

## SUPPLEMENTARY

| NaNTf <sub>2</sub> | Phase IV-III |                      | Phase III-II |                      | Phase II-I |                      | Eutectic |                      | melt |                      |
|--------------------|--------------|----------------------|--------------|----------------------|------------|----------------------|----------|----------------------|------|----------------------|
| / % mol            | T/ °C        | ΔH /Jg <sup>-1</sup> | T/ °C        | ΔH /Jg <sup>-1</sup> | T/ °C      | ΔH /Jg <sup>-1</sup> | T/ °C    | ΔH /Jg <sup>-1</sup> | T/°C | ΔH /Jg <sup>-1</sup> |
| 0                  | -84          | 4.6                  | 18           | 1.9                  | 42         | 0.1                  | -        | -                    | 91   | 24.7                 |
| 1                  | -84          | 5.6                  | 17           | 1.9                  | 42         | 0.1                  | 62       | 0.6                  | 89   | 20.7                 |
| 6                  | -85          | 4.0                  | 18           | 2.2                  | 42         | 0.1                  | 63       | 6.5                  | 80   | 12.9                 |
| 15                 | -84          | 4.1                  | 18           | 1.5                  | 42         | 0.1                  | 65       | 32.5                 |      |                      |
| 35                 | -87          | 0.3                  | 18           | 0.8                  | 46         | 0.1                  | 64       | 18.1                 | 82   | 2.6                  |
| 40                 | -87          | 0.3                  | 18           | 0.6                  | 46         | 0.2                  | 65       | 12.5                 | 81   | 3.8                  |
| 45                 | -86          | 0.3                  | 19           | 0.7                  | 46         | 0.2                  | 65       | 16.9                 | 81   | 4.8                  |
| 50                 | -86          | 0.3                  | 18           | 0.8                  | 42         | 0.2                  | 62       | 6.7                  | 82   | 5.8                  |

Table S1: Enthalpy (in J/g) for the phase transitions calculated from the area under the peaks in DSC traces and the corresponding transition temperatures of mixed systems

| Assignment | Raman<br>□/cm <sup>-1</sup> | FTIR<br>□/cm <sup>-1</sup> |
|------------|-----------------------------|----------------------------|
|------------|-----------------------------|----------------------------|

|  |          |          |
|--|----------|----------|
| $\square \text{CF}_3$  | 278(ms)  |          |
| $\square \text{CF}_3, \square_a \text{CS}$   | 297(m)   |          |
| $\square \text{SO}_2, \square \text{CF}_3, \square_a \text{CS}$  | 314(w)   |          |
| $\square \text{SO}_2$  | 341(w)   |          |
| $\square \text{SO}_2$  | 397(m)   | 397(vw)  |
| $\square \text{SO}_2$  |          | 408(w)   |
| $\square_a \text{CF}_3$  |          | 512(s)   |
|  | 537(vw)  |          |
| $\square \text{N-C}, \square_s \text{SO}_2$  | 552(w)   |          |
| $\square \text{N-C}, \square_s \text{SO}_2, \square_a \text{CF}_3, \square_a \text{R},$<br>$\square_{\text{ip}}^{\text{s}} \text{R}$ | 570(w)   | 568(s)   |
| $\square_a \text{CF}_3, \square_a \text{ip SO}_2, \square_s \text{N-SO}_2$   | 590(w)   |          |
| $\square_a \text{SO}_2, \square_{\text{op}}^{\text{a}} \text{R}, \square \square_s \text{SNS},$<br>$\square_a \text{op SO}_2$        |          | 611(vs)  |
| $\square_s \text{CF}_3, \square_s \text{N-SO}_2$   | 631(vw)  |          |
|  | 715(vw)  |          |
| $\square_s \text{CF}_3$  | 741(vs)  | 739(m)   |
| $\square_s \text{SNS}$   |          | 762(w)   |
| $\square \text{CS}$  | 798(vw)  | 790(m)   |
|  | 824(vw)  |          |
| <b>Ring mode</b>   | 880(vw)  | 879(vw)  |
| <b>Ring mode</b>   | 902(m)   |          |
| <b>Ring mode</b>   |          | 936(w)   |
| <b>Ring mode</b>   | 998(w)   | 999(w)   |
|  |          | 1035(vw) |
| $\square_a \text{R}, \square \text{CC}, \square \text{N-CH}_3, \square_a \text{SNS}, \square_a \text{SNS}$                           | 1054(w)  | 1052(s)  |
| $\square_s \text{SO}_2$  | 1141(m)  | 1137(s)  |
| $\square_s \text{R}, \square \text{N-CH}_3, \square_a \text{CF}_3,$  |          | 1177(vs) |
| $\square_s \text{CF}_3, \square \square \text{CH}_2$   | 1243(ms) |          |
| $\square_a \text{op SO}_2, \square \text{CH}_3, \square \square \square (\text{R})$  | 1336(w)  | 1333(m)  |
| $\square_a \text{ip SO}_2, \square \square \square (\text{R}), \square_a \text{ip SO}_2$   | 1355(w)  | 1347(m)  |
|  |          | 1405(vw) |
| $\square \text{CH}_3, \square_{\text{ip}}^{\text{a}} \text{R}$   |          | 1434(vw) |
| $\square \text{CH}_2, \square \text{CH}_3,$  | 1455(m)  |          |
| $\square \text{CH}_2, \square \text{CH}_3$   |          | 1467(w)  |
| $\square \text{CH}_2$  | 2852(w)  |          |
| $\square \text{CH}_2$  | 2904(s)  | 2904(w)  |
| $\square \text{CH}_2$  | 2962(w)  | 2964(vw) |
| $\square \text{CH}_2$  | 3000(s)  | 2997(s)  |
|  | 3041(w)  | 3042(w)  |

Table S2: Assignment of observed Raman and FTIR bands of  $[\text{C}_2\text{mpyr}][\text{NTf}_2]$  at room temperature based on literature reports [17, 47, 48, 50, 52] for related cations and anions.  
 [Letters representing the vibrational modes : v - stretching, δ - bending, τ - twisting, ρ - rocking, ω - wagging, ip - in phase, op - out of phase, s - symmetric, as - asymmetric Letters indicating relative intensities: vw - very weak, w - weak, m - medium, s - strong, vs - very strong]

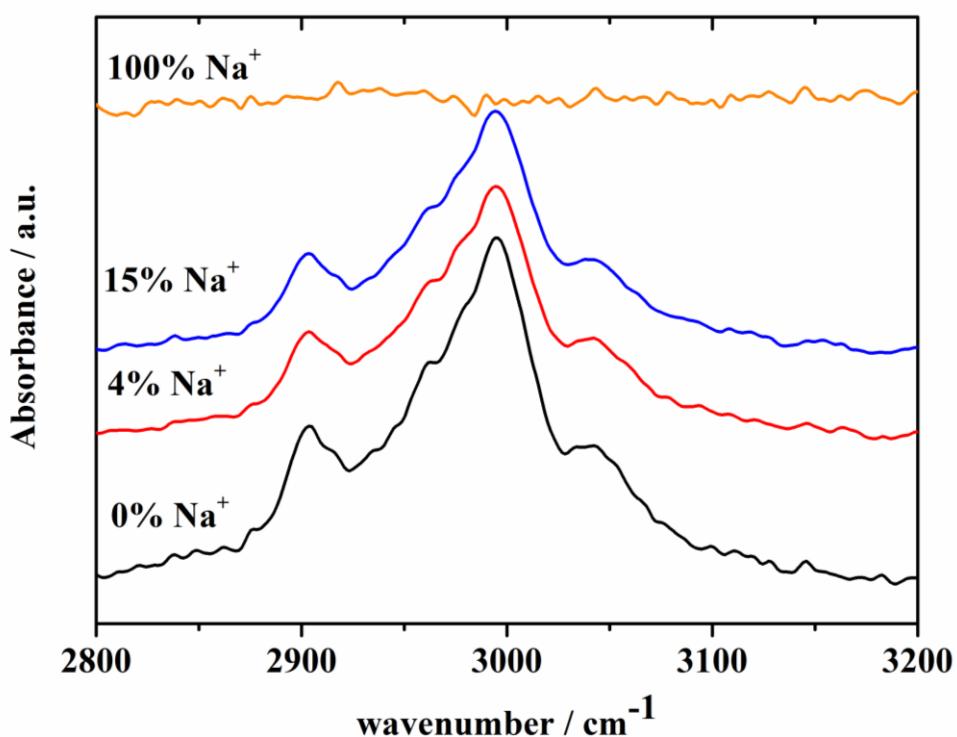


Figure S1. FTIR spectra of pure and mixed materials from  $2800 - 3200\text{cm}^{-1}$

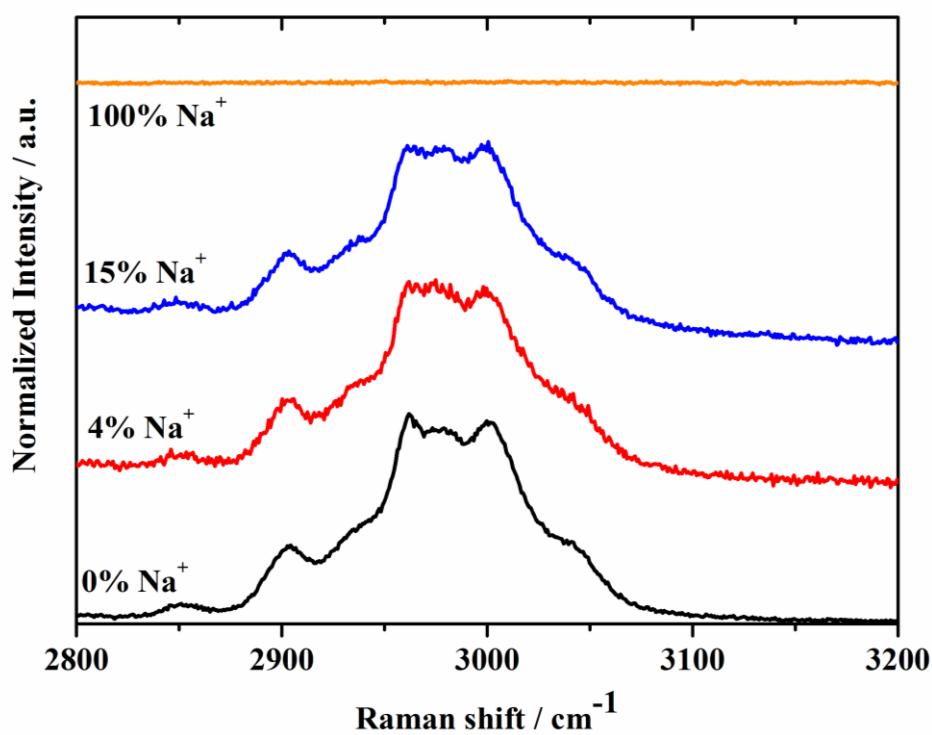


Figure S2. Raman spectra of pure and mixed materials from  $2800 - 3200 \text{ cm}^{-1}$