

Ionic Liquid-Based Fluorescein Colorimetric pH Nanosensors

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Synthesis of the ILs

[TTP]₂[FL] was synthesized using an ion exchange reaction where TTPCl was dissolved in dichloromethane (DCM) and mixed with Na₂FL dissolved in water. Phosphonium chloride and disodium fluorescein were taken in a molar ratio of 2:1. The mixture was stirred for 48 hrs following which the two layers were separated. The DCM layers were washed several times with water to remove the water soluble impurities. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The product was obtained as orange viscous (yield 88%). For the synthesis of [TTP][FL], at first Na₂FL was monoprotated by stirring in an acetate buffer of pH 5.5 and then the sodium ion was exchanged with the TTP cation in a 1:1 molar ratio using the same ion-exchange reaction mentioned above. The product obtained was an orange yellow sticky solid (yield 93%). Both products were characterized by ¹H-NMR and mass spectrometry.

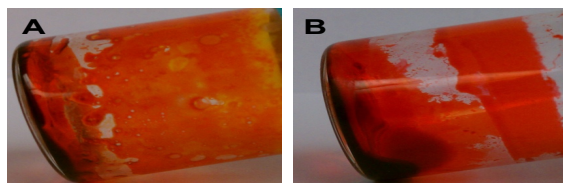


Fig S1: Pictures of the compounds (A) [TTP][FL] and (B) [TTP]₂[FL]

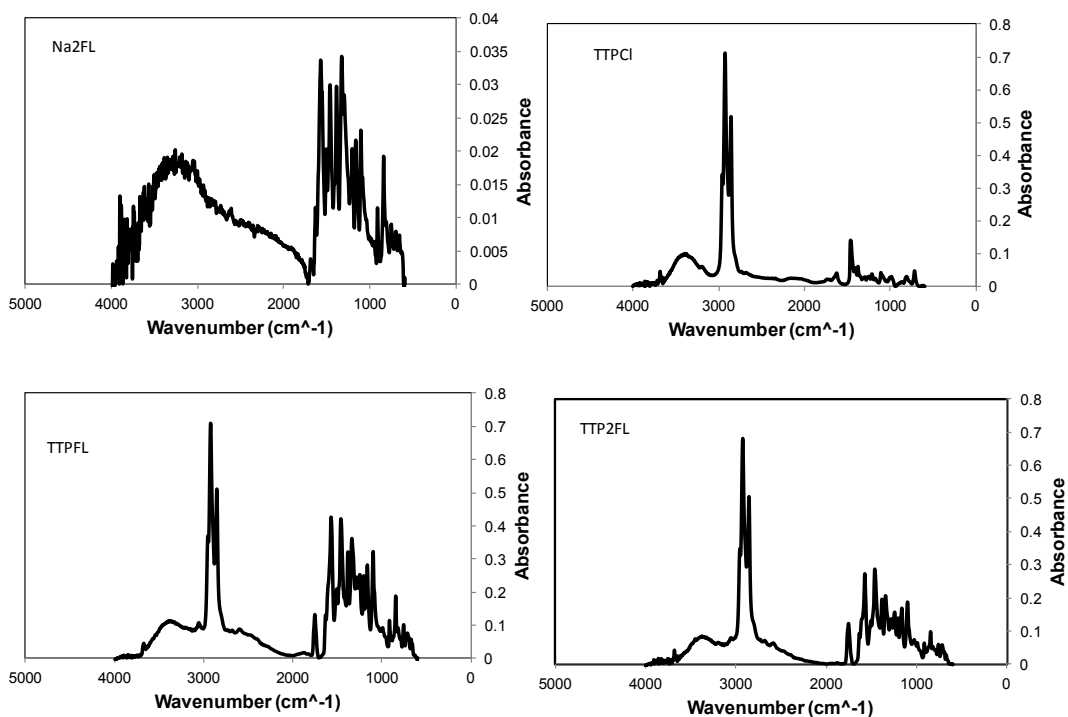


Fig S2. FTIR of the starting materials (top) and products (bottom).

^1H NMR characterization of $[\text{TTP}][\text{FL}]$ and $[\text{TTP}]_2[\text{FL}]$

$[\text{TTP}][\text{FL}]$

^1H -NMR (DMSO, 400 MHz): δ 7.95 (d, $J=8.32$, 1H), 7.55 (m, 2H), 7.13 (d, $J=7.44$ Hz, 1H), 6.57 (d, $J=9$ Hz, 2H), 6.34 (s, 1H), 6.30 (d, $J=8.88$ Hz, 2H), 2.15 (m, 8H), 1.45-1.23 (m, 48H), 0.85 (m, 12H).

$[\text{TTP}]_2[\text{FL}]$

^1H -NMR (DMSO, 400 MHz): δ 7.88 (d, $J=6.92$ Hz, 1H), 7.40 (m, 2H), 7.00 (d, $J=7.04$ Hz, 1H), 6.57 (d, $J=9.12$ Hz, 2H), 6.08 (m, 3H), 2.15 (m, 16H), 1.46-1.23 (m, 96H), 0.87 (m, 24H).

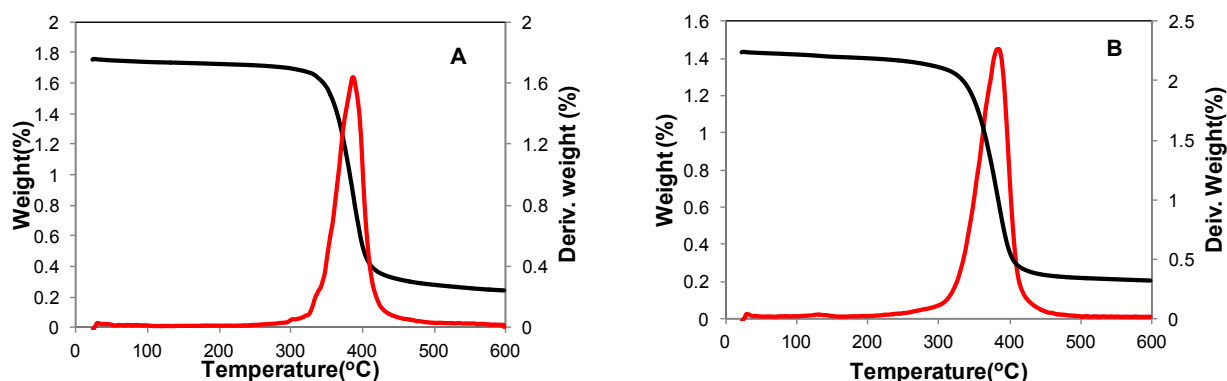


Fig S3. Thermogravimetric analysis of (A) $[\text{TTP}][\text{FL}]$ and (B) $[\text{TTP}]_2[\text{FL}]$.

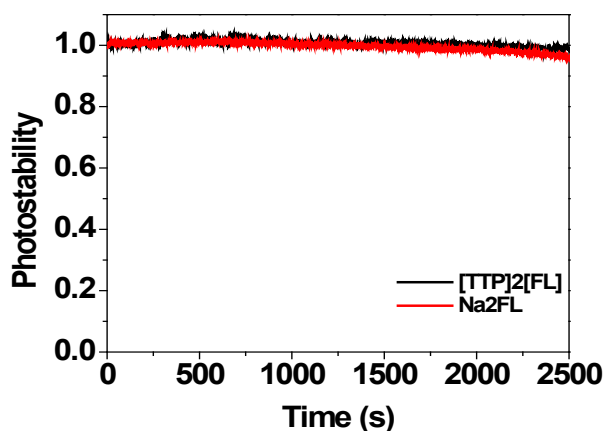


Figure S4: Photostabilities of $[\text{TTP}]_2[\text{FL}]$ nanoparticles compared to Na_2FL solution in water.

Table S1. Zeta Potential of [TTP][FL] and [TTP]₂[FL] nanodroplets at various pH values.

System	Zeta potential (mV)
[TTP] ₂ [FL] in water	+45.50
[TTP] ₂ [FL] in pH 7.4	+36.45
[TTP] ₂ [FL] in pH 5.4	-9.89
[TTP] ₂ [FL] in pH 4.0	+1.45
[TTP] ₂ [FL] in pH 2.2	+55.9
[TTP][FL] in water	+25.1
[TTP][FL] in pH 7.4	-12.35
[TTP][FL] in pH 5.4	-12.00
[TTP][FL] in pH 4.0	+0.09
[TTP][FL] in pH 2.2	+60.15