 ± 6	104 ± 6

Table S11. Summary of Parameters Associated with Microviscosity (η_μ/ns) of the Investigated DESs According to the VFT Model Using Equation: $\ln \eta_\mu = A + \frac{B}{T - T_0}$

DES	*A*	*B*	T_0/K	R^2	${}_aE_{a,\eta\mu}$/kJ mol^{-1}
Thy : Men					
1 : 1	−9.5 ± 3.6	4010 ± 2046	39 ± 73	0.9984	44.1 ± 17.0
1 : 2	1.6 ± 1.2	489 ± 267	210 ± 29	0.9892	46.6 ± 2.2
DA : Men					
1 : 1	−1.3 ± 3.6	1533 ± 1583	106 ± 112	0.9892	30.7 ± 13.1
1 : 2	−1.0 ± 2.2	895 ± 670	170 ± 55	0.9887	40.4 ± 5.6
Thy : DA					
2 : 1	1.7 ± 0.5	437 ± 103	209 ± 13	0.9980	41.2 ± 1.5
1 : 1	0.1 ± 0.7	1059 ± 279	132 ± 25	0.9991	28.4 ± 2.5
1 : 2	0.8 ± 0.7	733 ± 209	171 ± 21	0.9983	33.7 ± 2.0

[a] $E_{a,\eta}$ is calculated at T = (298.15 K). Standard deviations are given with ± sign.

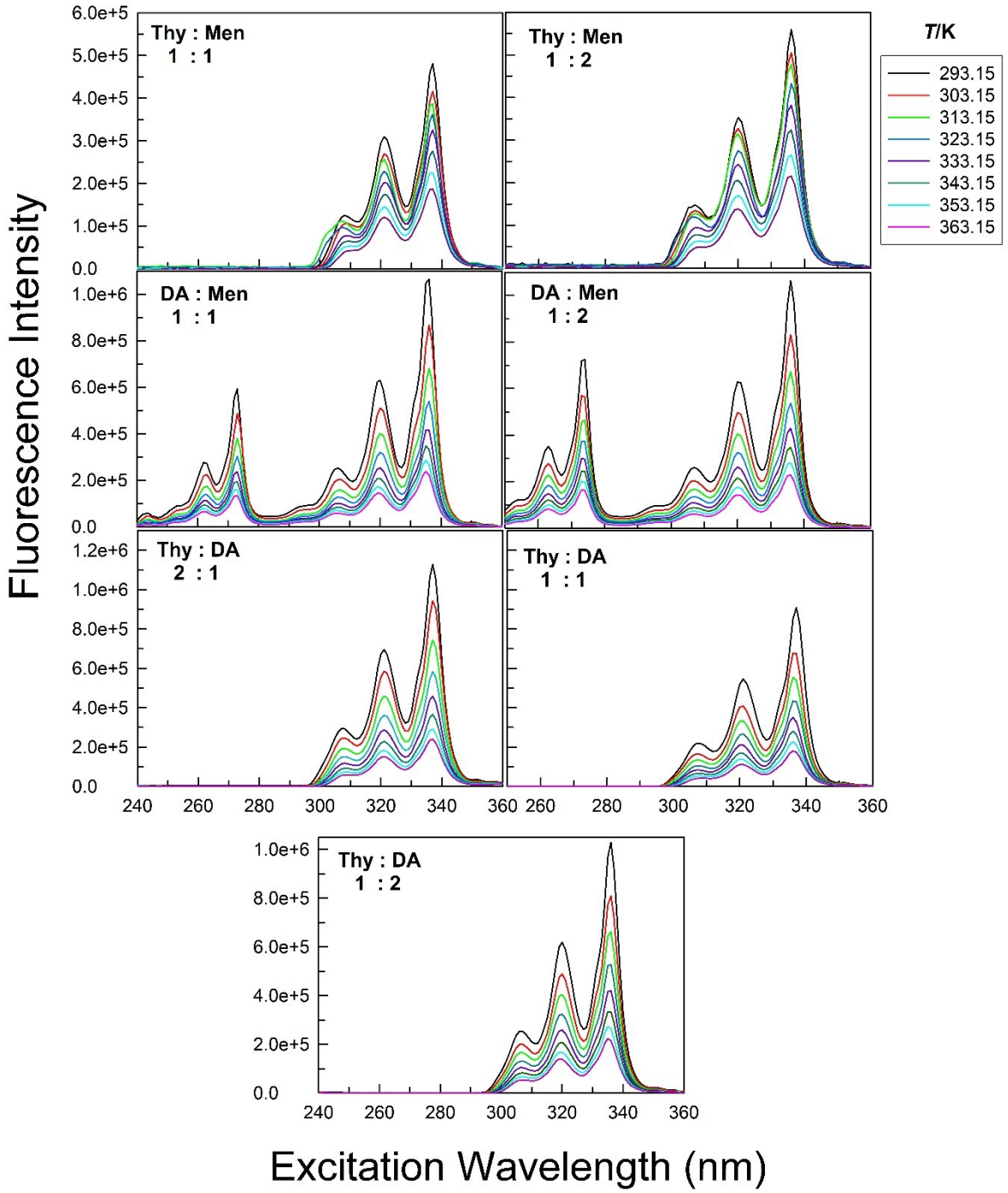

Figure S1. Steady-state fluorescence excitation spectra [λ_{em} = 373 nm; excitation and emission slits are 1.0 and 1.0 nm, respectively] of pyrene (10 μM) dissolved in the investigated DESs at different temperatures.

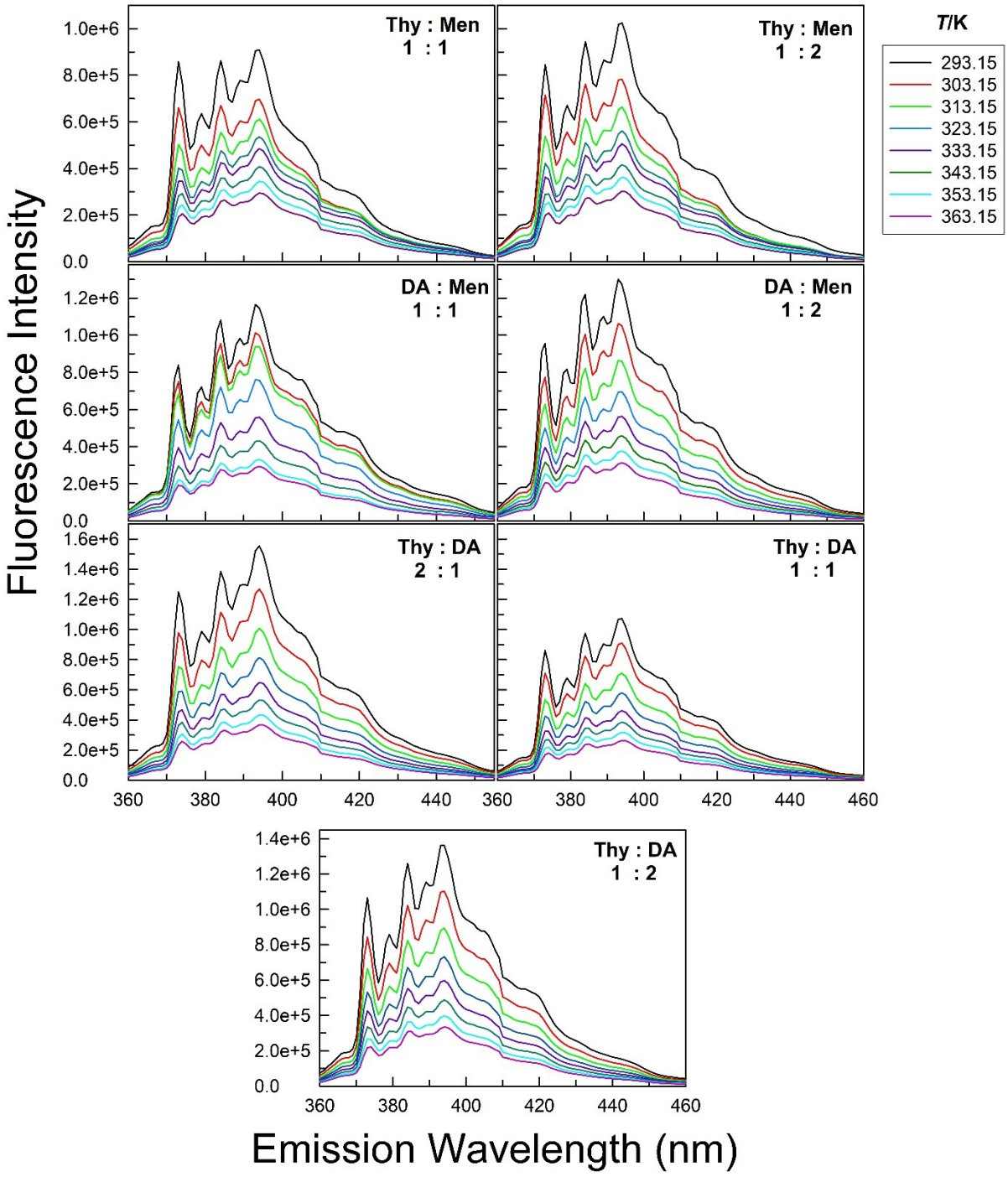

Figure S2. Steady-state fluorescence emission spectra [λ_{ex} = 337 nm; excitation and emission slits are 1.0 and 1.0 nm, respectively] of pyrene (10 μM) dissolved in the investigated DESs at different temperatures.

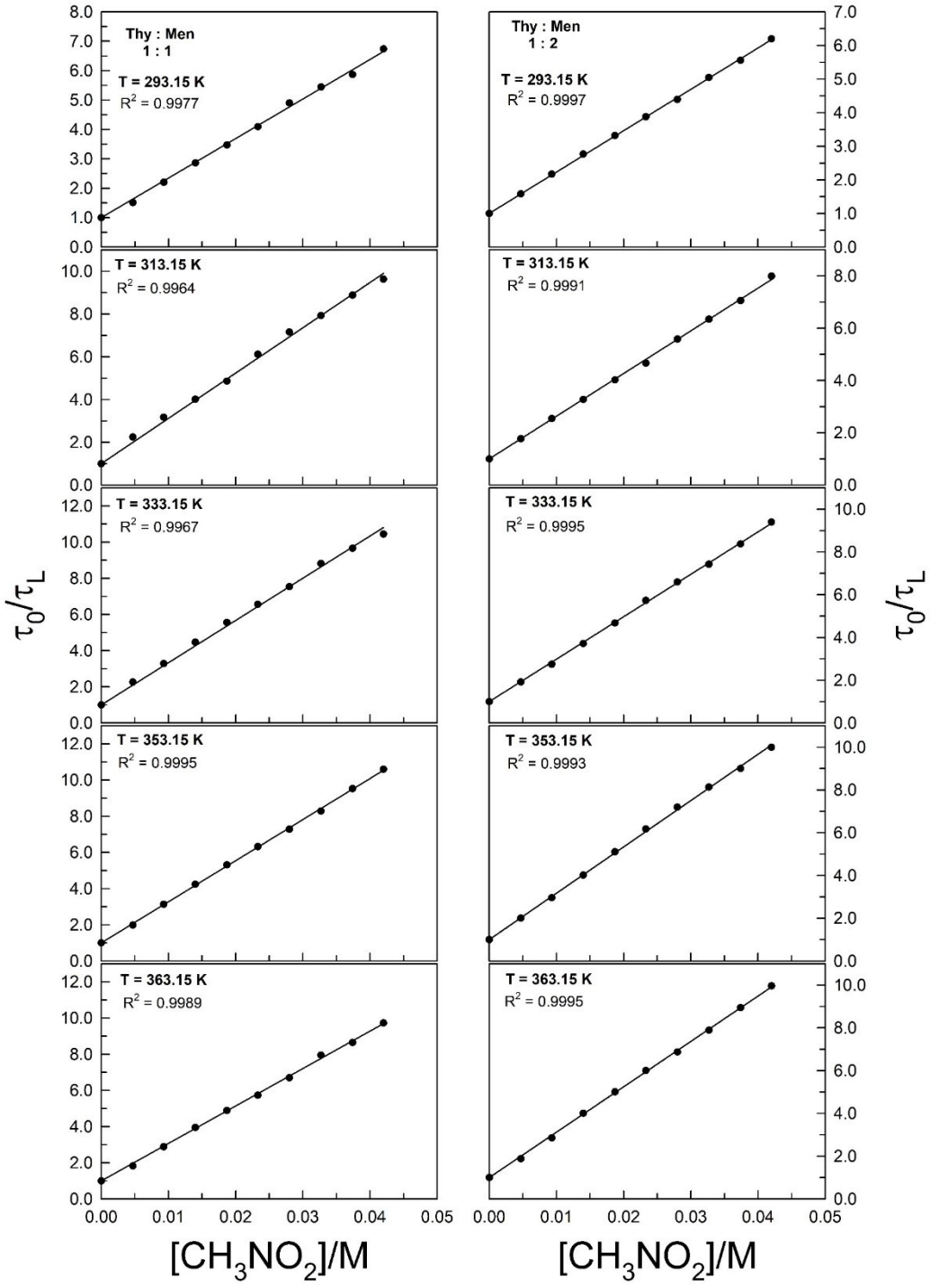

Figure S3. Plots of τ_0/τ *versus* [nitromethane] for pyrene (10 μM) within Thy : Men [1 : 1 (left) and 1 : 2 (right)] DES. Solid lines represent best fit to Stern-Volmer equation (**eq 1**). Estimated k_q (**eq 2**) at different temperatures are listed in **Table 2**. The error associated with τ_0/τ is $\leq \pm 5\%$.

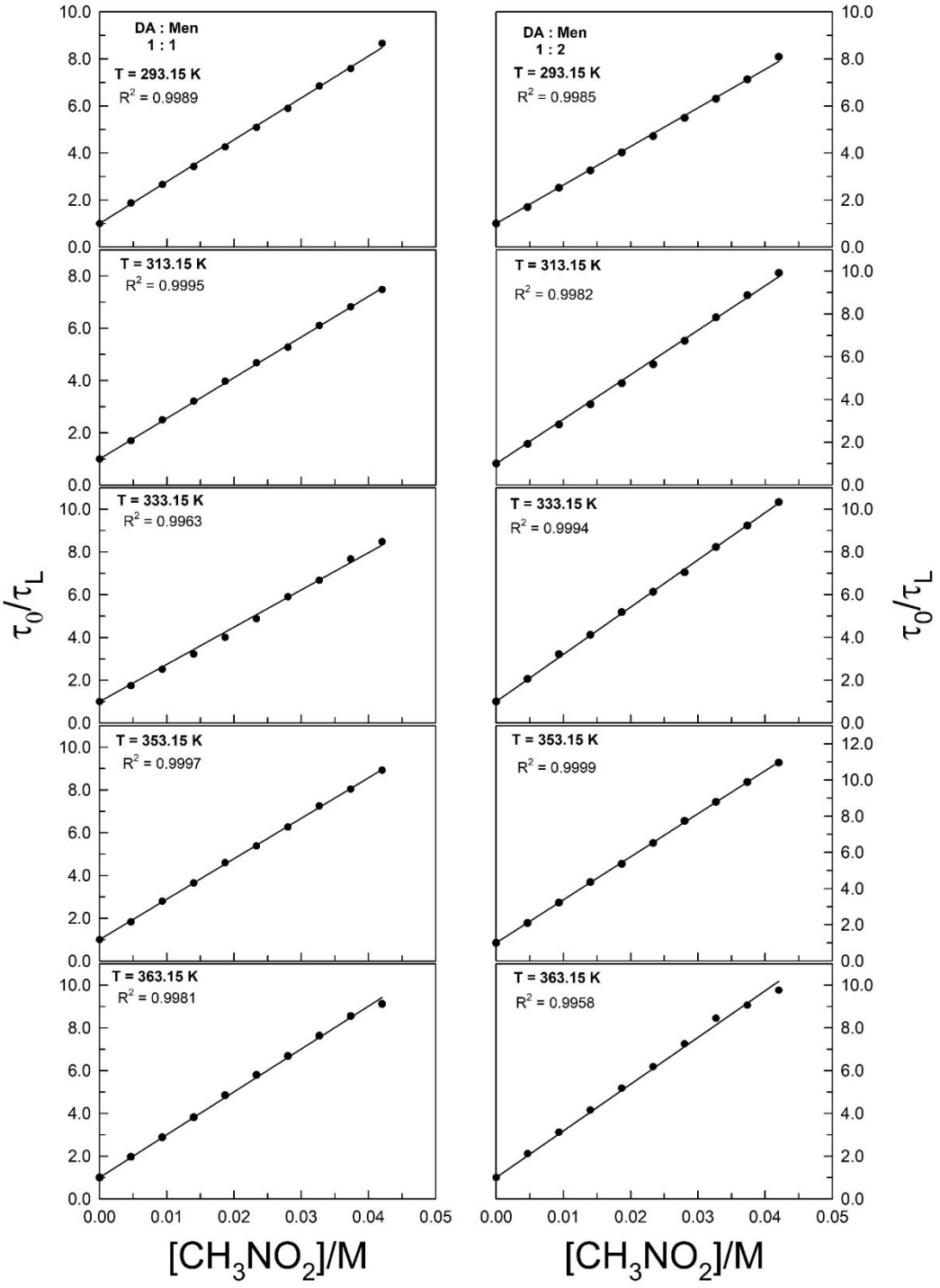

Figure S4. Plots of τ_0/τ *versus* [nitromethane] for pyrene (10 μM) within DA : Men [1 : 1 (left) and 1 : 2 (right)] DES. Solid lines represent best fit to Stern-Volmer equation (**eq 1**). Estimated k_q (**eq 2**) at different temperatures are listed in **Table 2**. The error associated with τ_0/τ is $\leq \pm 5\%$.

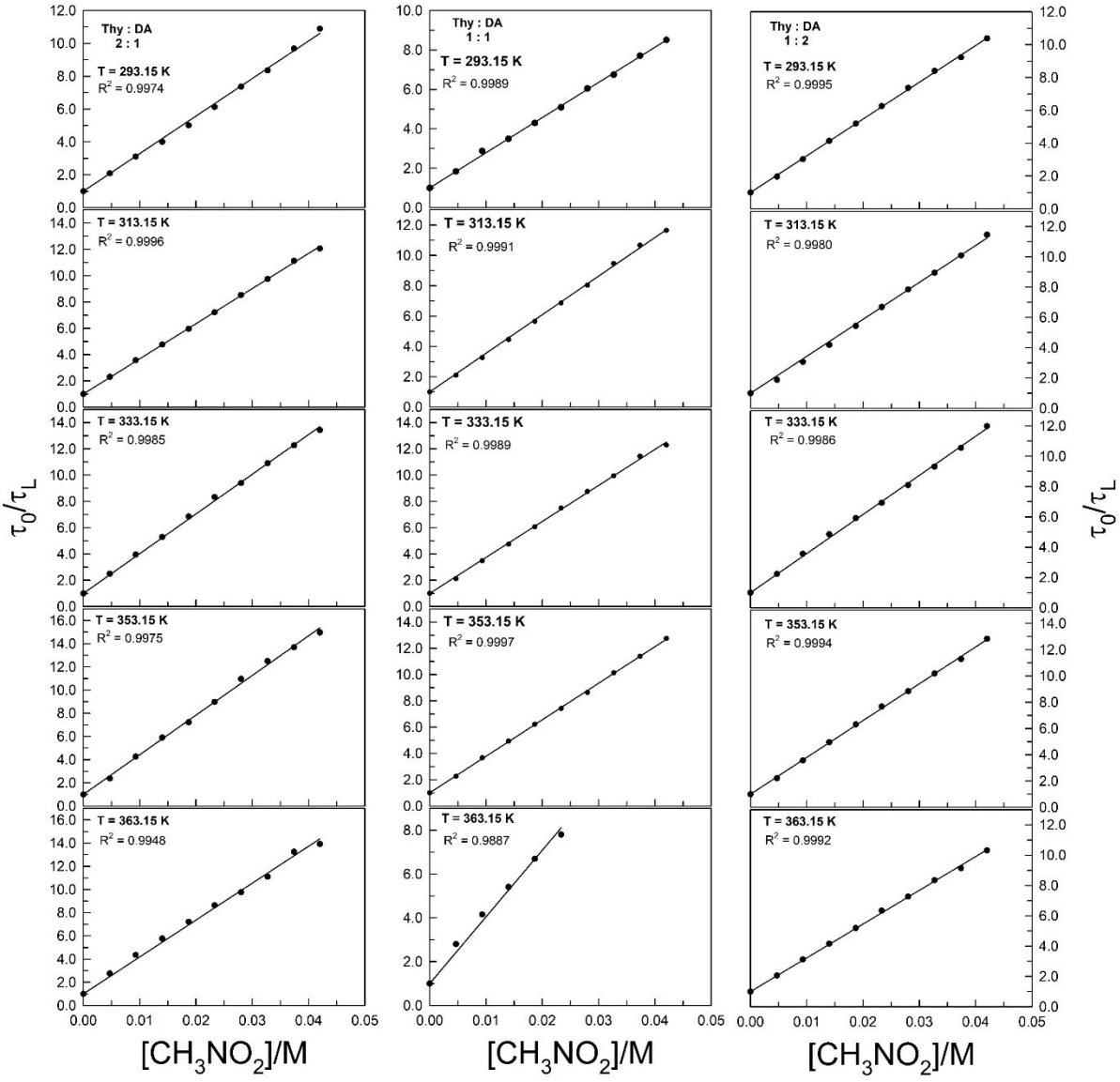

Figure S5. Plots of τ_0/τ *versus* [nitromethane] for pyrene (10 μM) within Thy : DA [2 : 1 (left), 1 : 1 (middle), and 1 : 2 (right)] DES. Solid lines represent best fit to Stern-Volmer equation (**eq 1**). Estimated k_q (**eq 2**) at different temperatures are listed in **Table 2**. The error associated with τ_0/τ is $\leq \pm 5\%$.

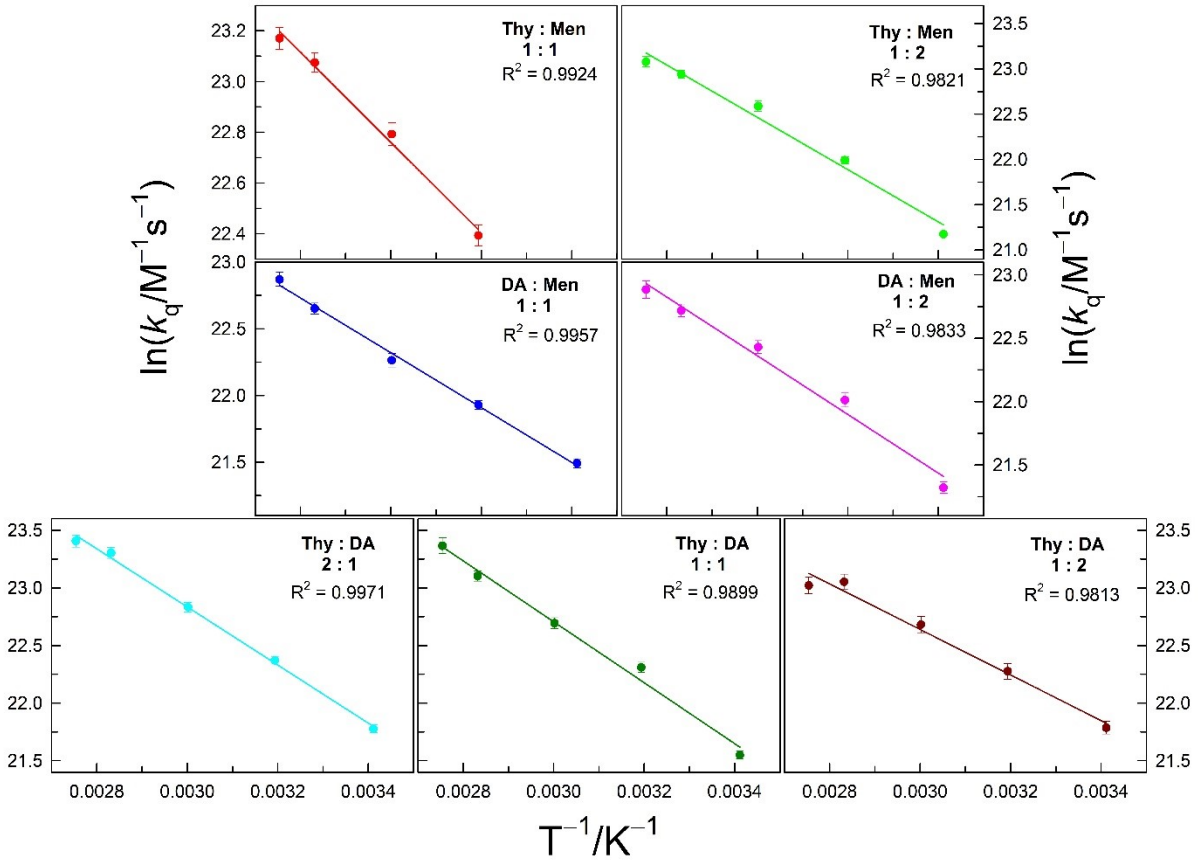

Figure S6. Variation of ln k_q with $1/T$ for pyrene-nitromethane fluorophore-quencher pair dissolved in the investigated DESs. Solid lines represent linear fit in agreement with empirical Arrhenius law. Recovered parameters − activation energy (E_a) and ln A are listed in **Table 3**.

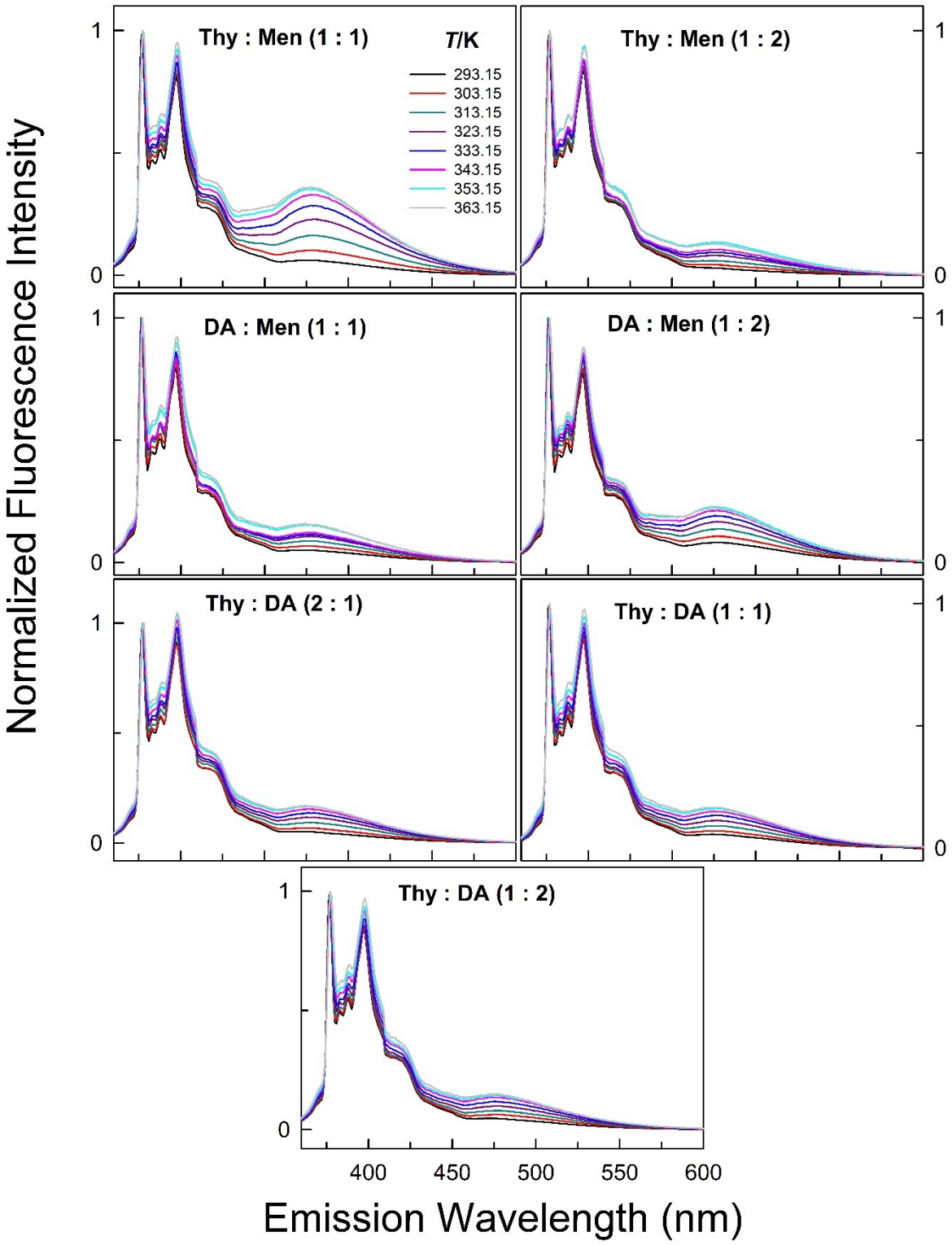

Figure S7. Normalized Fluorescence emission spectra of Py-PDMS-Py (10 μM, λ_{ex} = 340 nm; excitation and emission slits are 1.0 and 1.0 nm, respectively) dissolved in the investigated DESs at different temperatures (293.15 K – 363.15 K).

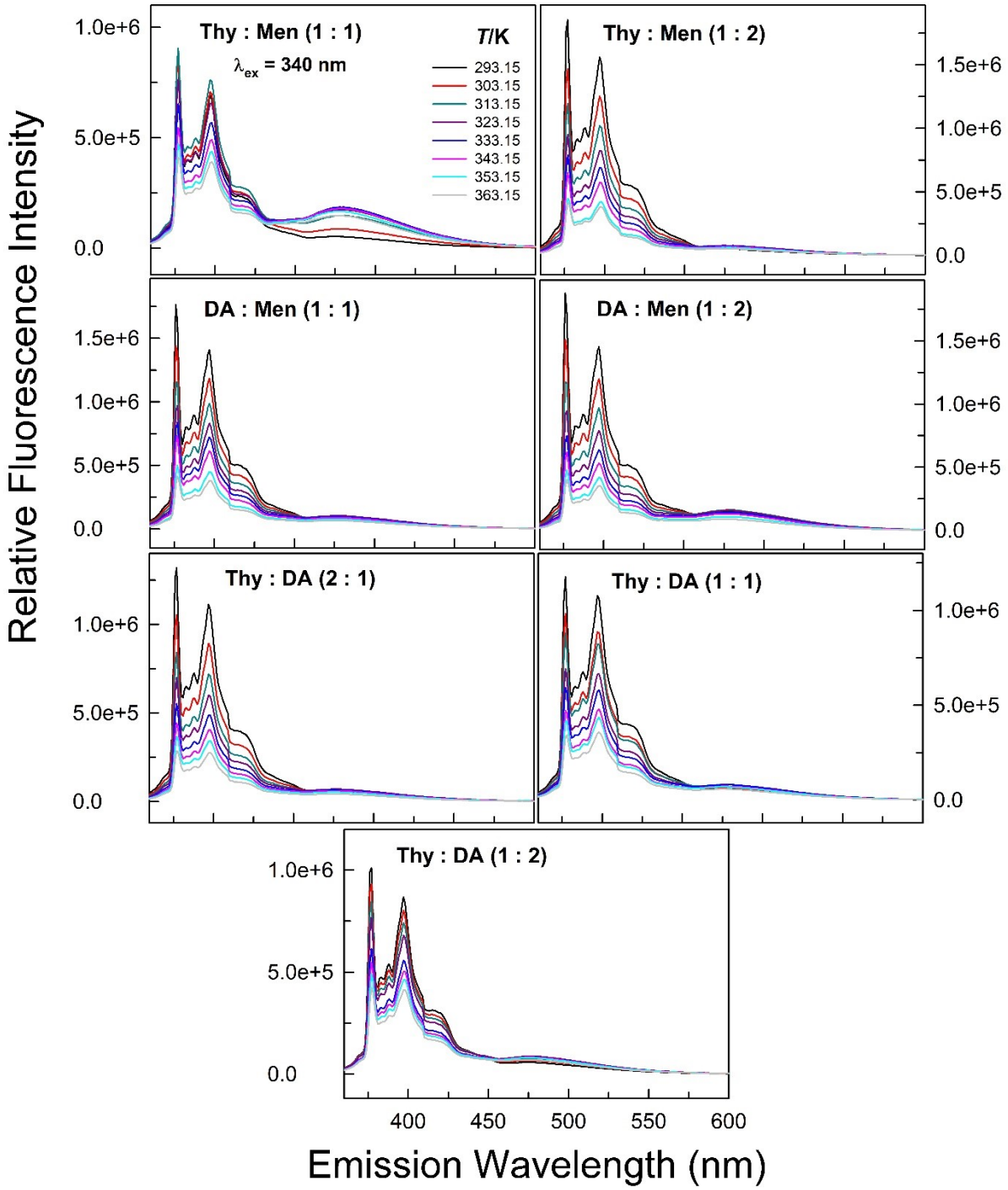

Figure S8. Relative Fluorescence emission spectra of Py-PDMS-Py (10 μM, λ_{ex} = 340 nm; excitation and emission slits are 1.0 and 1.0 nm, respectively) dissolved in the investigated DESs at different temperatures (293.15 K – 363.15 K).

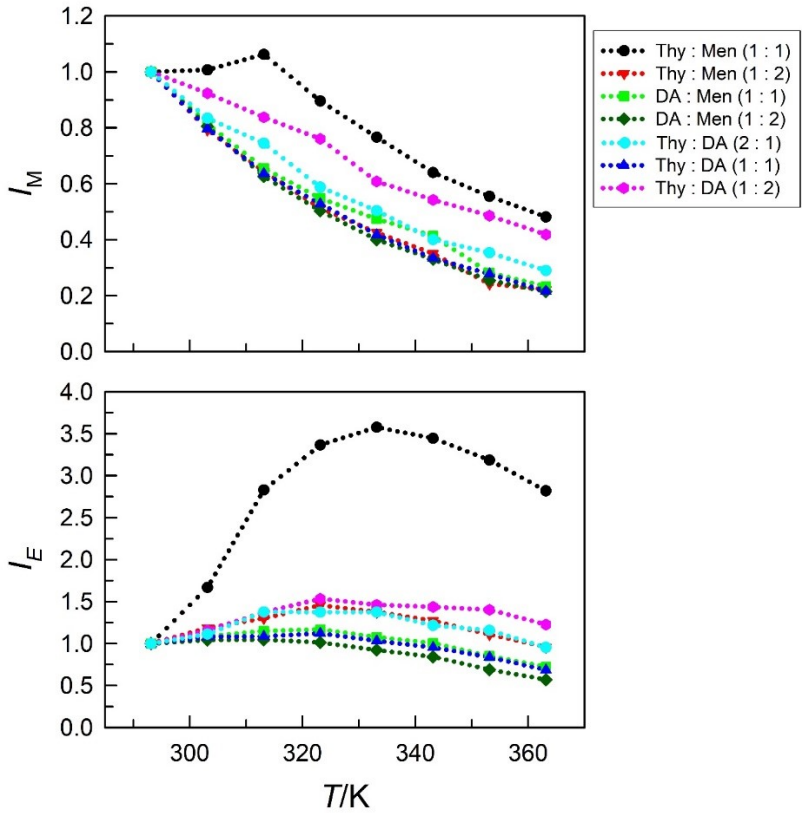

Figure S9. Variation of I_M and I_E with temperature for Py-PDMS-Py dissolved in the investigated DESs. The error associated with I_M and I_E is $\leq \pm 5\%$.

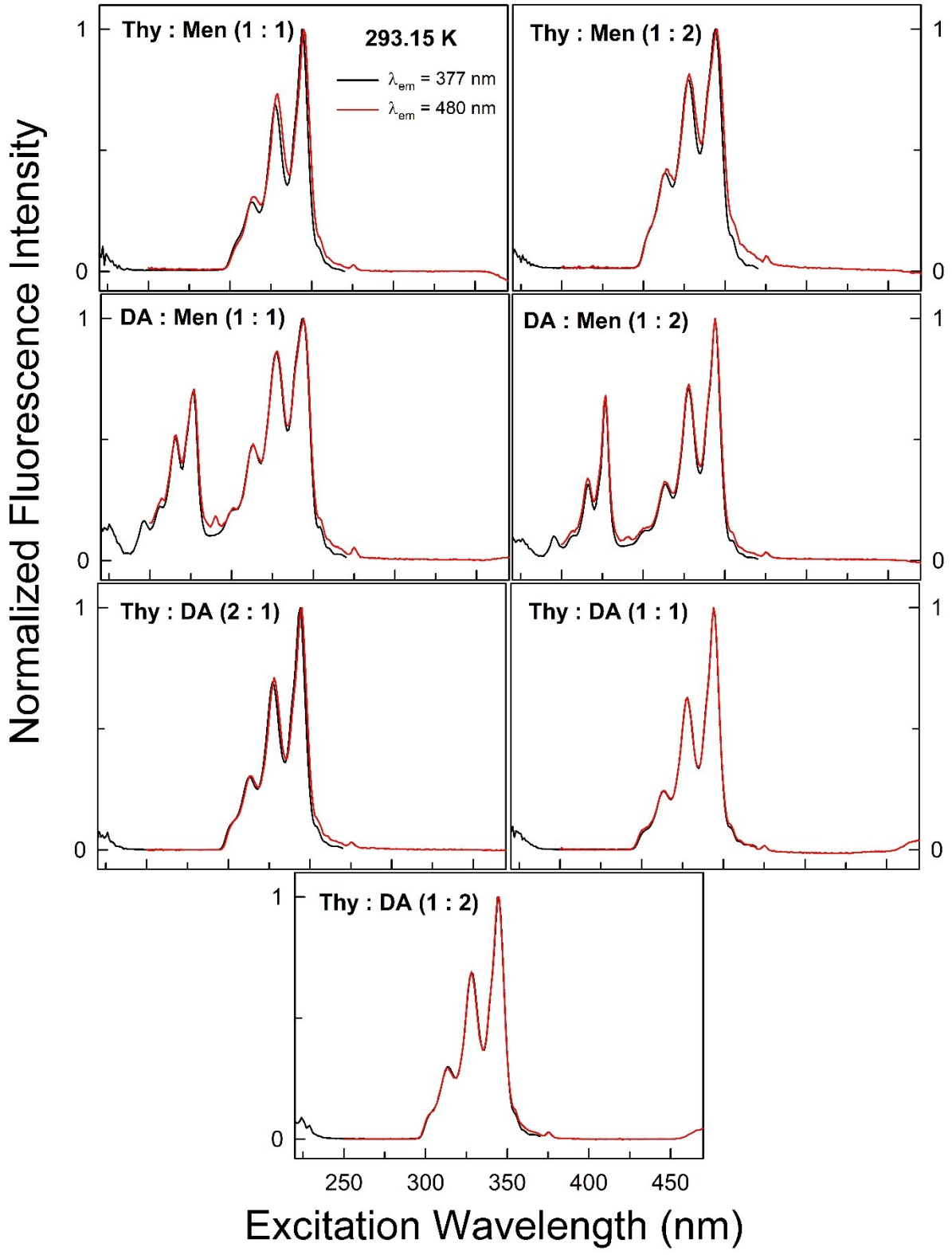

Figure S10. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 293.15 K.

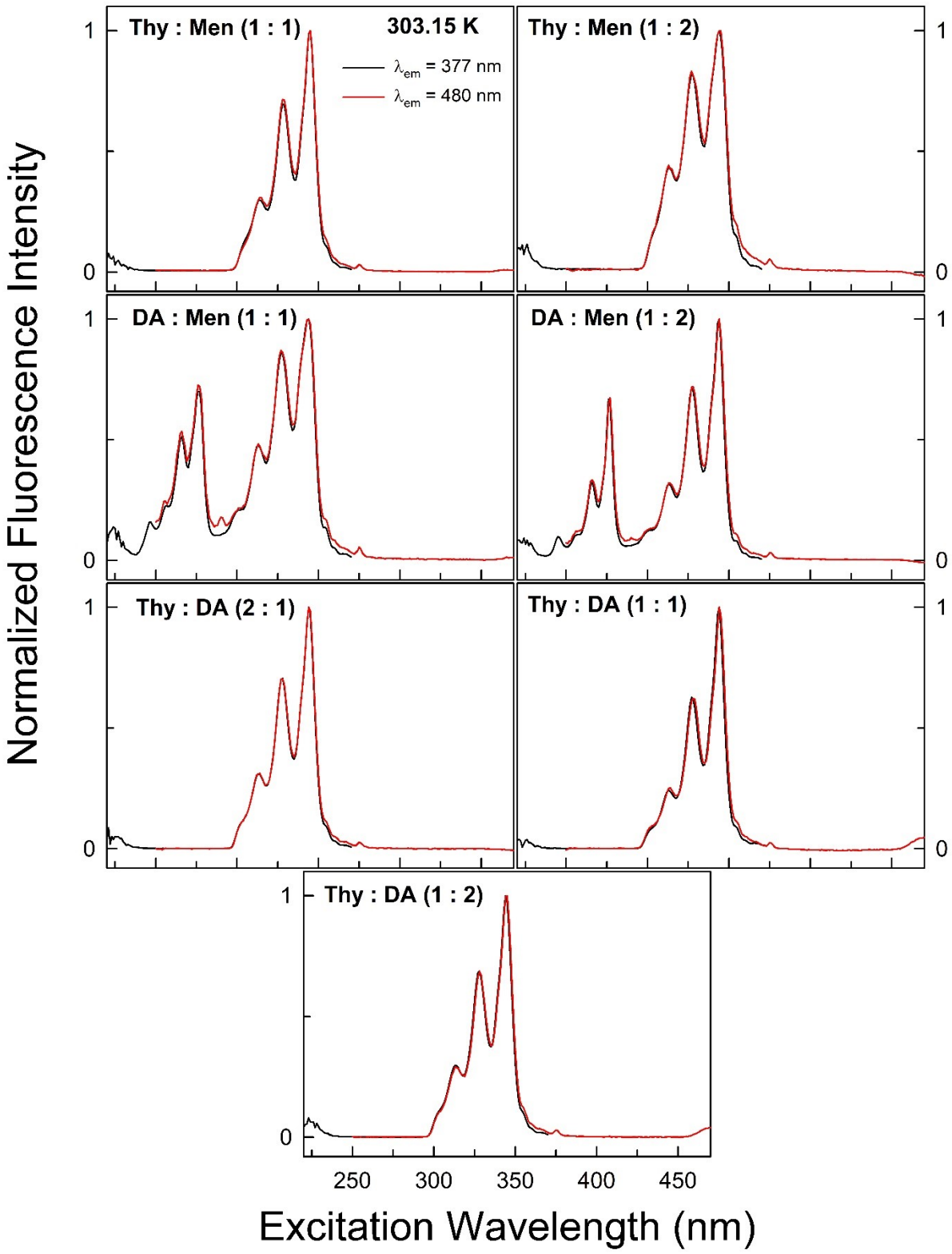

Figure S11. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 303.15 K.

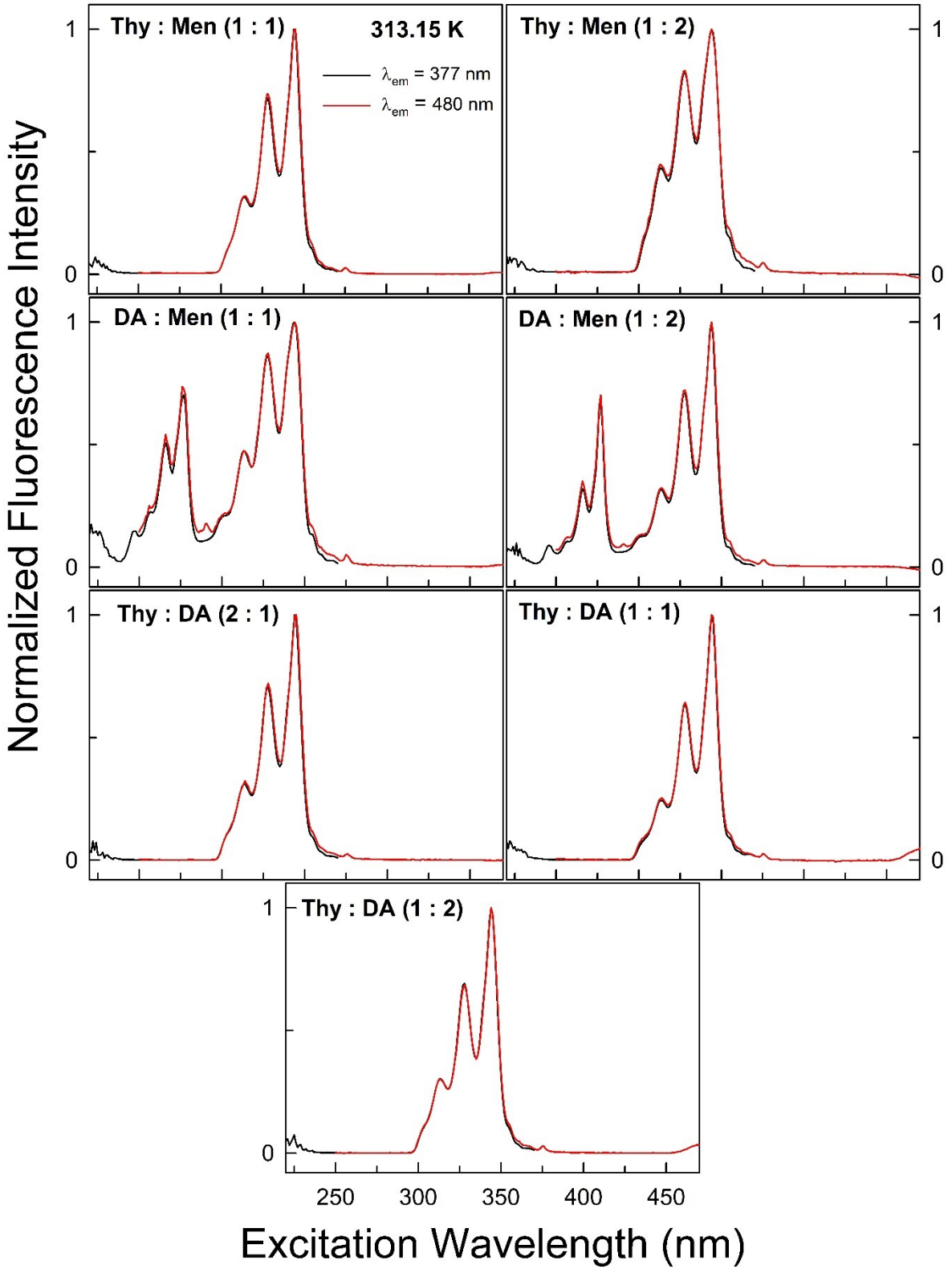

Figure S12. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 313.15 K.

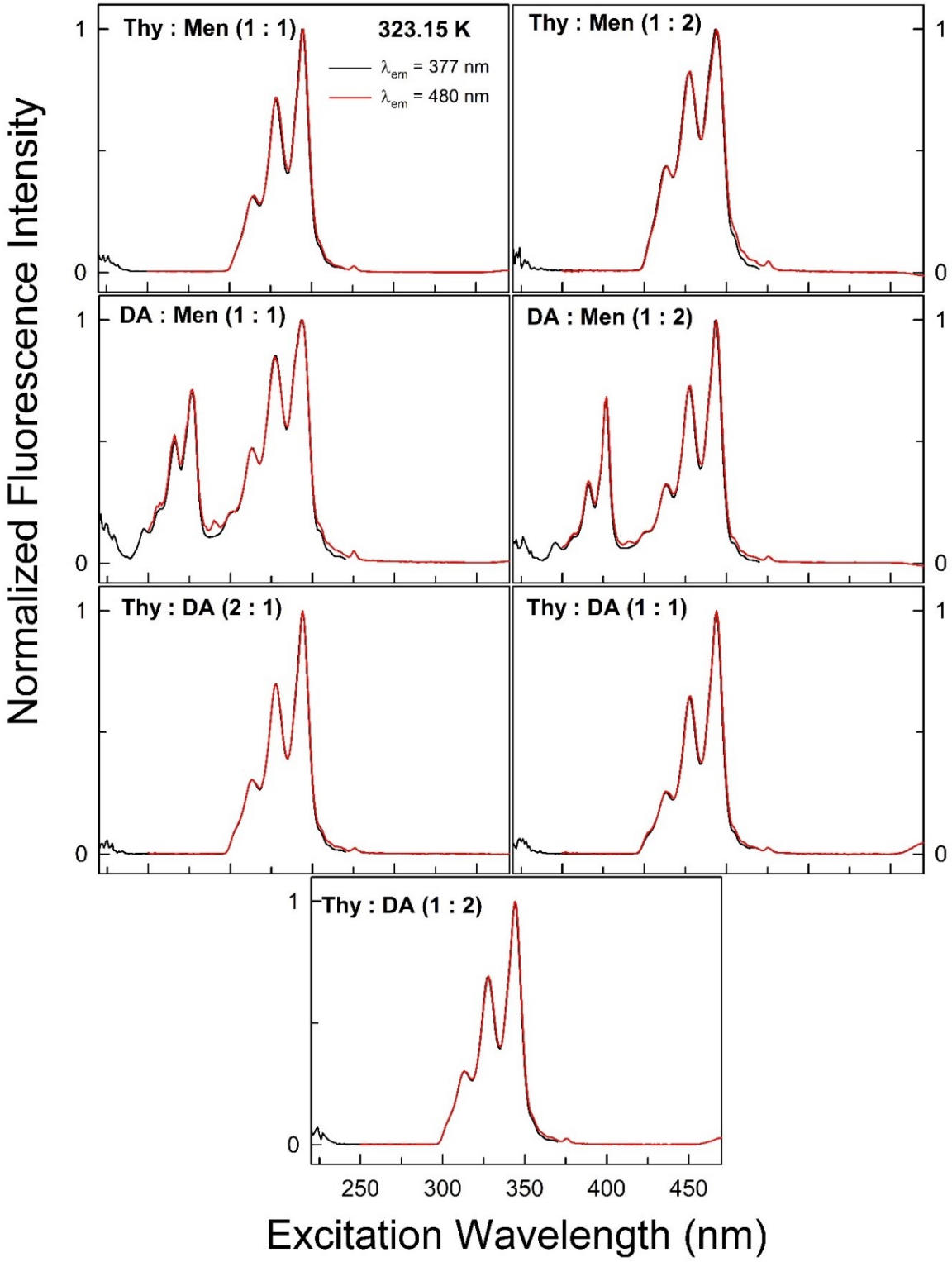

Figure S13. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 323.15 K.

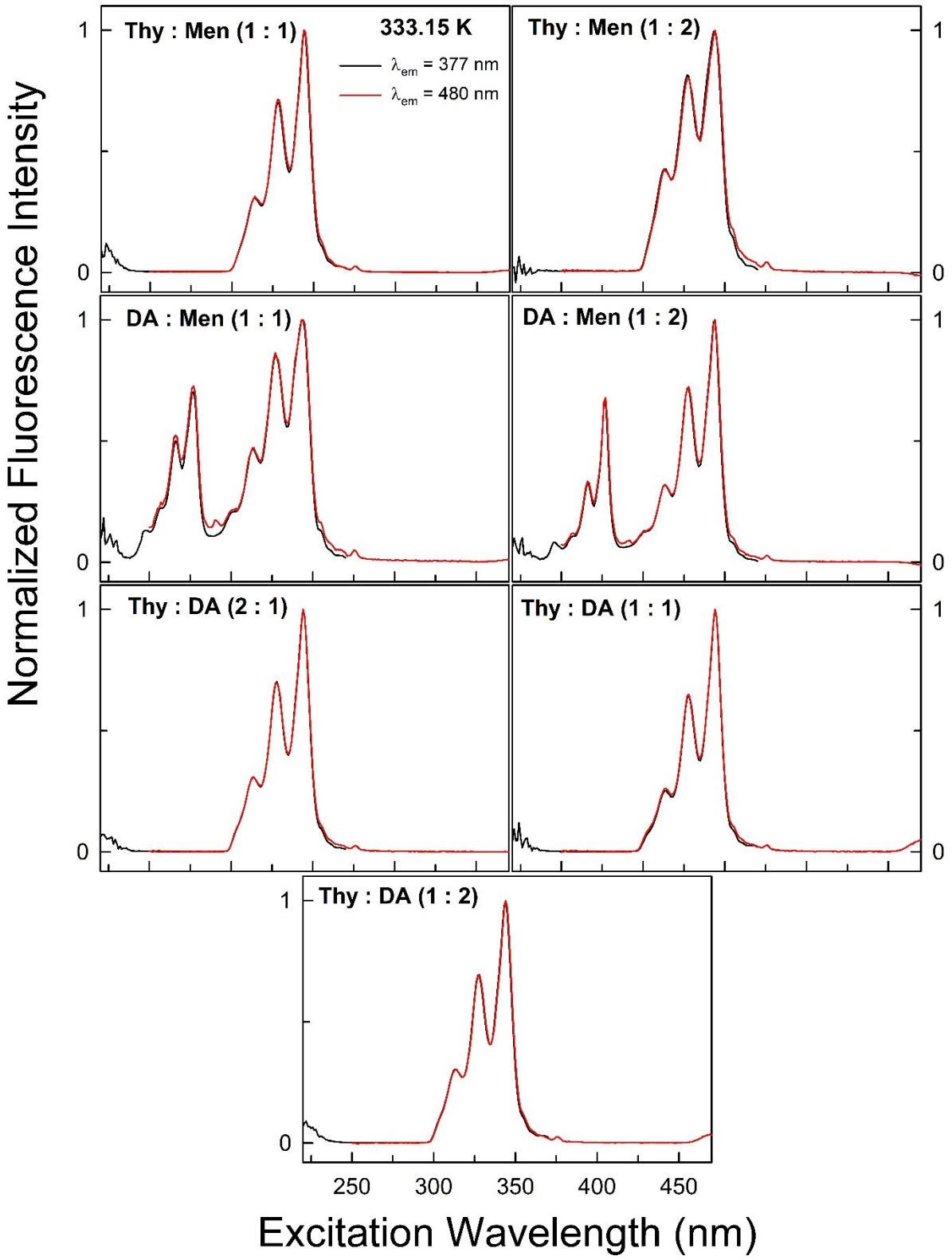

Figure S14. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 333.15 K.

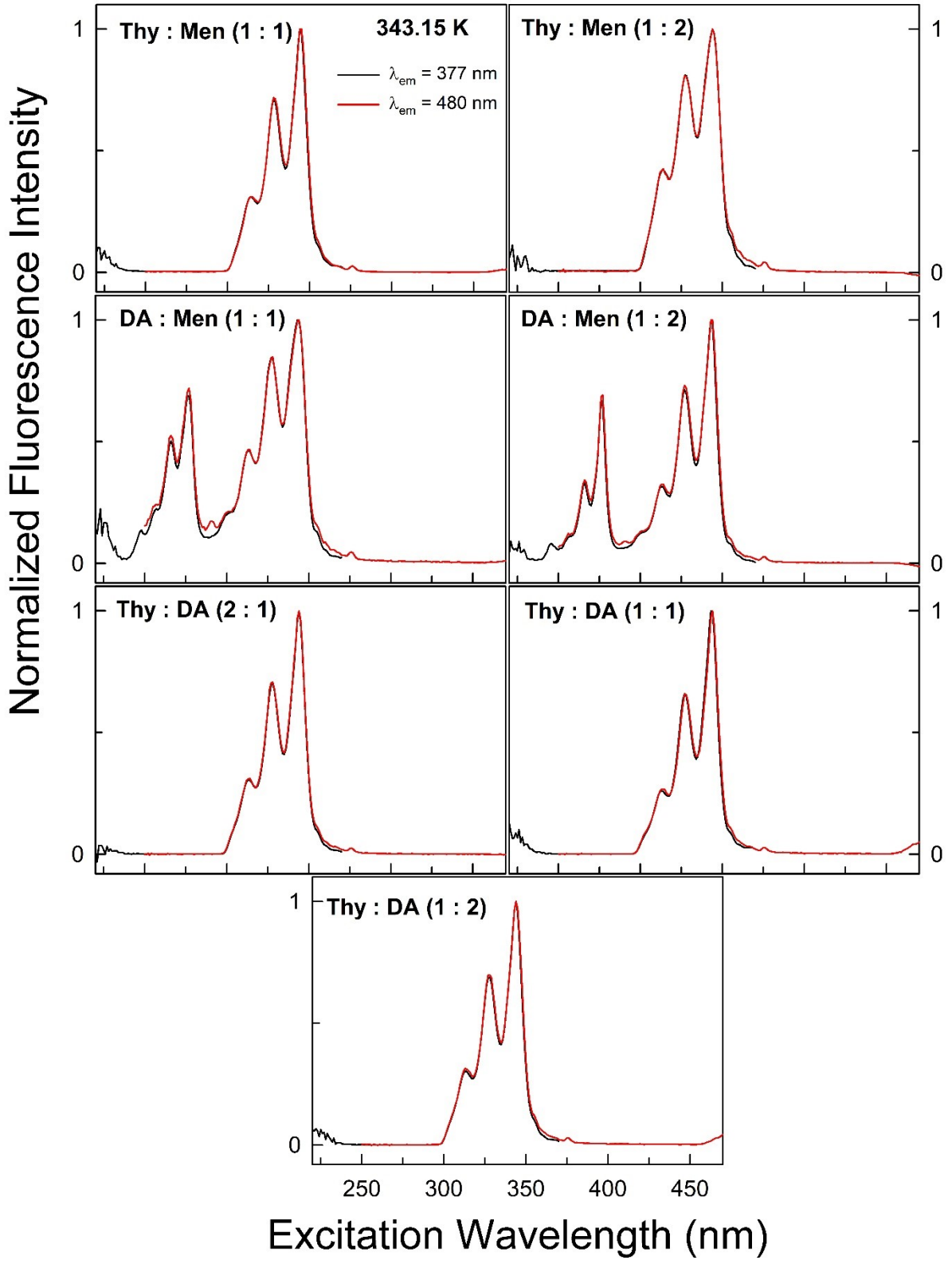

Figure S15. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 343.15 K.

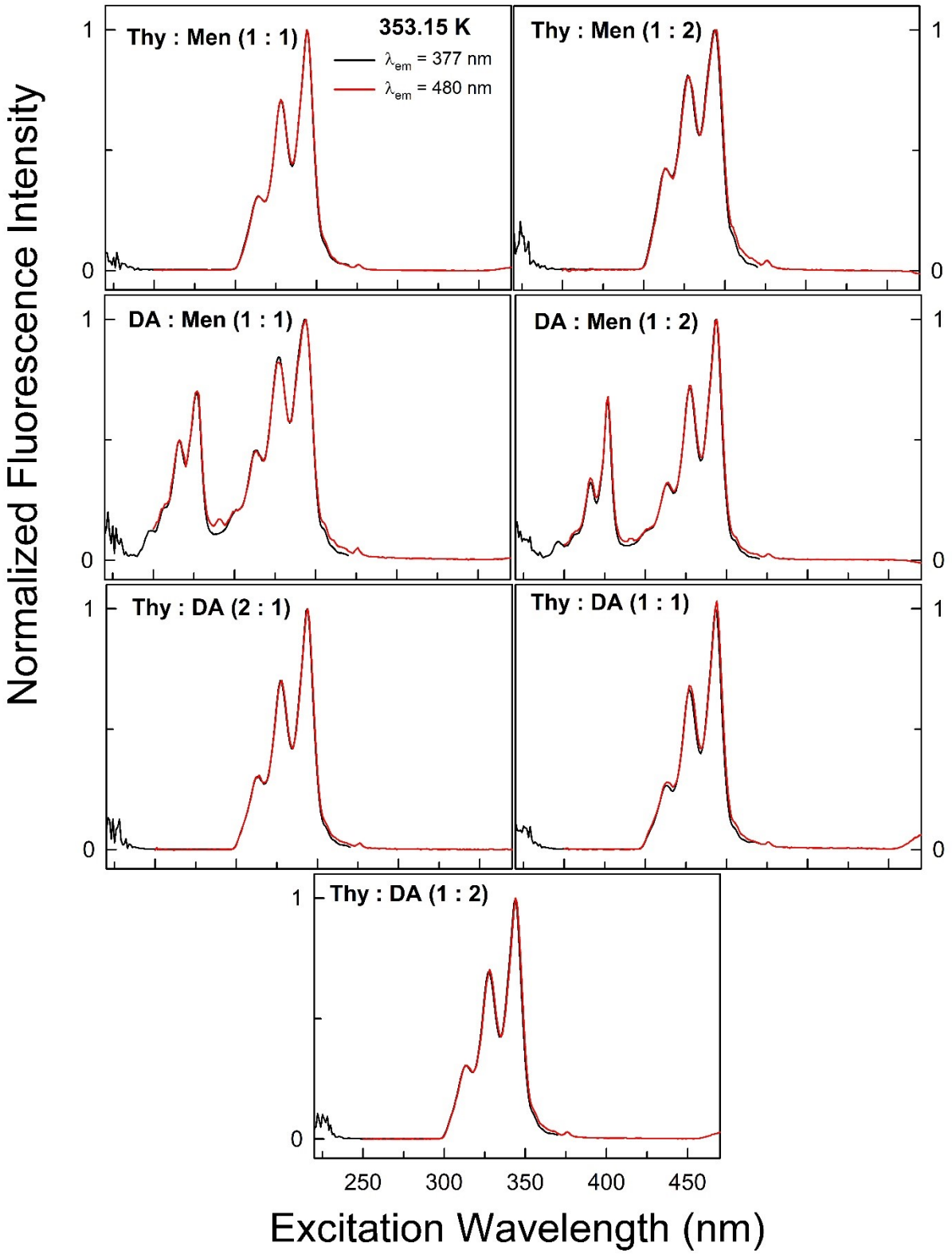

Figure S16. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 353.15 K.

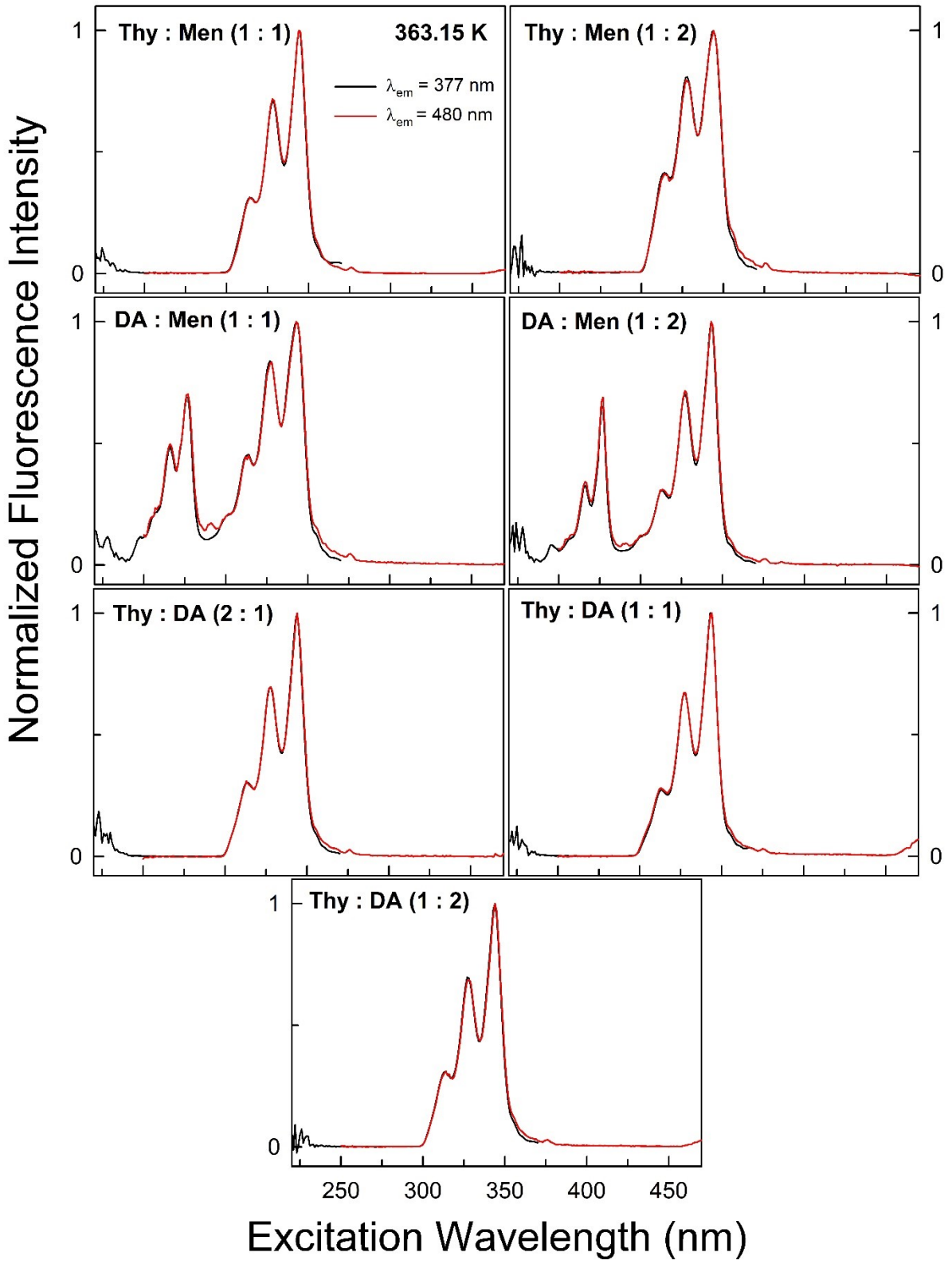

Figure S17. Normalized Fluorescence excitation spectra of Py-PDMS-Py (10 μM) dissolved in the investigated DESs; obtained with emission wavelengths fixed at 377 nm and 480 nm (emission and excitation slits are 1.0 and 1.0 nm, respectively) at 363.15 K.