

Electronic Supporting Information (ESI)

Ethanolamine-mediated microstructural transitions within terpenoid- and fatty acid-based deep eutectic solvents

Anjali 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	S4
Table S3	S5
Table S4	S6
Table S5	S7
Table S6	S8
Table S7	S9
Table S8	S10
Table S9	S11
Figure S1	S12
Figure S2	S13
Figure S3	S14
Figure S4	S15

Table S1. Description of Chemicals Used in This Work.

DES	Molar Mass (g/mol)	Composition
Thy : DA	322.48	1 : 1
Men : DA	328.53	1 : 1
Thy : Men	306.49	1 : 1

Table S2. Density ($\rho/\text{g}\cdot\text{cm}^{-1}$) Variation of MEA–Added DES system at Investigated Mole Fractions of MEA (χ_{MEA}) in the Temperature Range $T = 293 - 343$ K at Pressure $P = (0.1 \text{ MPa}\cdot\text{s})$.^a

χ_{MEA}	293 K	298 K	303 K	313 K	323 K	333 K	343 K
Thy : DA (1 : 1)							
0.0	0.933	0.930	0.927	0.918	0.910	0.906	0.901
0.09	0.940	0.937	0.934	0.925	0.918	0.913	0.908
0.17	0.946	0.943	0.940	0.931	0.924	0.920	0.914
0.23	0.952	0.949	0.946	0.937	0.930	0.926	0.920
0.29	0.957	0.953	0.950	0.942	0.935	0.930	0.925
0.33	0.961	0.957	0.955	0.946	0.939	0.935	0.930
0.41	0.969	0.964	0.959	0.951	0.944	0.939	0.934
0.50	0.978	0.975	0.972	0.964	0.957	0.952	0.947
1.00	1.016	1.012	1.009	0.999	0.992	0.987	0.982
Men : DA (1 : 1)							
0.0	0.900	0.896	0.894	0.885	0.878	0.873	0.869
0.09	0.906	0.903	0.900	0.892	0.885	0.880	0.876
0.17	0.912	0.909	0.906	0.898	0.891	0.887	0.882
0.23	0.917	0.914	0.911	0.903	0.896	0.892	0.887
0.29	0.922	0.919	0.916	0.908	0.901	0.897	0.892
0.33	0.926	0.923	0.920	0.912	0.905	0.900	0.896
0.38	0.931	0.928	0.925	0.917	0.910	0.906	0.901
0.41	0.934	0.931	0.929	0.920	0.914	0.909	0.904
0.47	0.941	0.938	0.935	0.927	0.920	0.916	0.911
0.50	0.925	0.942	0.940	0.931	0.924	0.920	0.915
1.00	1.016	1.012	1.009	0.999	0.992	0.987	0.982
Thy : Men (1 : 1)							
0.0	0.937	0.933	0.930	0.921	0.914	0.909	0.904
0.09	0.939	0.936	0.933	0.924	0.916	0.911	0.906
0.17	0.941	0.937	0.934	0.926	0.918	0.914	0.909
0.23	0.943	0.939	0.936	0.928	0.921	0.916	0.910
0.29	0.945	0.942	0.938	0.929	0.922	0.917	0.912
0.33	0.946	0.943	0.940	0.931	0.924	0.919	0.914
0.38	0.948	0.944	0.942	0.933	0.925	0.921	0.916
0.41	0.948	0.945	0.942	0.933	0.926	0.921	0.916
0.50	0.952	0.949	0.946	0.937	0.929	0.925	0.920
1.00	1.016	1.012	1.009	0.999	0.992	0.987	0.982

^aStandard Uncertainty u are $u(\rho) = 0.005$, $u(\chi_{\text{MEA}}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3 \text{ kPa}$, $u(\text{HBD} : \text{HBA})_{\text{DES}} = 0.05$.

Table S3. Dynamic Viscosity (η /mPa·s) of MEA-added DES System at Mole Fractions of MEA (x_{MEA}) in the Temperature Range 293 – 343 K at Pressure $P = 101.3$ kPa·s.^a

x_{MEA}	293 K	298 K	303 K	313 K	323 K	333 K	343 K
Thy : DA (1 : 1)							
0.00	15.08	12.00	9.720	6.930	5.030	3.800	2.960
0.09	27.22	21.22	16.63	10.90	7.549	5.447	4.096
0.17	49.75	37.27	28.41	17.77	11.81	8.251	6.004
0.23	85.58	62.58	46.96	27.98	17.97	12.17	8.617
0.29	162.9	115.0	85.00	47.00	29.84	18.86	12.87
0.33	233.2	164.8	118.3	66.06	39.74	26.01	17.24
0.41	670.9	453.3	314.1	163.0	91.92	52.74	32.72
0.50	1959	1211	801.6	373.2	191.0	103.0	62.07
1.00	24.08	18.93	15.15	10.06	6.962	5.037	3.775
Men : DA (1 : 1)							
0.00	20.41	15.92	12.81	8.540	6.000	4.410	3.470
0.09	36.94	28.25	21.76	13.80	9.183	6.460	4.760
0.17	58.66	44.04	33.62	20.58	13.48	9.252	6.681
0.23	87.33	63.68	47.57	28.20	17.95	12.02	8.492
0.29	137.6	97.34	70.57	39.64	24.26	15.74	10.77
0.33	157.0	113.6	82.64	48.11	29.61	19.18	12.97
0.38	302.2	211.2	151.3	83.62	48.43	29.72	19.50
0.47	745.2	509.6	354.0	183.1	101.5	58.52	36.55
0.50	949.6	593.0	412.1	208.9	113.9	66.07	42.06
1.00	24.08	18.93	15.15	10.06	6.962	5.037	3.775
Thy : Men (1 : 1)							
0.00	59.57	39.35	26.35	13.89	8.135	5.188	3.535
0.09	62.66	40.58	27.27	13.92	8.140	5.163	3.556
0.17	75.16	48.81	32.95	16.51	9.299	5.796	3.860
0.23	81.04	51.80	34.76	17.71	10.12	6.296	4.211
0.29	89.69	56.85	37.45	19.06	10.80	6.668	4.273
0.33	92.43	59.13	39.62	19.93	11.35	6.935	4.573
0.38	97.36	62.34	41.66	20.88	11.80	7.245	4.750
0.41	100.0	64.07	42.79	21.43	12.12	7.422	4.849
0.50	100.2	65.04	43.99	43.98	22.32	12.67	5.130
1.00	24.08	18.93	15.15	10.06	6.962	5.037	3.775

^aStandard Uncertainty u are $u(\eta) = 2\%$, $u(x_{\text{MEA}}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3\text{ kPa}$, $u(\text{HBD} : \text{HBA})_{\text{DES}} = 0.05$.

Table S4. Summary of Recovered Empirical Interaction Parameter (ε) and the Goodness-of-Fit (R^2) Obtained by Fitting Viscosity Data of MEA–Added DES System to Equation 1.^a

System	293 K	298 K	303 K	313 K	323 K	333 K	343 K
Thy : DA (1 : 1)							
ε	-8.00±0.08	-7.47±0.09	-7.19±0.07	-6.96±0.04	-6.19±0.09	-5.44±0.08	-5.14±0.09
R^2	0.999	0.999	0.999	0.999	0.999	0.998	0.999
Men : DA (1 : 1)							
ε	-6.06±0.07	-5.53±0.09	-5.64±0.07	-5.43±0.08	-5.12±0.08	-4.75±0.08	-4.87±0.09
R^2	0.996	0.996	0.996	0.996	0.996	0.996	0.997
Thy : Men (1 : 1)							
R^2	0.986	0.982	0.981	0.983	0.989	0.986	0.979

^aStandard Uncertainty u are $u(\eta) = 2\%$, $u(x_{MEA}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3\text{ kPa}$, $u(\varepsilon) = 0.05$, $u(\text{HBD : HBA})_{\text{DES}} = 0.05$, Standard deviation are provided with $\pm$ sign.

Table S5. Summary of Recovered Empirical Interaction Parameter (ε) and the Goodness of Fit (R^2) Obtained by Fitting Viscosity Data of MEA–Added (Thy : Men) DES system to Equation 2.^a

Systems	ε	K_1	R^2
293	3.77±0.08	2.593±0.082	0.992
298	4.95±0.09	3.279±0.090	0.990
303	5.89±0.07	3.761±0.095	0.991
313	6.02±0.06	3.675±0.098	0.986
323	5.79±0.09	3.282±0.099	0.981
333	6.89±0.08	3.945±0.089	0.989
343	7.06±0.08	4.167±0.089	0.993

^aStandard Uncertainty u are $u(\eta) = 2\%$, $u(x_{MEA}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3\text{ kPa.}$, $u(\varepsilon) = 0.05$, $u(\text{HBD} : \text{HBA})_{\text{DES}} = 0.05$. Standard deviation are provided with $\pm$ sign.

Table S6. Summary of Parameters Associated with Dynamic Viscosity of MEA–Added DES System at Investigated Mole Fractions of MEA (χ_{MEA}) in the Temperature Range $T = 293 - 343$ K at

Pressure $P = 101.3$ kPa. According to the VFT Model Using Equation^a: $\ln \eta = A + \frac{B}{T - T_0}$.

DES	<i>A</i>	<i>B</i>	T_0/K	r^2	${}^bE_{a,\eta}/\text{kJ}\cdot\text{mol}^{-1}$
Thy : DA (1 : 1)					
0.00	-3.03 ± 0.14	729 ± 189	165 ± 20	0.998	31.1 ± 1.8
0.09	-3.31 ± 0.30	823 ± 148	168 ± 21	1.000	36.6 ± 1.1
0.17	-3.16 ± 0.28	830 ± 178	175 ± 23	1.000	41.4 ± 1.1
0.23	-3.31 ± 0.18	923 ± 138	173 ± 13	1.000	44.8 ± 1.4
0.29	-3.84 ± 0.16	1126 ± 145	166 ± 14	0.999	48.9 ± 1.6
0.33	-3.47 ± 0.30	1086 ± 135	171 ± 20	0.999	50.5 ± 1.7
0.41	-6.19 ± 0.40	2038 ± 164	132 ± 15	1.000	55.3 ± 1.8
0.50	-4.85 ± 0.35	1614 ± 146	163 ± 24	0.999	66.2 ± 2.0
1.00	-4.12 ± 0.42	1070 ± 124	146 ± 25	1.000	34.3 ± 1.8
Men : DA (1 : 1)					
0.00	-2.68 ± 0.24	624 ± 136	183 ± 22	0.999	35.5 ± 2.0
0.09	-4.12 ± 0.34	1071 ± 136	146 ± 11	1.000	34.7 ± 2.9
0.17	-3.60 ± 0.12	905 ± 137	167 ± 14	1.000	39.7 ± 3.0
0.23	-3.63 ± 0.58	978 ± 125	166 ± 20	1.000	42.0 ± 3.2
0.29	-3.57 ± 0.23	992 ± 125	176 ± 21	1.000	49.9 ± 3.3
0.33	-4.39 ± 0.14	1319 ± 114	153 ± 22	1.000	47.0 ± 3.7
0.38	-5.22 ± 0.19	1632 ± 112	143 ± 24	1.000	51.2 ± 3.7
0.47	-6.28 ± 0.16	2109 ± 165	129 ± 15	1.000	55.5 ± 2.9
0.50	-3.59 ± 0.15	1233 ± 156	175 ± 19	0.999	60.6 ± 1.8
Thy : Men (1 : 1)					
0.00	-3.42 ± 0.14	622 ± 176	210 ± 20	1.000	60.2 ± 2.9
0.09	-3.41 ± 0.19	621 ± 174	210 ± 21	1.000	60.1 ± 2.8
0.17	-3.93 ± 0.39	731 ± 135	204 ± 23	1.000	62.4 ± 2.2
0.23	-3.567 ± 0.39	674 ± 167	208 ± 24	1.000	62.6 ± 2.1
0.29	-3.65 ± 0.67	694 ± 133	208 ± 25	1.000	63.6 ± 1.8
0.33	-3.86 ± 0.35	750 ± 155	203 ± 26	1.000	62.7 ± 2.0
0.38	-3.84 ± 0.53	753 ± 135	203 ± 27	1.000	63.0 ± 1.9
0.41	-3.90 ± 0.53	770 ± 187	202 ± 28	1.000	62.9 ± 1.8
0.50	-3.96 ± 0.52	806 ± 189	199 ± 20	1.000	61.2 ± 1.4

^aStandard Uncertainty u are $u(\chi_{\text{MEA}}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3\text{ kPa}$, $u(\text{HBD} : \text{HBA})_{\text{DES}} = 0.05$. ^b $E_{a,\eta}$ is calculated at 298 K. Standard deviation are provided with $\pm$ sign.

Table S7. Kamlet–Taft Parameters, Dipolarity/Polarizability (π^*), HBD Acidity (α), and HBA Basicity (β) of the MEA–Added (Thy : DA) DES System at Investigated Mole Fractions of MEA (χ_{MEA}) at Temperature $T = 298 \text{ K}$.^a

χ_{MEA}	Kamlet - Taft Parameters		
	π^*	α	β
0.00	0.86 ± 0.05	0.93 ± 0.05	0.28 ± 0.05
0.09	0.91 ± 0.04	0.91 ± 0.05	0.24 ± 0.04
0.17	1.00 ± 0.06	0.73 ± 0.04	0.21 ± 0.03
0.23	0.97 ± 0.04	0.86 ± 0.05	0.25 ± 0.04
0.29	1.01 ± 0.05	0.79 ± 0.04	0.34 ± 0.04
0.33	1.06 ± 0.06	0.75 ± 0.05	0.43 ± 0.05
0.38	1.10 ± 0.03	0.72 ± 0.04	0.43 ± 0.06
0.41	1.10 ± 0.05	0.74 ± 0.04	0.45 ± 0.04
0.44	1.10 ± 0.02	0.74 ± 0.03	0.43 ± 0.05
0.47	1.10 ± 0.04	0.74 ± 0.06	0.53 ± 0.06
0.50	1.10 ± 0.04	0.74 ± 0.05	0.55 ± 0.04
1.00	1.01 ± 0.05	0.7^*	0.71 ± 0.05

* α calculated from E_{T} (30) and extracted from ref. 34. ^aStandard Uncertainty u are $u(\pi^*) = 0.07$, $u(\alpha) = 0.07$, $u(\beta) = 0.07$, $u(T) = 1\text{K}$, $u(p) = 0.3 \text{ kPa}$, $u(\text{HBD} : \text{HBA})_{\text{DES}} = 0.05$. Standard deviation are provided with $\pm$ sign.

Table S8. Steady-state Anisotropy of Perylene (4 μ M) at $\lambda_{\text{em}} = 440$ nm [Xenon Lamp ($\lambda_{\text{ex}} = 404$ nm; Excitation and Emission Slits are 2 nm and 2 nm, respectively] Dissolved in MEA-added (Thy : DA) DES System at Investigated Mole Fraction MEA in the Temperature Range $T = 283$ to 343 K at Pressure $P = 101.3$ kPa $\cdot$ s^a.

χ_{MEA}	T/K							
	283	293	298	303	313	323	333	343
0.00	0.0237	0.0152	0.0122	0.0098	0.0068	0.0045	0.0031	0.0024
0.09	0.0336	0.0193	0.0237	0.0139	0.0089	0.0066	0.0049	0.0035
0.23	0.0586	0.0398	0.0313	0.0256	0.0169	0.0157	0.0082	0.0063
0.33	0.0787	0.0539	0.0451	0.0365	0.0259	0.0163	0.0129	0.0099
0.38	0.0901	0.0642	0.0534	0.0439	0.0306	0.0214	0.0162	0.0120
0.41	0.0979	0.0695	0.0586	0.0492	0.0340	0.0245	0.0179	0.0128
0.47	0.1102	0.0825	0.0709	0.0607	0.0432	0.0324	0.0244	0.0193
0.50	0.1183	0.0874	0.0738	0.0653	0.0452	0.0364	0.0253	0.0229
1.00	0.0370	0.0238	0.0191	0.0155	0.0103	0.0073	0.0049	0.0030

^aStandard Uncertainty u are $u(\chi_{\text{MEA}}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3$ kPa, $u(\text{HBD} : \text{HBA})_{\text{DES}} = 0.05$.

Table S9. Rotational Reorientation Times (θ) Recovered from the Fit of the Time-Dependent Fluorescence Anisotropy Decay to Single Exponential Function for MEA-added (Thy : DA) DES System at Investigated Mole Fractions of MEA (χ_{MEA}) at Temperature $T = 298 \text{ K}$.^a

Perylene				DPH		
χ_{MEA}	$\theta \text{ (ns)}$	r_0	χ^2	$\theta \text{ (ns)}$	r_0	χ^2
0.00	0.38	0.133	0.98	0.94	0.289	0.98
0.09	0.60	0.158	1.07	1.25	0.292	1.01
0.17	0.96	0.158	1.12	1.86	0.304	1.11
0.23	0.90	0.211	1.16	2.42	0.300	1.10
0.29	1.20	0.209	1.09	3.20	0.288	1.03
0.33	1.80	0.184	1.14	4.65	0.289	1.22
0.38	1.87	0.257	1.47	5.64	0.289	1.21
0.41	2.80	0.209	1.26	6.96	0.289	1.42
0.44	3.09	0.209	1.22	7.80	0.280	1.46
0.47	3.47	0.214	1.27	9.20	0.281	1.70
0.50	3.60	0.217	1.31	14.5	0.277	1.73
1.00	0.73	0.234	1.20	2.61	0.340	1.12

^aStandard Uncertainty u are $u(\chi_{\text{MEA}}) = 0.05$, $u(T) = 1\text{K}$, $u(p) = 0.3 \text{ kPa}$, $u(\theta) = 0.05$, $u(r_0) = 0.005$, $u(\text{HBD : HBA})_{\text{DES}} = 0.05$.

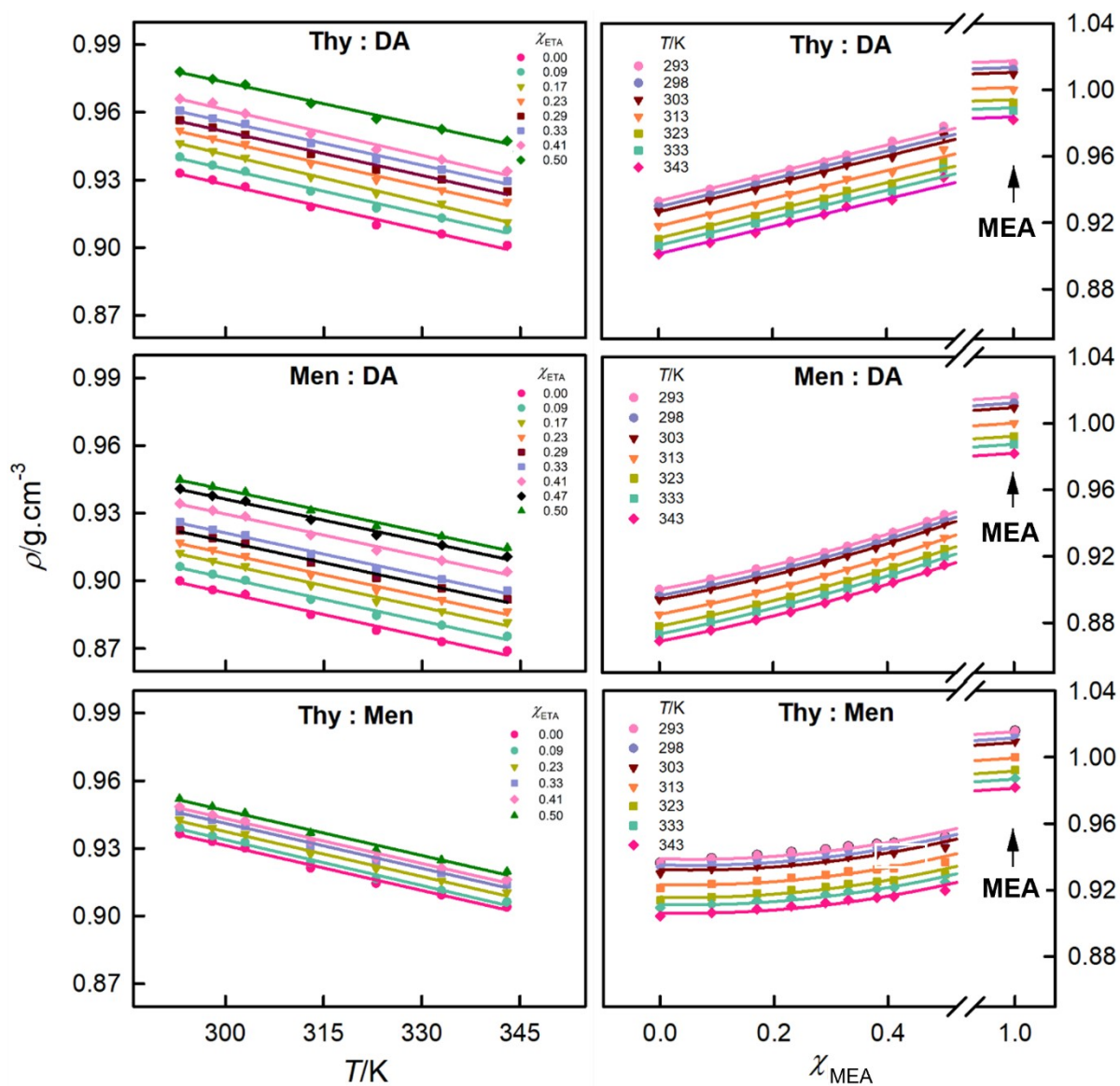


Figure S1. Densities (ρ) of MEA-added DES systems at investigated mole fractions of MEA (χ_{MEA}) at pressure $P = (0.1 \text{ MPa})$ and temperature $T = (293 \text{ K to } 343 \text{ K})$. Solid lines represent outcomes of the linear regression analysis for all the investigated systems except mole fraction dependence of density in (Men : DA) system and (Thy : Men) system where solid line represent fit to quadratic equation: $\rho = \rho_o + a\chi_{\text{MEA}} + \chi_{\text{MEA}}^2$. Standard deviation estimated for the density measurement is $\pm 0.005 \text{ g/cm}^3$.

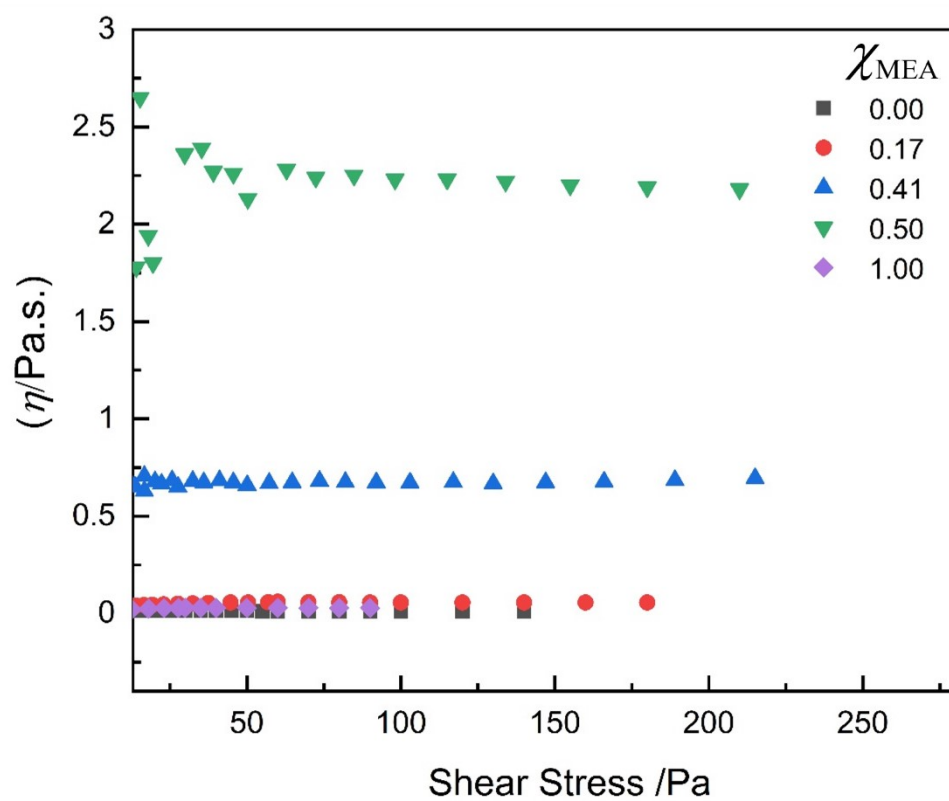


Figure S2. Dynamic viscosity (η) versus shear stress for MEA-added (Thy : DA) DES system at investigated mole fraction of MEA (χ_{MEA}) at 298 K. The uncertainty associated with viscosity measurements is 2%.

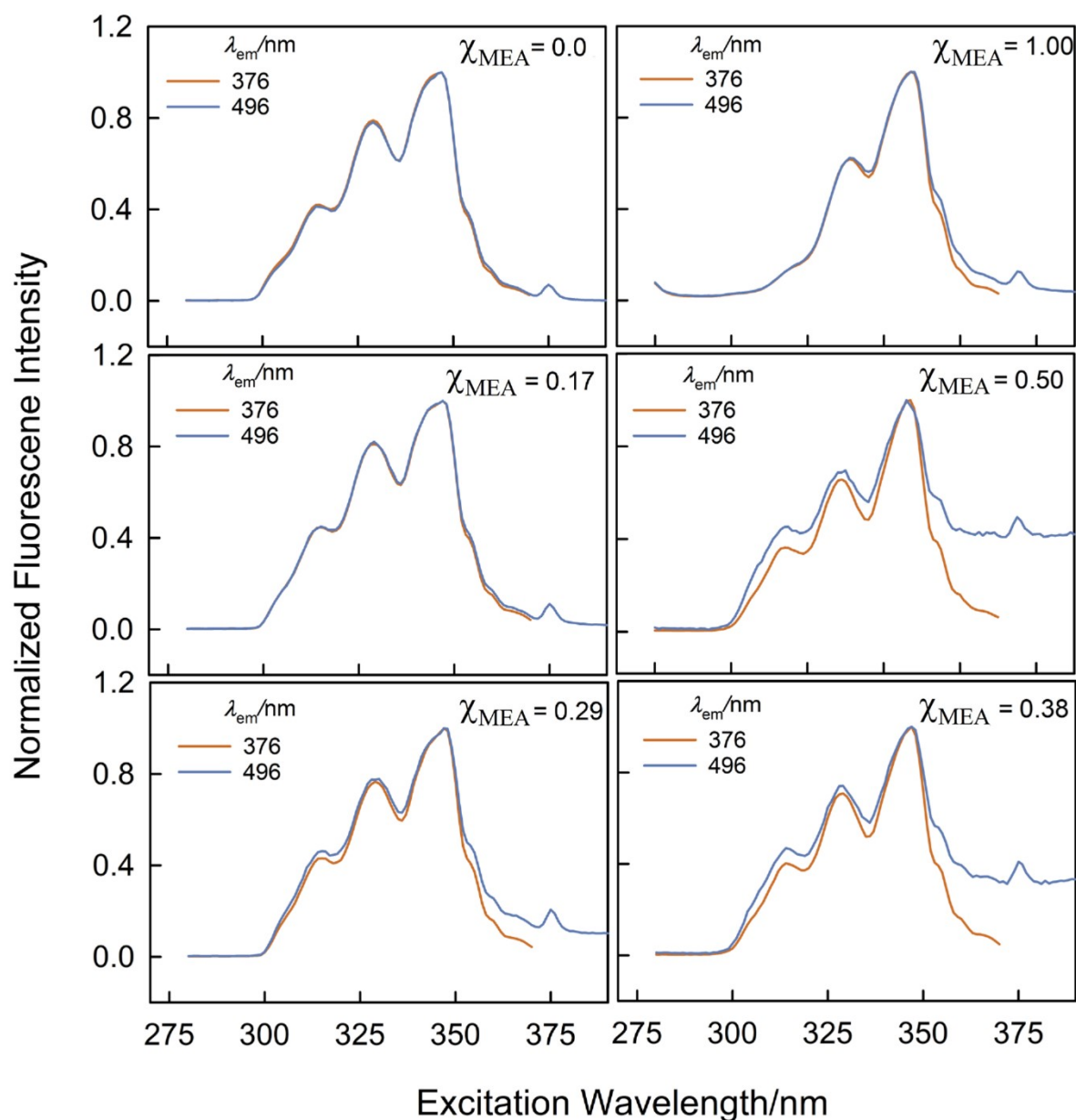


Figure S3. Fluorescence excitation spectra of BPP (10 μ M) dissolved in MEA-added (Thy : DA) DES system at investigated mole fractions of MEA (χ_{MEA}) while monitoring the emission at 376 nm (monomer emission) and 496 nm (excimer emission) [emission and excitation slits are 1 nm and 1 nm, respectively] at 298 K.

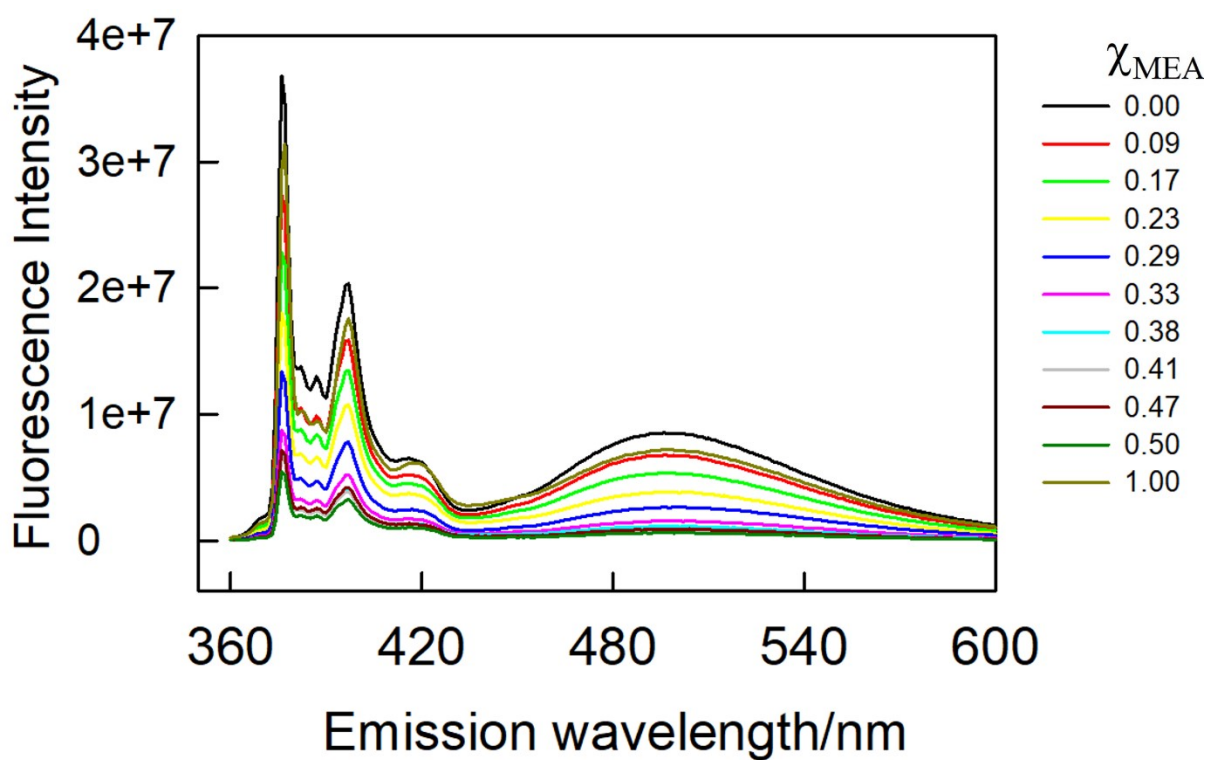


Figure S4. Steady-state fluorescence emission spectra of BPP [$10 \mu\text{M}$; $\lambda_{\text{ex}} = 347 \text{ nm}$ (Xe arc lamp); excitation and emission slits are 1 nm and 1 nm, respectively] in MEA-added (Thy : DA) DES system at investigated mole fractions of MEA (χ_{MEA}) at 298 K.