Electronic Supporting Information

Highly stable ionic liquid-in-water emulsions as a new class of fluorescent sensors for metal ions: the study case of Fe^{3+} sensing.

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Table S1. Protonation constants of NEA and OAcH (H_2O/EtOH 50:50 (v/vol), NaCl 0.1 M, 298 K) and $(NEAH)^+/(OAc)^-$ (H_2O solution, NaCl 0.1 M, 298 K).

Reaction	LogK
$(NEA) + H^+ = (NEAH)^+$	8.41 (2)
$(OAc)^- + H^+ = (OAcH)$	5.70 (6)
$(NEA)/(OAc)^- + H^+ = (NEAH)^+/(OAc)^-$	10.9[a]
$(NEAH)^+/(OAc)^- + H^+ = (NEAH)^+/(OAcH)$	2.9 (1)

[a]Only a rough estimation of the equilibrium costant for protonation of $(NEA)/(OAc)^-$ can be given due to partial formation of sodium oleate micelles above pH 10.

Table S2. Formation constants of the Fe^{3+} complexes with NEA (H_2O/EtOH 50:50 (v/v), NaCl 0.1 M, 298 K) and with $(NEAH)^+/(OAc)^-$ (H_2O solution, NaCl 0.1 M, 298 K)

Reaction	LogK
$2(NEA) + Fe^{3+} = [(NEA)_2Fe]^{3+}$	17.85 (9)
$[(NEA)_2Fe]^{3+} + OH^- = [(NEA)_2Fe(OH)]^{2+}$	11.08 (6)
$[(NEA)_2Fe(OH)]^{2+} + 3OH^- = [(NEA)_2Fe(OH)_4]^-$	6.9 (2)
$2(NEA)/(OAc)^- + Fe^{3+} = [((NEA)/(OAc)^-)_2Fe]^+$	22.95 (6)

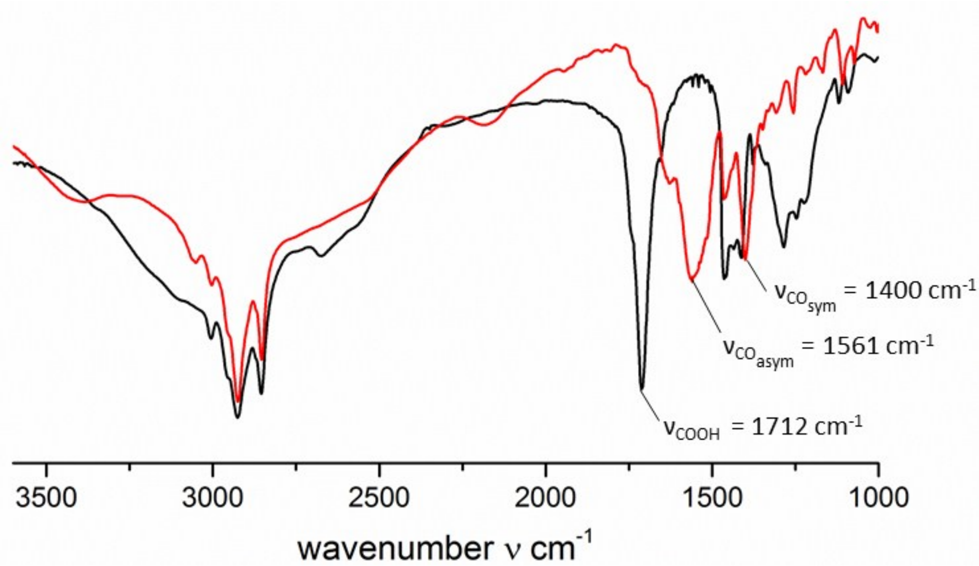

Figure S1. FT-IR spectra of oleic acid (black) and $(NEAH)^+/(OAc)^-$ salt (red).

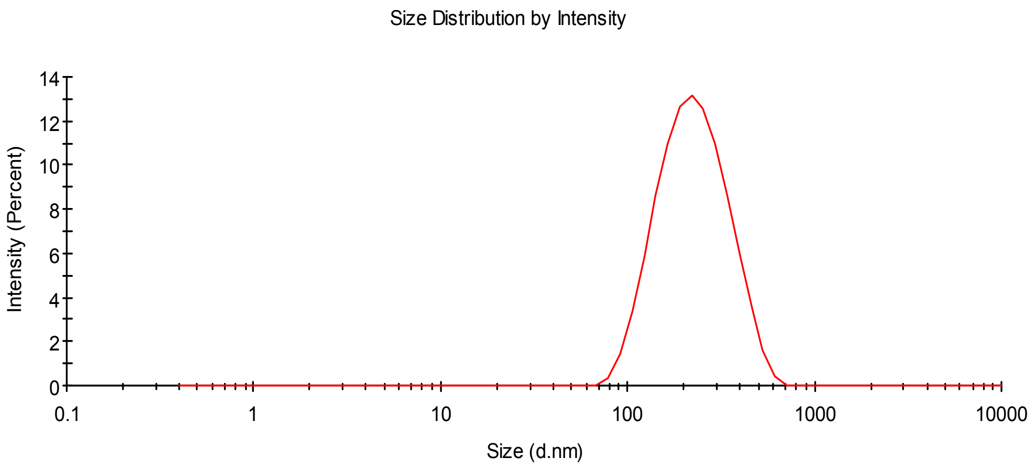

Figure S2. Dynamic light scattering of $(NEAH)^+/(OAc)^-$ [$8.82 \cdot 10^{-5}$ M] in milli-Q water (pH = 8.2). The average hydrodynamic parameter is 200 nm with a polydispersity index of 0.2.

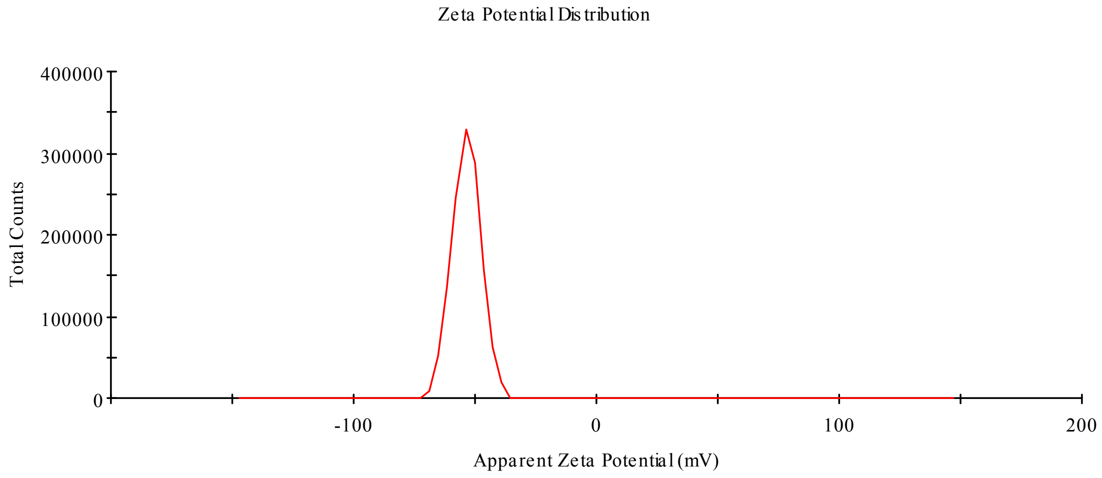

Figure S3. ζ-potential of $(NEAH)^{+}/(OAc)^{-}$ [$8.82 \cdot 10^{-5}$ M] in milli-Q water, pH = 8.2. ζ-potential is -53 ± 1 mV.

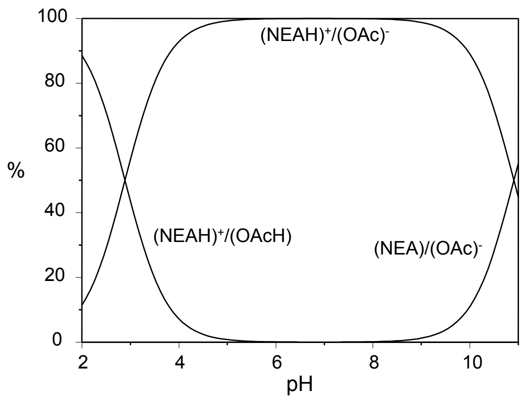

Figure S4. Distribution diagram of the protonated forms of $(NEA)/(OAc)^{-}$ (H_2O solution, NaCl 0.1 M, 298 K, $(NEA)/(OAc)^{-}$ = $1 \cdot 10^{-3}$ M).

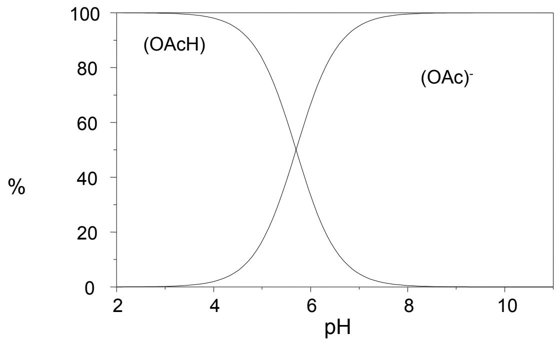

Figure S5. Distribution diagram for the protonated forms of OAcH (H_2O/EtOH 1:1 (v/v), NaCl 0.1 M, T = 298 K, [OAcH] = $1\cdot10^{-3}$M).

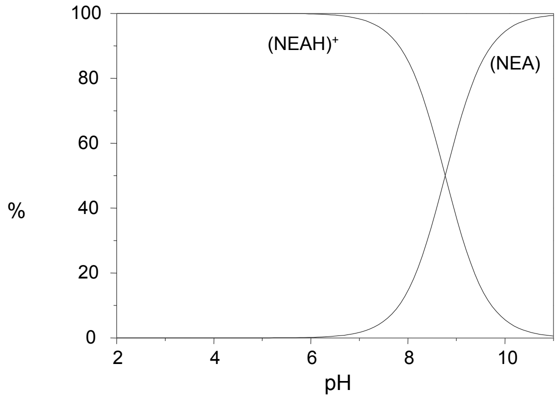

Figure S6. Distribution diagram for the protonated forms of NEA (H_2O/EtOH 1:1 (v/v), NaCl 0.1 M, T = 298 K, [NEA] = $1\cdot10^{-3}$M).

Table S3. Comparison of dimension and zeta potential of the emulsion in pure water and in NaCl 0.1 M.

Number	Conc IL (M)	Solvent	pH	Diameter average (nm)	Z potential
1	$8.82{\cdot}10^{-5}$	H_2O	7.0	**209**	**-53**
2	8.8210^{-5}	NaCl (0.1 M)	7.0	**335**	**-58**
3	8.8210^{-5}	NaCl(0.1 M)	10.7	**100/400**	**-56**

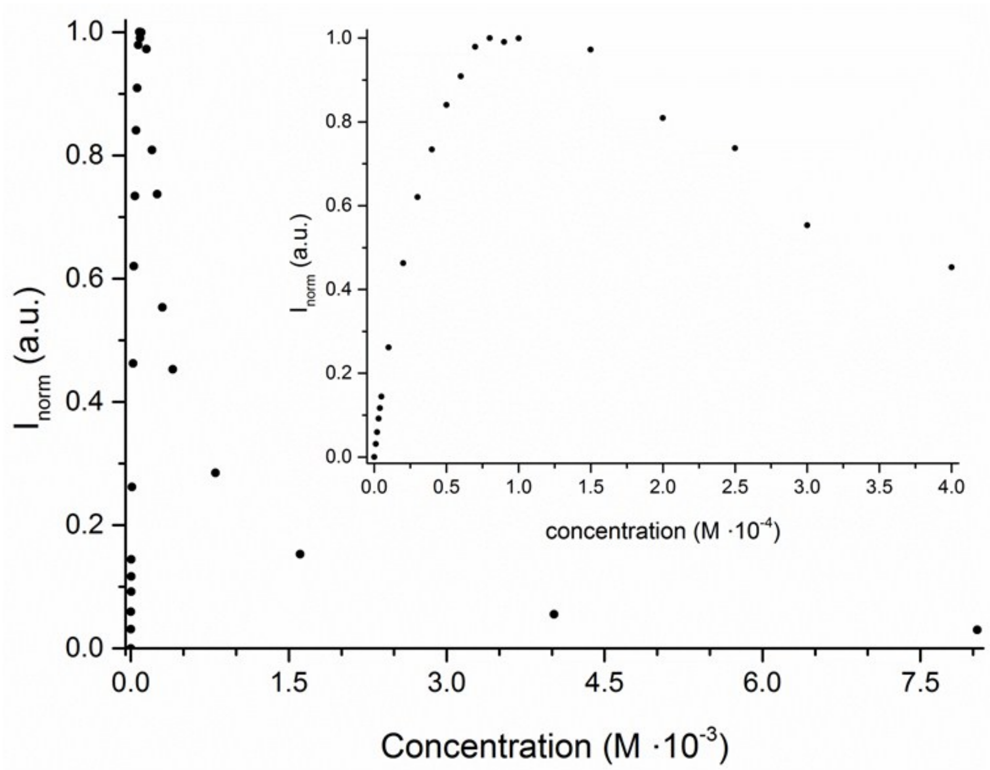

Figure S7. Changes in the fluorescence intensity of $(NEAH)^+/(OAc)^-$ *vs*. concentration (M) in the range $8.0 \cdot 10^{-3}$ M- $1.0 \cdot 10^{-6}$ M. Inset: zoom in the concentration range $4.0 \cdot 10^{-4}$ M- $1.0 \cdot 10^{-6}$ M.

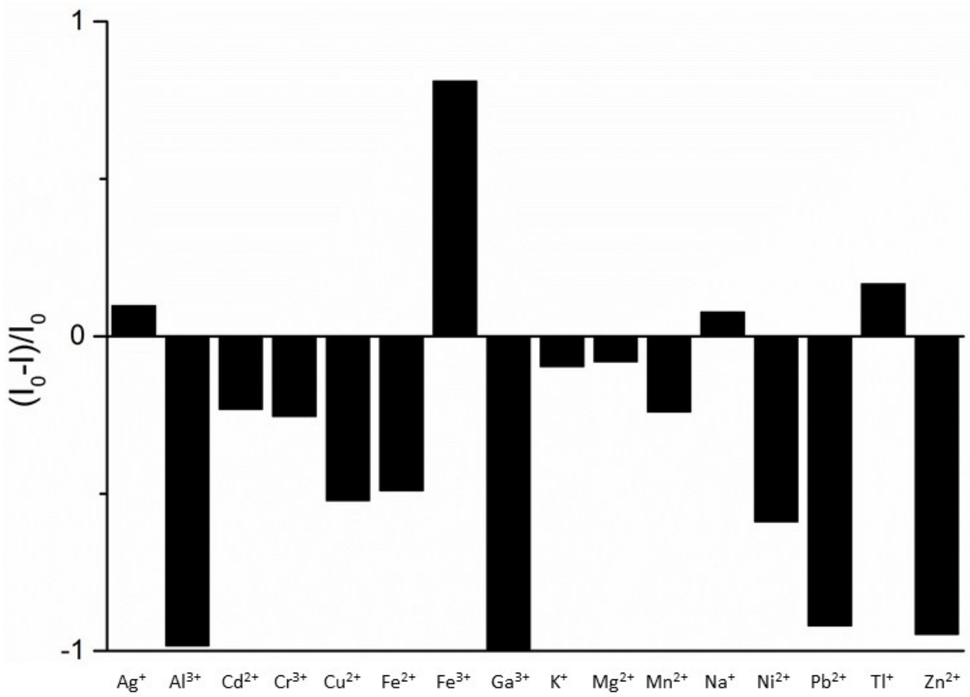

Figure S8. Changes in the fluorescence intensity reported as $(I_0-I)/I_0$ of $(NEAH)^+/(OAc)^-$ emulsion in water (λ_{em} = 333 nm, λ_{exc} = 281 nm) upon addition of 10 equivalents of different metal ions. ($(NEAH)^+/(OAc)^-$ = $8.82\cdot10^{-5}$ M, $[M]^{n+}$ = Ag^+, Al^{3+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ga^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Tl^+, and Zn^{2+}).

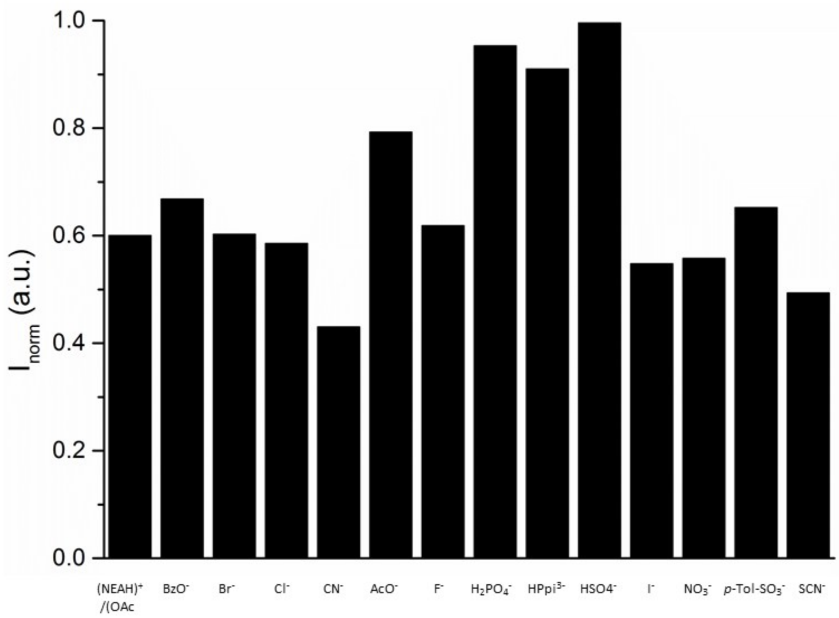

Figure S9. Changes in the fluorescence intensity of $(NEAH)^+/(OAc)^-$ emulsion in water (λ_{em} = 333 nm, λ_{exc} = 281 nm) upon addition of 10 equivalents of different anions. ($(NEAH)^+/(OAc)^-$ = $8.82\cdot10^{-5}$ M, $[A]^{n-}$ = BzO^-, Br^-, Cl^-, CN^-, AcO^-, F^-, $H_2PO_4^-$, $HPpi^{3-}$, HSO_4^-, I^-, NO_3^-, *p*-Tol-SO_3^- and SCN^-).

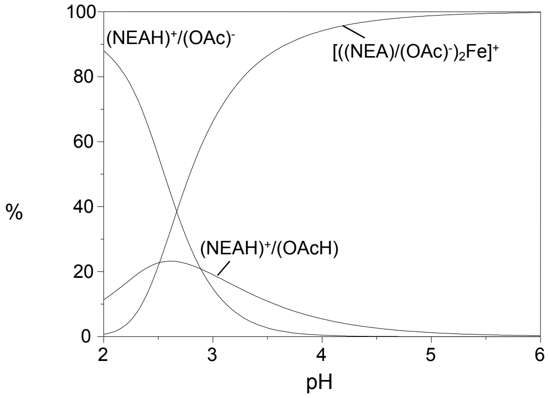

Figure S10. Distribution diagram of the complexes of (NEA)/(AOc)$^-$ emulsion with Fe^{3+} (aqueous solution, NaCl 0.1 M, T = 298 K, [NEA] = [Fe^{3+}] = $1{\cdot}10^{-3}$ M).

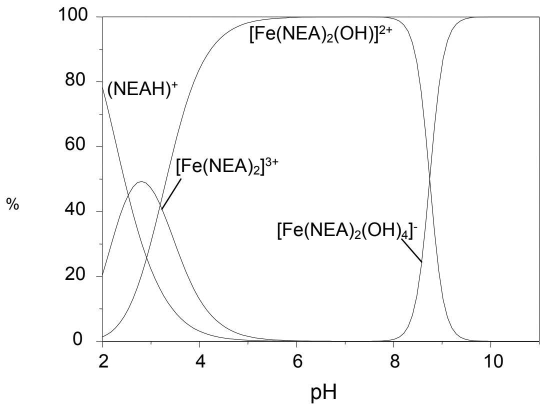

Figure S11. Distribution diagram of the complexes of NEA with Fe^{3+} (H_2O/EtOH 1:1 (v/v), NaCl 0.1 M, T = 298 K, [NEA] = [Fe^{3+}] = $1{\cdot}10^{-3}$ M).