Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supporting Information (ESI)

Excimer formation of 6-(1-pyrenyl)hexyl-11(1-pyrenyl) undecanoate within ionic liquid and cosolvent modified ionic liquid mixture

Rewa Rai[a] and Siddharth Pandey[a*]

[a]*Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi – 110016, India.*

[*]Corresponding Author. Phone: +91-11-26596503, Fax: +91-11-26581102,

E-mail: sipandey@chemistry.iitd.ac.in

Table S1. Recovered best global fitted intensity decay parameters for **1** dissolved in [bmim][PF_6], TEG and their equimolar mixture at different temperatures.

T (^{o}C)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
				TEG				
10	378	131			1.00			4.76
	480	131			1.00			10.58
	378	114	60.6		0.99	0.01		0.99
	480	114	60.6		0.57	-0.43		2.41
	378	112	59.1	431	0.87	0.12	-0.01	1.01
	480	112	59.1	431	0.57	-0.43	0.00	1.93
30	378	100			1.00			12.16
	480	100			1.00			26.43
	378	68.4	49.2		0.90	0.10		1.02
	480	68.4	49.2		0.52	-0.48		1.30
	378	67.2	48.7	2.1	0.84	0.01	0.15	1.01
	480	67.2	48.7	2.1	0.49	-0.47	0.04	0.98
50	378	82.6			1.00			25.62
	480	82.6			1.00			46.37

T (^{o}C)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
50	378	48.4	32.9		0.37	0.63		1.00
	480	48.4	32.9		0.51	-0.49		1.30
	378	51.0	26.7	5.6	0.50	0.41	0.09	0.96
	480	51.0	26.7	5.6	0.48	-0.47	0.05	1.02
70	378	54.6			1.00			24.33
	480	54.6			1.00			35.16
	378	40.9	17.2		0.39	0.61		1.04
	480	40.9	17.2		0.52	-0.48		1.02
	378	39.4	13.8	8.5	0.44	0.52	0.03	0.94
	480	39.4	13.8	8.5	0.36	-0.48	0.16	0.89
90	378	42.0			1.00			13.90
	480	42.0			1.00			20.81
	378	36.1	8.2		0.49	0.51		1.01
	480	36.1	8.2		0.54	-0.46		1.02
	378	34.4	10.1	34.0	0.49	0.03	-0.48	0.94
	480	34.4	10.1	34.0	-0.39	-0.10	0.51	0.77

T (^{o}C)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
				[bmim][PF_6]				
10	378	124			1.00			1.60
	480	124			1.00			4.42
	378	115	54.2		0.99	0.01		1.10
	480	115	54.2		0.63	-0.37		3.12
	378	116	40.0	3.3	0.93	0.06	0.01	1.03
	480	116	40.0	3.3	0.34	-0.25	0.41	1.02
30	378	102			1.00			4.52
	480	102			1.00			10.14
	378	82.8	43.1		0.97	0.03		1.00
	480	82.8	43.1		0.56	-0.44		1.76
	378	84.8	35.3	2.5	0.82	0.07	0.11	0.96
	480	84.8	35.3	2.5	0.44	-0.37	0.19	1.02
50	378	81.1			1.00			11.83
	480	81.1			1.00			24.61
	378	57.5	33.1		0.87	0.13		1.02
	480	57.5	33.1		0.54	-0.46		1.49

T (^{o}C)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
50	378	52.4	32.2	2.0	0.85	0.01	0.14	0.89
	480	52.4	32.2	2.0	0.49	-0.45	0.06	0.89
70	378	55.1			1.00			18.16
	480	55.1			1.00			31.41
	378	36.1	22.9		0.75	0.25		1.00
	480	36.1	22.9		0.52	-0.48		1.11
	378	36.0	21.2	4.1	0.73	0.17	0.11	0.98
	480	36.0	21.2	4.1	0.49	-0.47	0.04	0.91
90	378	40.5			1.00			21.16
	480	40.5			1.00			26.99
	378	27.4	13.9		0.59	0.41		1.02
	480	27.4	13.9		0.53	-0.47		1.01
	378	29.0	14.1	14.3	0.50	0.50	0.00	0.91
	480	29.0	14.1	14.3	0.54	-0.46	0.00	0.90

T (^{o}C)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
Equimolar mixture ([bmim][PF_6] + TEG)								
10	378	138			1.00			2.65
	480	138			1.00			7.77
	378	118	55.4		0.99	0.01		1.06
	480	118	55.4		0.51	-0.49		2.90
	378	120	43.0	3.1	0.93	0.02	0.05	1.01
	480	120	43.0	3.1	0.36	-0.29	0.35	1.01
30	378	121			1.00			11.51
	480	121			1.00			30.80
	378	78.7	50.0		0.99	0.01		1.04
	480	78.7	50.0		0.53	-0.47		1.89
	378	80.1	40.2	2.2	0.87	0.05	0.08	0.90
	480	80.1	40.2	2.2	0.46	-0.42	0.11	0.97
50	378	79.8			1.00			23.34
	480	79.8			1.00			45.29
	378	49.5	35.2		0.76	0.24		1.04
	480	49.5	35.2		0.51	-0.49		1.25

T (^{o}C)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
50	378	46.6	32.5	2.8	0.90	0.01	0.09	0.91
	480	46.6	32.5	2.8	0.50	-0.48	0.03	0.91
70	378	55.9			1.00			30.38
	480	55.9			1.00			42.77
	378	33.9	21.2		0.55	0.45		0.98
	480	33.9	21.2		0.52	-0.48		1.09
	378	35.8	17.2	6.6	0.56	0.39	0.05	0.89
	480	35.8	17.2	6.6	0.45	-0.47	0.08	0.94
90	378	37.7			1.00			18.98
	480	37.7			1.00			25.88
	378	28.1	11.0		0.49	0.51		0.99
	480	28.1	11.0		0.53	-0.47		1.00
	378	24.1	14.1	14.0	0.01	0.50	0.50	0.69
	480	24.1	14.1	14.0	0.17	-0.49	0.33	0.76

Table S2. Decay parameters (τ_1, τ_2 and A = α_{12}/α_{11}) for **1** dissolved in [bmim][PF_6], TEG and their equimolar mixture at different temperatures based on Scheme 2.

T (ºC)	τ_1 (ns)	τ_2 (ns)	A
		[bmim][PF_6]	
10	114 (± 2)	61.0 (± 0.4)	0.02
30	83.5 (± 1.3)	44.2 (± 2.2)	0.06
50	58.1 (± 1.5)	32.6 (± 1.0)	0.17
70	37.7 (± 3.2)	23.2 (± 0.6)	0.40
90	27.7 (± 0.7)	13.7 (± 0.4)	0.69
		Equimolar Mixture ([bmim][PF_6] + TEG)	
10	120 (± 4)	56.8 (± 1.8)	0.01
30	79.2 (± 1.0)	49.3 (± 1.4)	0.03
50	50.9 (± 1.4)	34.2 (± 2.0)	0.30
70	34.4 (± 1.0)	21.0 (± 0.5)	0.86
90	28.1 (± 1.0)	11.3 (± 0.5)	0.99
		TEG	
10	111 (± 7)	61.0 (± 0.8)	0.04
30	69.2 (± 2.0)	48.5 (± 1.5)	0.17
50	49.9 (± 3.0)	31.2 (± 1.8)	1.46
70	41.2 (± 1.5)	17.0 (± 0.4)	1.60
90	35.7 (± 1.6)	8.4 (± 0.3)	1.11

Table S3. Fluorescence lifetimes (τ_0) and excited-state intensity decay rates ($k_M = 1/\tau_0$) for 1-methylpyrene dissolved in [bmim][PF_6], TEG and their equimolar mixture at different temperatures.

T (^oC)	τ_0 (ns)	k_M (10^6, s^{-1})
	[bmim][PF_6]	
10	137 (± 2)	7.3 (± 0.1)
30	131 (± 2)	7.7 (± 0.1)
50	107 (± 1)	9.3 (± 0.1)
70	100 (± 1)	10.1 (±0.1)
90	82 (± 3)	12.2 (±0.2)
	Equimolar mixture ([bmim][PF_6] + TEG)	
10	139 (± 4)	7.2 (± 0.2)
30	127 (± 8)	7.9 (± 0.5)
50	110 (± 8)	9.1 (± 0.7)
70	98 (± 1)	10.2 (± 0.1)
90	83 (± 2)	12.1 (±0.3)
	TEG	
10	140 (± 1)	7.2 (± 0.1)
30	131 (± 3)	7.7 (± 0.2)
50	124 (± 1)	8.1 (± 0.1)
70	135 (± 2)	7.4 (± 0.1)
90	130 (± 1)	7.7 (± 0.1)

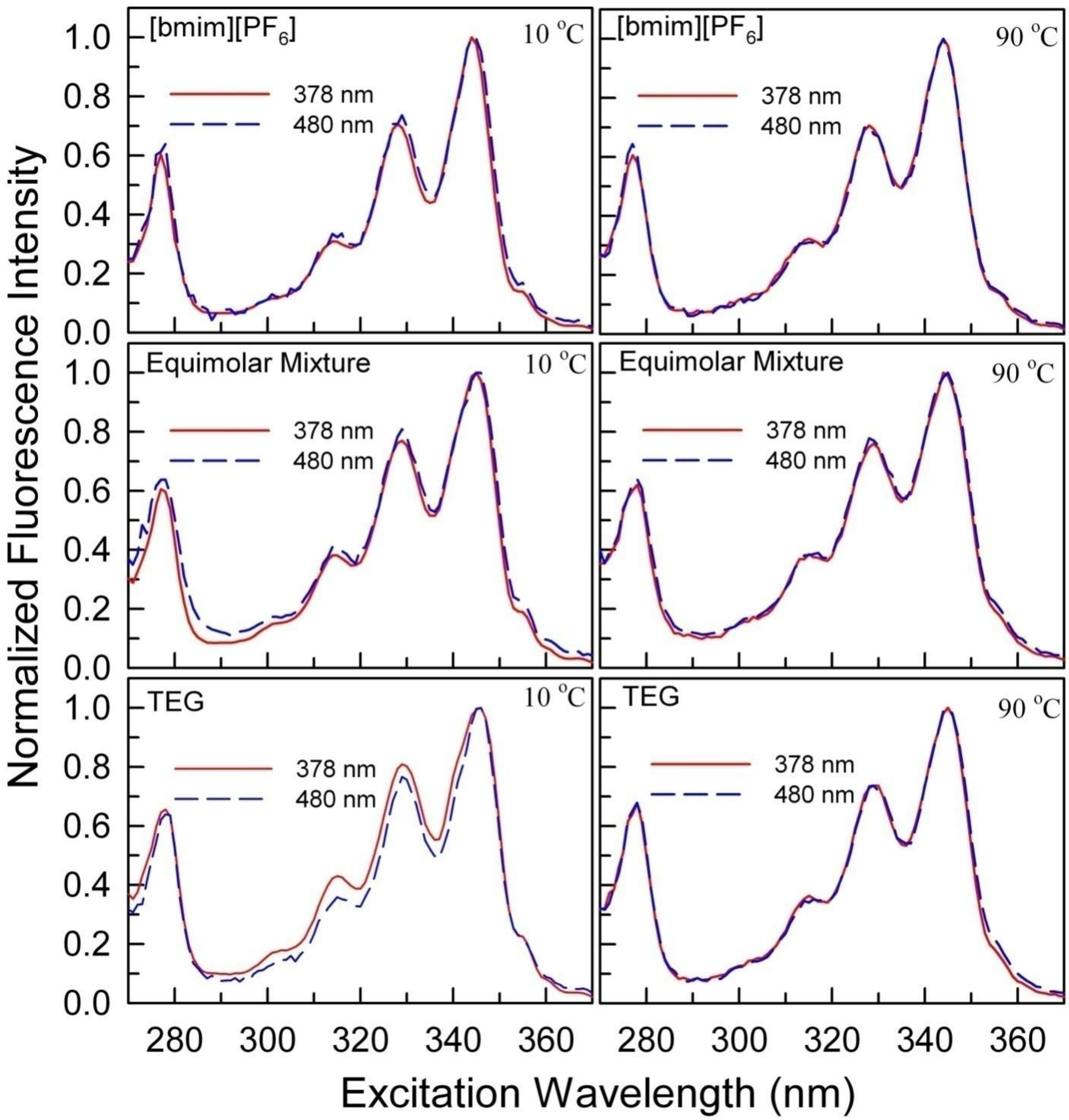

Figure S1. Normalized steady-state emission wavelength-dependent excitation spectra of **1** dissolved in [bmim][PF_6] (top two panels), equimolar mixture (middle two panels) and TEG (bottom two panels) when emission is monitored at 378 nm (—) and 480 nm (– –) at 10 ºC (left panels) and 90 ºC (right panels).