Electronic Supplementary Information (ESI)

Pyrene aggregation at unprecedented low concentrations in (lanthanide metal salt + urea) deep eutectic solvents

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Experimental Methods

DESs were prepared by mixing lanthanum nitrate hexahydrate (>99% from Sigma-Aldrich) and gadolinium nitrate hexahydrate (>99% from Sigma-Aldrich) with urea (99%, SRL) in respective molar ratio followed by stirring under gentle heating (~313 K) until a homogeneous, colorless liquid was formed. Pyrene (>99%) was purchased from Sigma-Aldrich and used without further processing.

The pre-calculated amount of pyrene was weighed using an analytical balance with a precision of ±0.1 mg and dissolved in ethanol and the prepared stock solution was stored at stored at 4±1°C to retard any photochemical reactions. An appropriate amount of the stock was transferred to the 1-cm path length quartz cuvette and ethanol was evaporated using a gentle stream of high purity nitrogen gas. DES was added in pre-calculated amount to achieve the desired final concentration of the pyrene. A Jobin-Yvon Fluorolog-3 (model FL-3-11) modular spectrofluorometer equipped with a 450 W Xe arc lamp as the excitation source and single-grating monochromators as wavelength selection devices with a photomultiplier tube as the detector is used to collect steady state emission and excitation spectra. All the acquired spectra were duly corrected by subtracting the spectral responses from suitable blanks. Horiba-Jobin Yvon, Inc. Fluorocube time-correlated single photon counting (TCSPC) fluorimeter was used to acquire lifetime excited decay time. Pyrene was excited using a 340 nm UV-pulsed NanoLED-340 source having pulse width <1.0 ns and the emission was collected using Peltier-cooled red-sensitive TBX-04 PMT detection module at the respective emission maxima wavelength. The data was collected with DAQ-MCA-3 Series (P7882) multichannel analyzer. The instrument response function (IRF) was obtained using a scattering solution of glycogen in water (glycogen from bovine liver, Type IX, Aldrich). The excited-state intensity decays were analyzed using DAS6 analysis software and were fitted to the desired decay models. Further data analysis was performed using SigmaPlot v14 software.

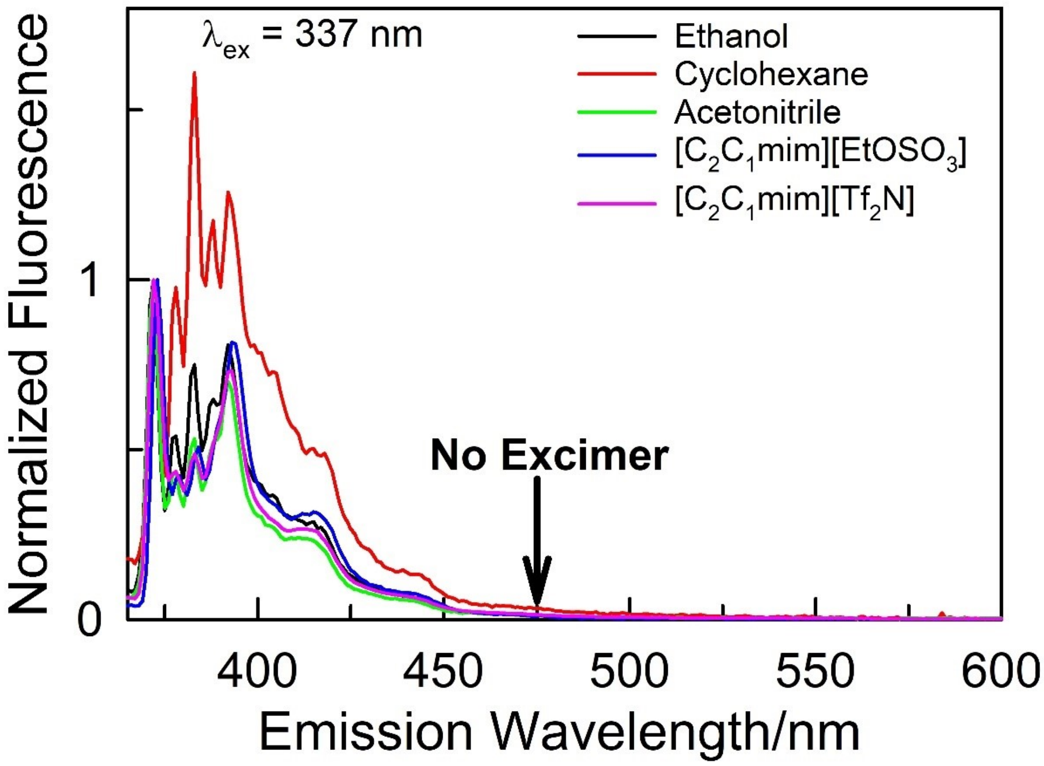

Fig. S1 Normalized fluorescence emission spectra of 20 μM pyrene dissolved in select organic solvents and ionic liquids under ambient conditions.

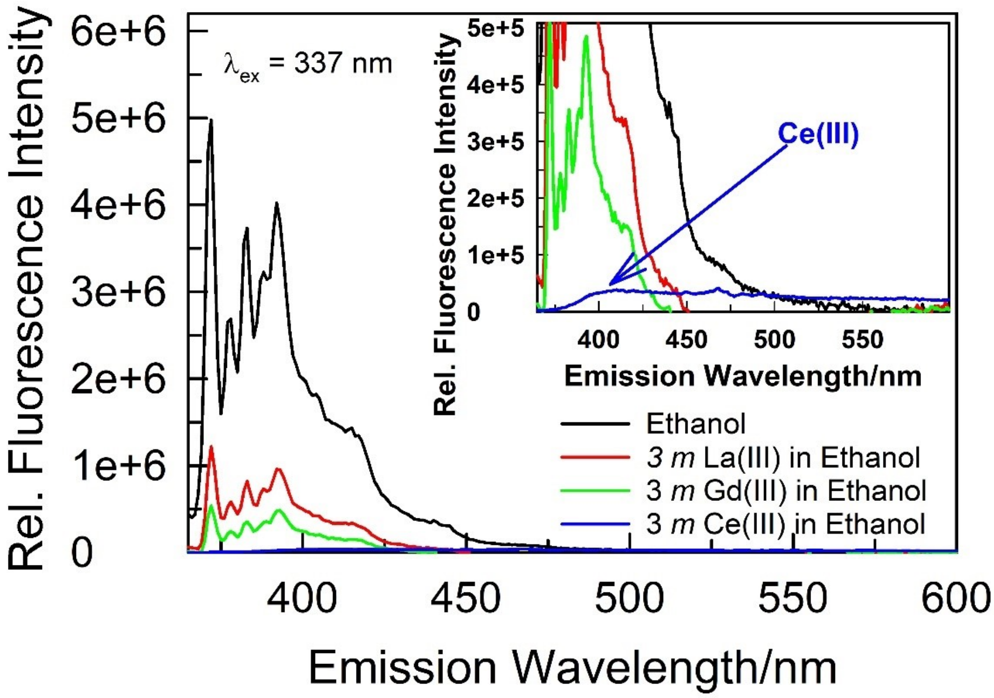

Fig. S2 Fluorescence emission spectra of 20 μM pyrene dissolved in ethanol and in 3 *m* metal salt added ethanol under ambient conditions. Inset shows corresponding spectra highlighting the absence of pyrene emission in the presence of 3 *m* Ce(III).

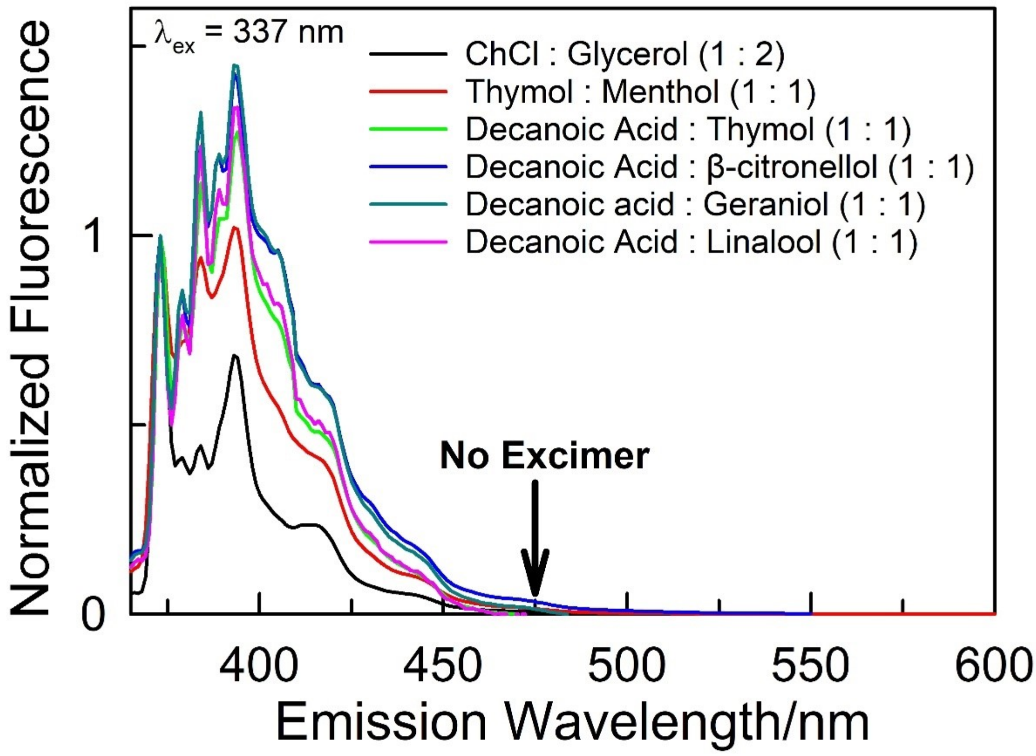

Fig. S3 Normalized fluorescence emission spectra of 20 μM pyrene dissolved in various DESs under ambient conditions.

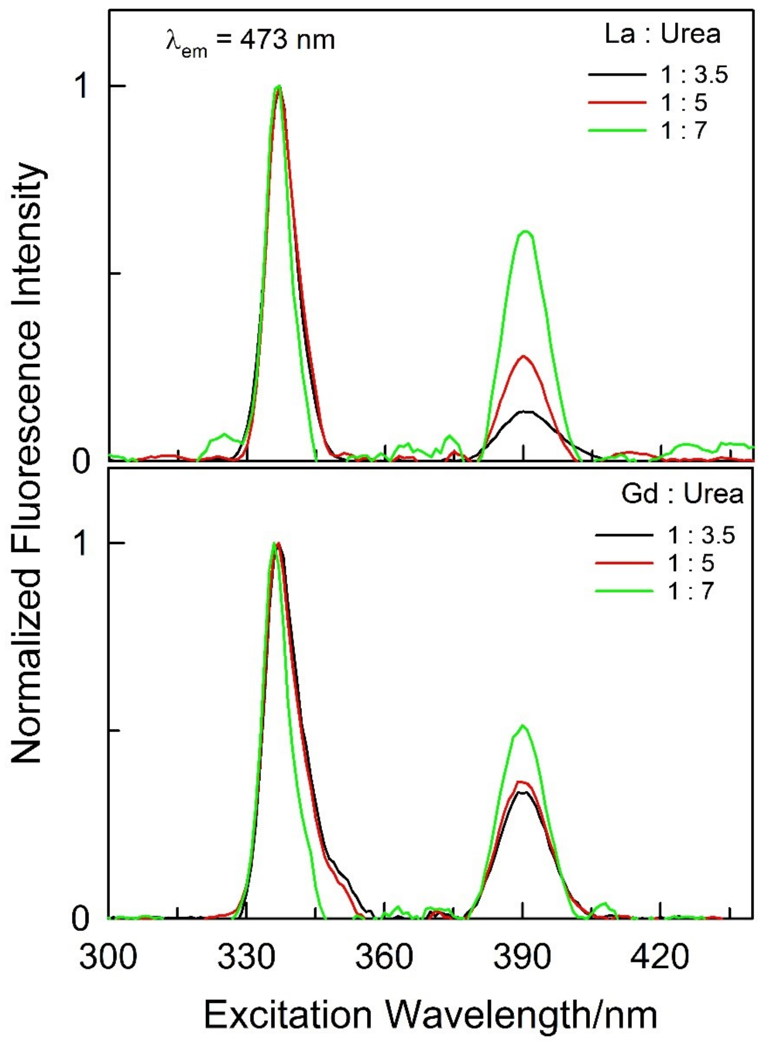

Fig. S4 Normalized fluorescence excitation spectra of 20 μM pyrene dissolved in various metal-based DESs under ambient conditions.

Table S1. Recovered excited-state intensity decay parameters for pyrene (20 μM; excitation with 340 nm NanoLED) dissolved in various metal-based DESs. Errors associated with decay times are ≤ ±5% and with preexponential factors are ≤ ±5%.

T/K	λ_{em}	τ_1 (ns)/α_1	τ_2 (ns)/α_2	χ^2
		1 : 3.5 (La : Urea)		
293.15	373	0.37		4.38
		0.22/0.99	9.07/0.01	1.37
	473	39.54		2.27
		0.69/0.76	41.05/0.24	1.13
298.15	373	0.49		4.28
		0.32/0.99	9.16/0.01	1.04
	473	36.37		3.82
		0.79/0.74	37.56/0.26	1.37
303.15	373	0.31		4.52
		0.14/1.00	6.75/0.00	1.12
	473	32.98		3.38
		0.76/0.74	34.31/0.26	1.30
313.15	373	0.29		4.89
		0.04/1.00	5.74/0.00	1.41
	473	27.65		2.68
		0.83/0.75	29.12/0.25	1.32
323.15	373	0.24		4.11
		0.09/1.00	4.93/0.00	1.05
	473	21.30		3.60
		1.40/0.75	24.30/0.25	1.10
		1 : 5 (La : Urea)		
298.15	373	0.70		3.94
		0.52/0.99	9.34/0.01	1.10
	473	34.37		2.78
		0.70/0.78	35.85/0.22	1.37
303.15	373	0.61		4.04
		0.42/0.98	6.25/0.02	1.07
	473	32.61		2.91
		0.59/0.78	33.76/0.22	1.38
313.15	373	0.53		2.98
		0.37/0.99	5.97/0.01	1.00
	473	25.91		3.97
		0.78/0.86	27.64/0.14	1.18
323.15	373	0.45		3.24
		0.31/0.99	4.17/0.01	1.01
	473	20.03		4.05
		1.01/0.80	22.74/0.20	1.26
		1 : 7 (La : Urea)		
293.15	373	1.25		2.83
		0.48/0.85	2.25/0.15	1.37
	473	35.16		4.44
		1.41/0.86	40.14/0.14	1.13
298.15	373	1.15		2.08
		0.72/0.90	2.55/0.10	1.32
	473	34.36		3.67
		1.07/0.83	36.97/0.17	1.22

303.15	373	1.09		2.04
		0.75/0.96	3.73/0.04	1.12
	473	30.08		4.04
		1.12/0.85	33.52/0.15	1.18
313.15	373	0.87		2.15
		0.67/0.97	3.52/0.03	1.11
	473	25.09		4.67
		1.08/0.85	28.31/0.15	1.24
323.15	373	0.76		1.93
		0.62/0.01	4.51/0.99	1.07
	473	18.94		4.53
		1.04/0.85	22.05/0.15	1.15
		1 : 3.5 (Gd : Urea)		
293.15	373	0.35		3.04
		0.23/0.99	5.55/0.01	1.12
	473	23.39		2.41
		1.11/0.65	24.89/0.35	1.16
298.15	373	0.30		2.56
		0.19/0.99	5.61/0.01	1.05
	473	20.62		2.82
		1.15/0.67	22.64/0.33	1.20
303.15	373	0.37		3.30
		0.19/0.99	4.75/0.01	0.93
	473	18.89		2.87
		1.06/0.71	20.88/0.29	1.14
313.15	373	0.31		3.97
		0.14/0.99	4.52/0.01	0.98
	473	15.53		3.28
		1.27/0.72	18.08/0.28	1.21
323.15	373	0.14		3.04
		0.13/0.99	4.51/0.01	0.94
	473	12.90		3.39
		1.28/0.73	15.39/0.27	1.26
		1 : 5 (Gd : Urea)		
293.15	373	0.85		2.75
		0.62/0.98	11.38/0.02	1.02
	473	37.83		2.97
		0.75/0.80	39.31/0.20	1.32
298.15	373	0.66		3.42
		0.47/0.99	7.89/0.01	1.15
	473	34.48		3.25
		0.89/0.78	36.18/0.22	1.37
303.15	373	0.63		3.46
		0.39/0.98	5.79/0.02	1.24
	473	30.73		3.59
		0.99/0.79	33.12/0.21	1.22
313.15	373	0.45		2.73
		0.34/0.99	5.66/0.01	0.90
	473	24.51		4.00
		1.00/0.80	27.11/0.20	1.19
323.15	373	0.39		3.38
		0.29/0.99	5.24/0.01	0.97
	473	19.34		4.15
		0.99/0.83	22.00/0.17	1.06

		1 : 7 (Gd : Urea)		
293.15	373	1.26		1.60
		0.97/0.97	6.14/0.03	0.92
	473	36.56		5.21
		1.34/0.89	41.32/0.11	1.19
298.15	373	1.06		1.56
		0.83/0.97	4.65/0.03	0.82
	473	32.46		4.78
		1.30/0.88	36.79/0.12	1.11
303.15	373	1.00		1.83
		0.62/0.91	2.24/0.09	1.27
	473	28.47		5.22
		1.20/0.89	33.10/0.11	1.11
313.15	373	0.86		1.67
		0.68/0.98	4.26/0.02	0.89
	473	22.17		5.80
		1.19/0.89	26.89/0.11	1.09
323.15	373	0.68		1.64
		0.54/0.98	4.22/0.02	0.82
	473	17.28		5.28
		1.10/0.88	21.40/0.12	1.10