

**Two water-rich amphiphilic and hydrophilic coordination polymers:
syntheses, structures and proton conduction behaviors in Nafion
composite membranes**

Zhipeng Huan, Huiqi Zou, Na Wang, Jing Lu, Houting Liu*, Suna Wang*, Yunwu Li*

Table S1 The selected bond lengths and angels of compounds **1-2**.

| Compound 1 | | | |
|---------------------|------------|---------------------|------------|
| Cd(1)-O(7) | 2.268(4) | Cd(1)-O(1) | 2.284(4) |
| Cd(1)-O(4)#1 | 2.348(5) | Cd(1)-O(3)#1 | 2.486(4) |
| Cd(1)-O(2) | 2.650(4) | Cd(1)-N(1) | 2.338(6) |
| Cd(1)-N(2) | 2.324(6) | Cd(2)-O(9) | 2.284(5) |
| Cd(2)-O(5) | 2.219(4) | Cd(2)-O(8) | 2.314(5) |
| O(7)-Cd(1)-O(1) | 98.88(17) | O(7)-Cd(1)-N(2) | 93.00(18) |
| O(1)-Cd(1)-N(2) | 137.69(18) | O(7)-Cd(1)-N(1) | 162.3(2) |
| O(1)-Cd(1)-N(1) | 88.2(2) | N(2)-Cd(1)-N(1) | 71.2(2) |
| O(7)-Cd(1)-O(4)#1 | 103.31(17) | O(1)-Cd(1)-O(4)#1 | 83.95(15) |
| N(2)-Cd(1)-O(4)#1 | 132.37(17) | N(1)-Cd(1)-O(4)#1 | 93.6(2) |
| O(7)-Cd(1)-O(3)#1 | 88.43(15) | O(1)-Cd(1)-O(3)#1 | 136.85(16) |
| N(2)-Cd(1)-O(3)#1 | 83.57(17) | N(1)-Cd(1)-O(3)#1 | 97.51(18) |
| O(4)#1-Cd(1)-O(3)#1 | 53.11(14) | O(7)-Cd(1)-O(2) | 81.15(14) |
| O(1)-Cd(1)-O(2) | 52.00(14) | N(2)-Cd(1)-O(2) | 90.64(16) |
| N(1)-Cd(1)-O(2) | 90.72(17) | O(4)#1-Cd(1)-O(2) | 135.59(14) |
| O(3)#1-Cd(1)-O(2) | 167.81(14) | O(5)-Cd(2)-O(9)#2 | 88.33(19) |
| O(5)-Cd(2)-O(8) | 91.63(17) | O(5)-Cd(2)-O(9) | 91.67(19) |
| O(5)#2-Cd(2)-O(8) | 88.37(17) | O(9)#2-Cd(2)-O(8) | 88.9(2) |
| O(9)-Cd(2)-O(8) | 91.1(2) | O(5)-Cd(2)-O(8)#2 | 88.37(17) |
| Compound 2 | | | |
| Zn(1)-O(1) | 1.992(4) | Zn(1)-O(2) | 2.144(4) |
| Zn(1)-O(3) | 2.156(3) | Zn(2)-O(5) | 2.040(3) |
| Zn(2)-O(6) | 2.102(3) | Zn(2)-O(7) | 2.141(3) |
| Zn(2)-O(8) | 2.101(3) | Zn(2)-O(9) | 2.170(3) |
| Zn(2)-O(10) | 2.032(3) | | |
| O(1)#1-Zn(1)-O(1) | 104.0(4) | O(1)-Zn(1)-O(2)#1 | 94.12(16) |
| O(1)-Zn(1)-O(2) | 83.86(16) | O(2)#1-Zn(1)-O(2) | 176.7(2) |
| O(1)-Zn(1)-O(3)#1 | 156.35(18) | O(2)#1-Zn(1)-O(3)#1 | 95.97(15) |
| O(2)-Zn(1)-O(3)#1 | 86.85(14) | O(1)-Zn(1)-O(3) | 98.3(2) |
| O(2)-Zn(1)-O(3) | 95.97(15) | O(3)#1-Zn(1)-O(3) | 61.04(17) |
| O(10)-Zn(2)-O(5) | 173.76(15) | O(10)-Zn(2)-O(8) | 89.94(13) |
| O(5)-Zn(2)-O(8) | 93.80(14) | O(10)-Zn(2)-O(6) | 90.50(13) |

| | | | |
|------------------|-----------|------------------|------------|
| O(5)-Zn(2)-O(6) | 86.10(13) | O(8)-Zn(2)-O(6) | 176.11(15) |
| O(5)-Zn(2)-O(7) | 90.99(13) | O(7)-Zn(2)-O(9) | 178.83(15) |
| O(6)-Zn(2)-O(7) | 87.93(14) | O(8)-Zn(2)-O(7) | 88.18(14) |
| O(5)-Zn(2)-O(9) | 88.93(14) | O(8)-Zn(2)-O(9) | 92.99(14) |
| O(6)-Zn(2)-O(9) | 90.90(14) | O(10)-Zn(2)-O(9) | 85.89(14) |
| O(10)-Zn(2)-O(7) | 94.12(14) | | |

Symmetry codes: compound **1** #1 $x-1, y, z$; #2 $-x+2, -y+2, -z+1$; #3 $x+1, y, z$; compound **2** #1 $-x+2, y, -z+1$.

Table S2 The hydrogen bond parameters of compounds **1** and **2**.

| D-H \cdots A | d(H \cdots A) | \angle DHA | d(D \cdots A) |
|--------------------------------|-----------------|--------------|-----------------|
| Compound 1 | | | |
| O7-H \cdots O6 ^a | 1.862 | 169.18 | 2.702 |
| O7-H \cdots O10 | 1.879 | 177.55 | 2.728 |
| O8-H \cdots O6 | 2.281 | 115.28 | 2.754 |
| O8-H \cdots O2 ^b | 2.204 | 133.27 | 2.855 |
| O10-H \cdots O4 ^c | 2.052 | 147.73 | 2.808 |
| O10-H \cdots O1 ^d | 2.390 | 115.02 | 2.855 |
| Compound 2 | | | |
| O1-H \cdots O12 ^e | 2.012 | 175.47 | 2.860 |
| O1-H \cdots O6 ^f | 1.850 | 158.37 | 2.658 |
| O2-H \cdots O12 ^g | 2.044 | 163.17 | 2.868 |
| O2-H \cdots O8 ^h | 2.365 | 120.19 | 2.888 |
| O6-H \cdots O11 | 2.088 | 113.54 | 2.549 |
| O6-H \cdots O12 ⁱ | 2.272 | 123.57 | 2.832 |
| O7-H \cdots O11 ^j | 1.831 | 176.25 | 2.680 |
| O7-H \cdots O9 ^k | 2.428 | 160.99 | 3.243 |
| O8-H \cdots O3 ^l | 2.210 | 138.24 | 2.900 |
| O8-H \cdots O4 | 2.012 | 127.17 | 2.614 |
| O9-H \cdots O4 ^m | 1.915 | 165.12 | 2.745 |
| O9-H \cdots O12 ⁿ | 2.332 | 149.03 | 3.092 |

Symmetry codes: compound **1** a $-x+1, -y+1, -z+1$; b $x, y+1, z$; c $-x+2, -y+1, -z+1$; d $-x+1, -y+1, -z+1$; e $x+1/2, y+3/2, z$; f $-x+2, y+1, -z+1$; g $-x+3/2, y+3/2, -z$; h $-x+3/2, y+1/2, -z$; i $-x+3/2, y+1/2, -z$; j $-x+3/2, y+1/2, -z$; k $x, y, z-1$; l $x-1/2, y-1/2, z$; m $-x+3/2, y-1/2, -z+1$; n $-x+3/2, y+1/2, -z+1$.

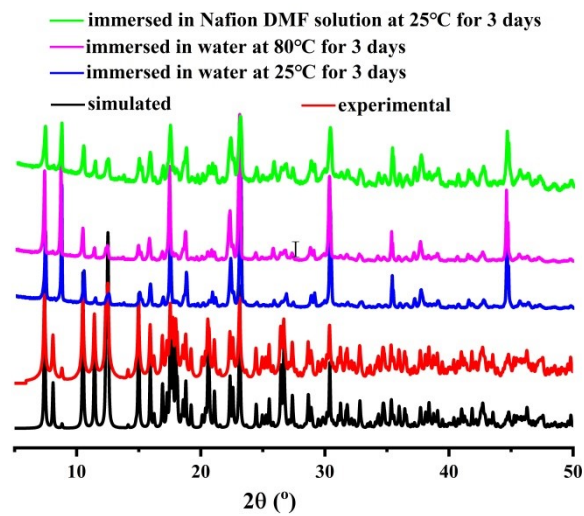
Table S3. Proton conductivities ($S \cdot cm^{-1}$) of pure Nafion membrane and **1**/Nafion-x composite membranes at different temperatures

| T (K) | pure Nafion | 1 /Nafion-3 | 1 /Nafion-5 | 1 /Nafion-7 |
|-------|-----------------------|-----------------------|------------------------|-----------------------|
| 308 | 2.55×10^{-3} | 2.42×10^{-3} | 6.02×10^{-3} | 3.90×10^{-3} |
| 313 | 2.95×10^{-3} | 2.47×10^{-3} | 6.21×10^{-3} | 4.54×10^{-3} |
| 318 | 3.48×10^{-3} | 3.59×10^{-3} | 6.85×10^{-3} | 5.05×10^{-3} |
| 323 | 4.19×10^{-3} | 4.55×10^{-3} | 7.73×10^{-3} | 4.79×10^{-3} |
| 328 | 4.76×10^{-3} | 5.55×10^{-3} | 8.26×10^{-3} | 5.37×10^{-3} |
| 333 | 5.43×10^{-3} | 6.62×10^{-3} | 8.50×10^{-3} | 6.20×10^{-3} |
| 338 | 6.26×10^{-3} | 7.64×10^{-3} | 9.19×10^{-3} | 6.11×10^{-3} |
| 343 | 7.00×10^{-3} | 8.51×10^{-3} | 9.39×10^{-3} | 7.12×10^{-3} |
| 348 | 7.45×10^{-3} | 9.32×10^{-3} | 10.20×10^{-3} | 7.91×10^{-3} |
| 353 | 8.48×10^{-3} | 9.86×10^{-3} | 10.92×10^{-3} | 8.81×10^{-3} |

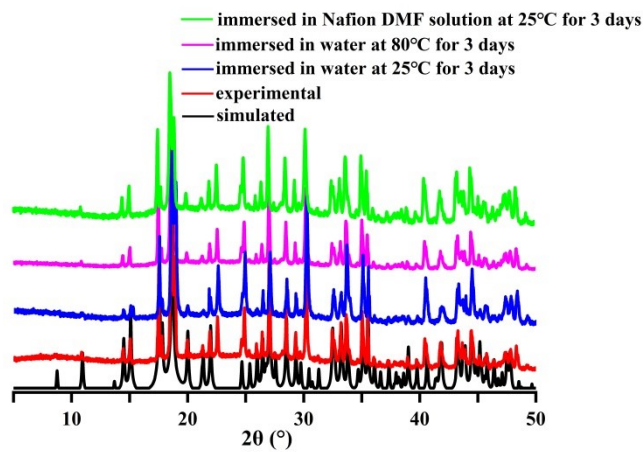
Table S4. Proton conductivities ($S \cdot cm^{-1}$) of pure Nafion membrane and **2**/Nafion-x composite membranes at different temperatures

| T (K) | pure Nafion | 2 /Nafion-1 | 2 /Nafion-3 | 2 /Nafion-5 |
|-------|-----------------------|-----------------------|-----------------------|-----------------------|
| 308 | 2.55×10^{-3} | 2.95×10^{-3} | 4.44×10^{-3} | 4.36×10^{-3} |
| 313 | 2.95×10^{-3} | 3.99×10^{-3} | 5.03×10^{-3} | 4.85×10^{-3} |
| 318 | 3.48×10^{-3} | 4.75×10^{-3} | 5.62×10^{-3} | 5.26×10^{-3} |
| 323 | 4.19×10^{-3} | 5.20×10^{-3} | 6.03×10^{-3} | 5.73×10^{-3} |
| 328 | 4.76×10^{-3} | 6.38×10^{-3} | 6.73×10^{-3} | 6.43×10^{-3} |
| 333 | 5.43×10^{-3} | 6.97×10^{-3} | 7.79×10^{-3} | 7.30×10^{-3} |
| 338 | 6.26×10^{-3} | 7.65×10^{-3} | 8.94×10^{-3} | 7.83×10^{-3} |

| | | | | |
|-----|-----------------------|------------------------|------------------------|------------------------|
| 343 | 7.00×10^{-3} | 8.36×10^{-3} | 10.42×10^{-3} | 9.02×10^{-3} |
| 348 | 7.45×10^{-3} | 9.42×10^{-3} | 12.10×10^{-3} | 9.94×10^{-3} |
| 353 | 8.48×10^{-3} | 10.65×10^{-3} | 13.18×10^{-3} | 11.41×10^{-3} |



(a)



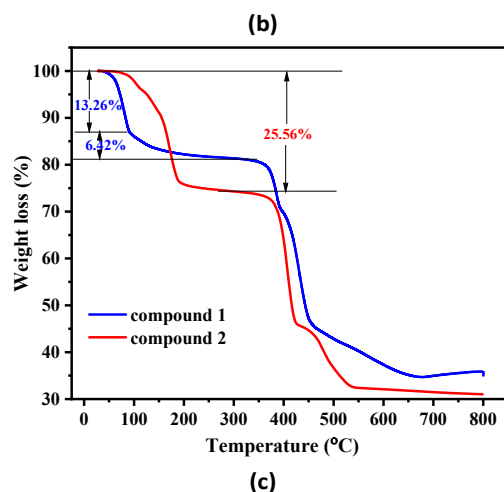


Fig. S1 Simulated, experiment water treatment and Nafion DMF treatment sample PXRD patterns of compounds **1** (a) and **2** (b); the TG curves of of compounds **1** and **2** (c).

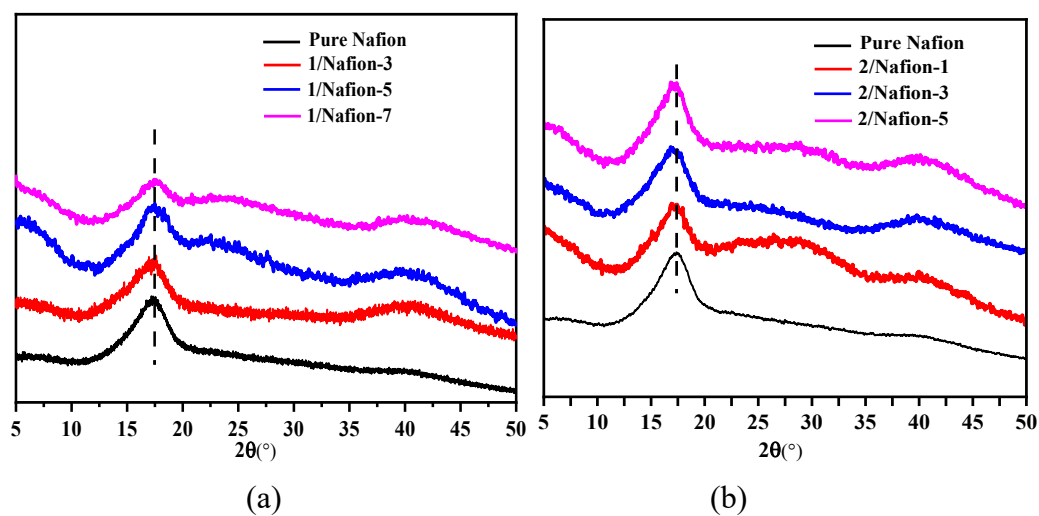


Fig. S2 PXRD of pure Nafion and **1**/Nafion-x (a) and PXRD of pure Nafion and **2**/Nafion-x (b).

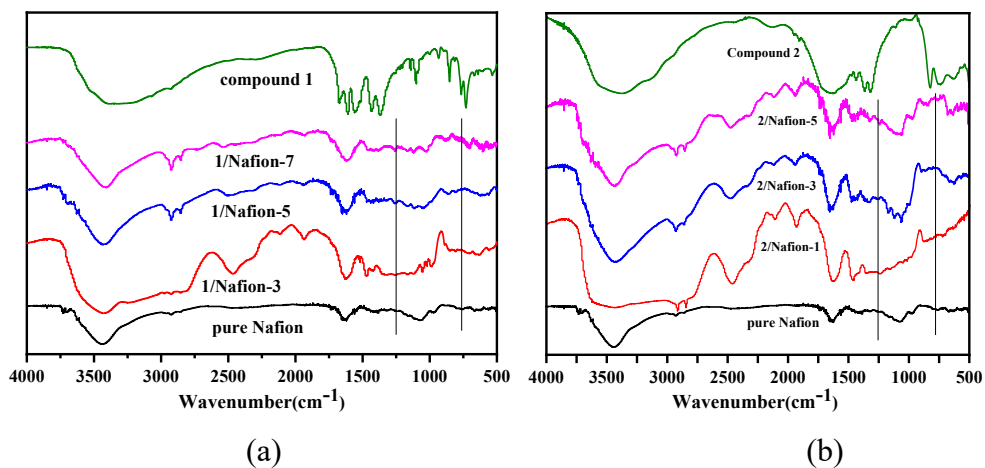


Fig. S3 IR spectra of pure Nafion and 1/Nafion-x (a) and PXRD of pure Nafion and 2/Nafion-x (b).

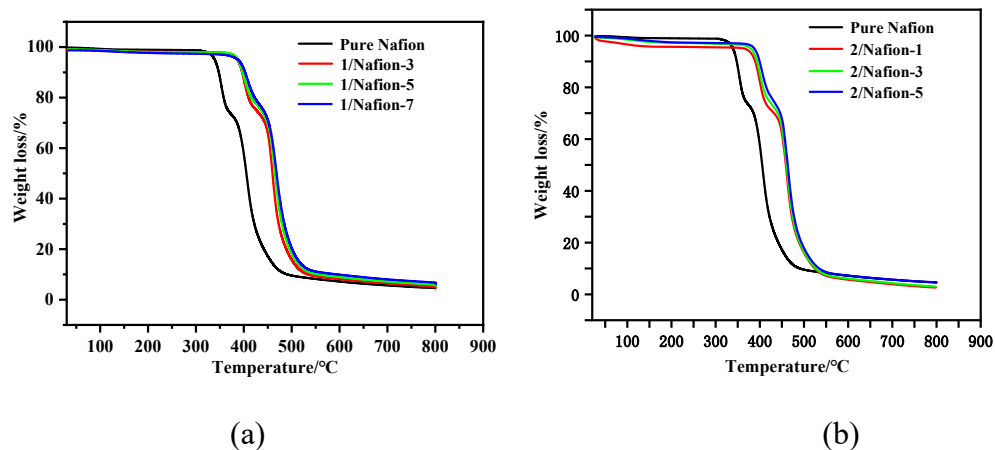


Fig. S4 TG curves of pure Nafion and 1/Nafion-x (a) and PXRD of pure Nafion and 2/Nafion-x (b).

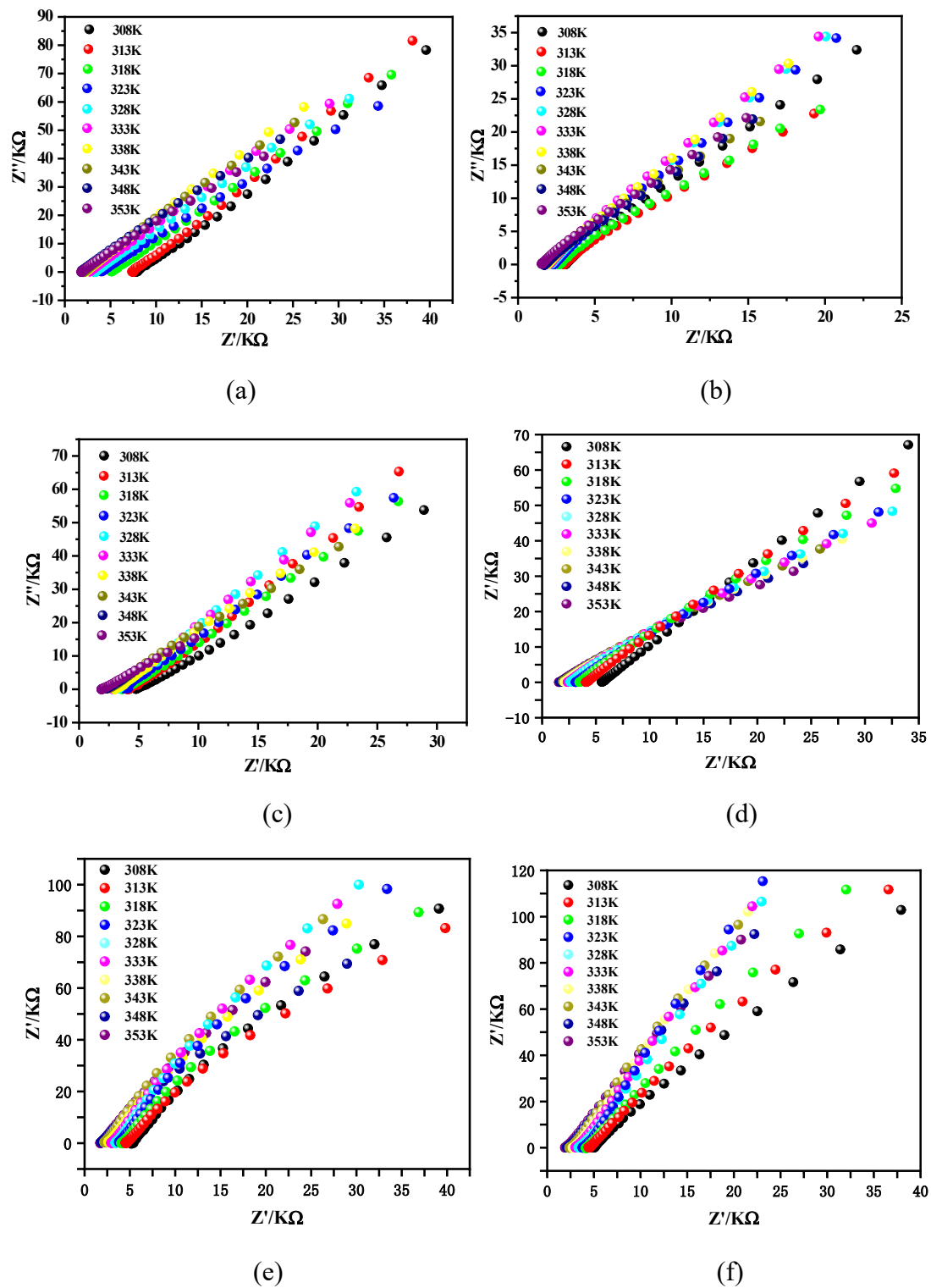


Fig. S4 Nyquist curves of 1/Nafion-3(a), 1/Nafion-5(b), 1/Nafion-7(c), 2/Nafion-1(d), 2/Nafion-3(e) and 2/Nafion-5(f) composite membranes at different temperatures.