

Novel anion exchange membrane based on poly(pentafluorostyrene) substituted with mercaptotetrazole pendant groups and its blend with polybenzimidazole for vanadium redox flow battery application

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Table S1. Optimization for PPFSt-MTZ synthesis.

| Entry | Solvent | Equivalents of 1-(2-Dimethylaminoethyl)-5-mercaptotetrazole | Reaction conditions | Substitution Results* |
|-------|-----------|---|---------------------|------------------------------|
| 1 | NMP / MEK | 5 | 80 °C, 18 hours | Low substitution (1% DOS) |
| 2 | MEK | 1 | 55 °C, 72 hours | No substitution |
| 3 | NMP / MEK | 5 | 80 °C, 72 hours | Low substitution (15% DOS) |
| 4 | NMP / MEK | 5 | 95 °C, 72 hours | Used in this study (41% DOS) |
| 5 | NMP / MEK | 5 | 95 °C, 168 hours | 40 % DOS |

* Degree of substitution (DOS) was calculated by F-NMR

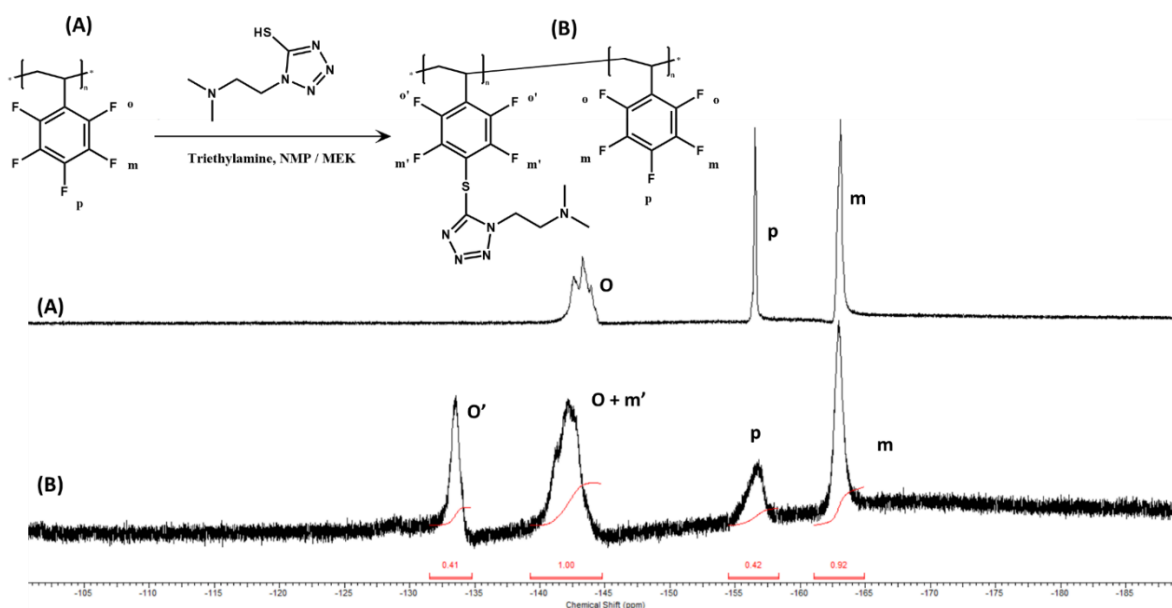


Figure S1. Calculation of degree of substitution confirming 41%.

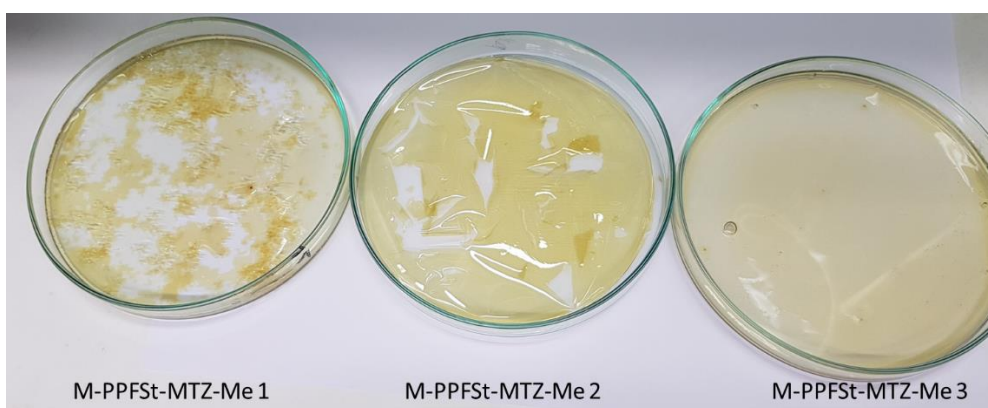


Figure S2. Photographs of the blend membranes.

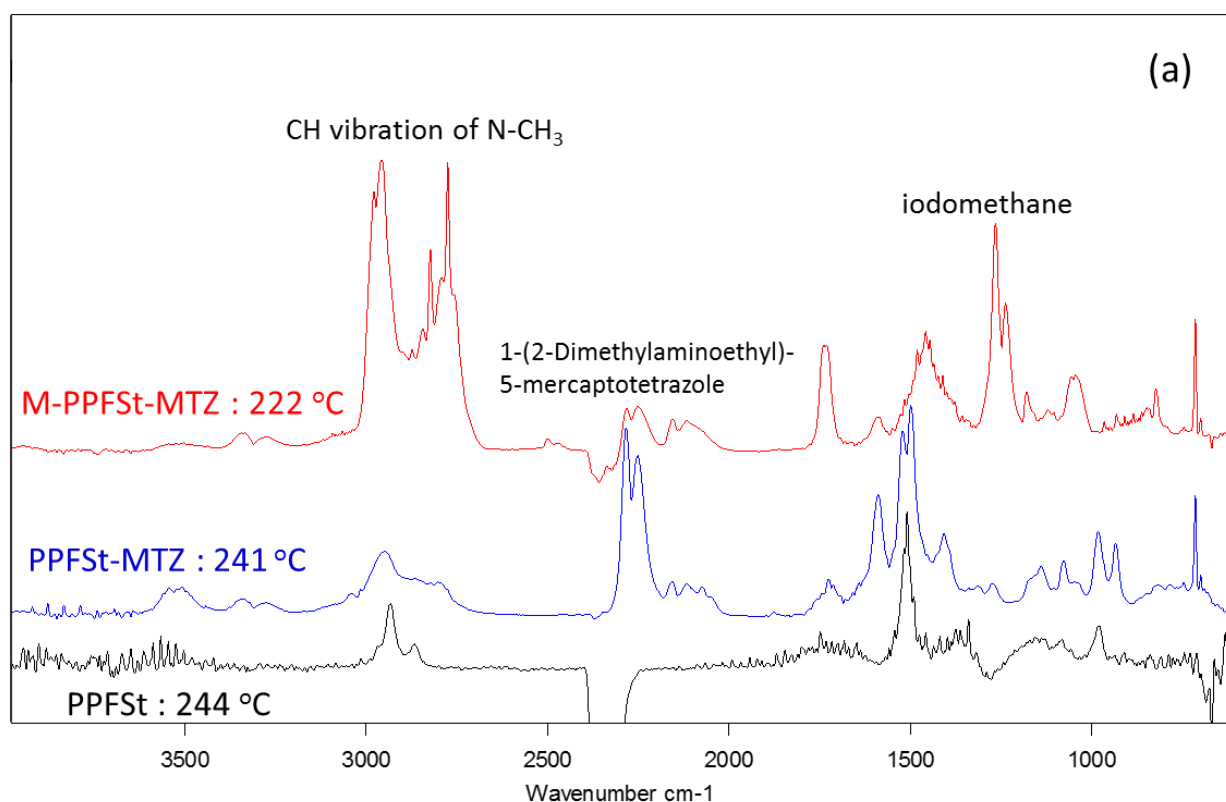
Table S2. The blend membranes preparation.

| Membrane | M-PPFSt-MTZ : F6-PBI (by weight) | Membrane formation (see Figure S2) |
|------------------|-------------------------------------|---------------------------------------|
| M-PPFSt-MTZ-Me 1 | 9 : 1 | Brittle |
| M-PPFSt-MTZ-Me 2 | 8 : 2 | Brittle |
| M-PPFSt-MTZ-Me 3 | 7 : 3 | Ductile |
| M-PPFSt-MTZ-Me 4 | 6 : 4 | Ductile |

The blend membrane of M-PPFSt-MTZ-Me 3 was mechanically stable after drying the

solvent. Therefore, blend membranes of M-PPFSt-MTZ-Me 3 and M-PPFSt-MTZ-Me 4 were prepared as larger membranes onto glass plate for the investigation in this study.

As seen in the Figure S3 (a), a strong peak 2957 cm^{-1} can be assigned to C-H vibration of N-CH₃ from the 1-(2-dimethylaminoethyl)-5-mercaptopotetrazole. A strong peak at 1264 cm^{-1} can be assigned to the iodomethane by a nucleophilic substitution of iodide. The peaks at 2200 and 2400 cm^{-1} can be assigned to the loss of side chains, 1-(2-dimethylaminoethyl)-5-mercaptopotetrazole. Above 340°C , polymer main back bone degradation was observed for all polymers, PPFSt, PPFSt-MTZ and M-PPFSt-MTZ (Figure S3 (b)).



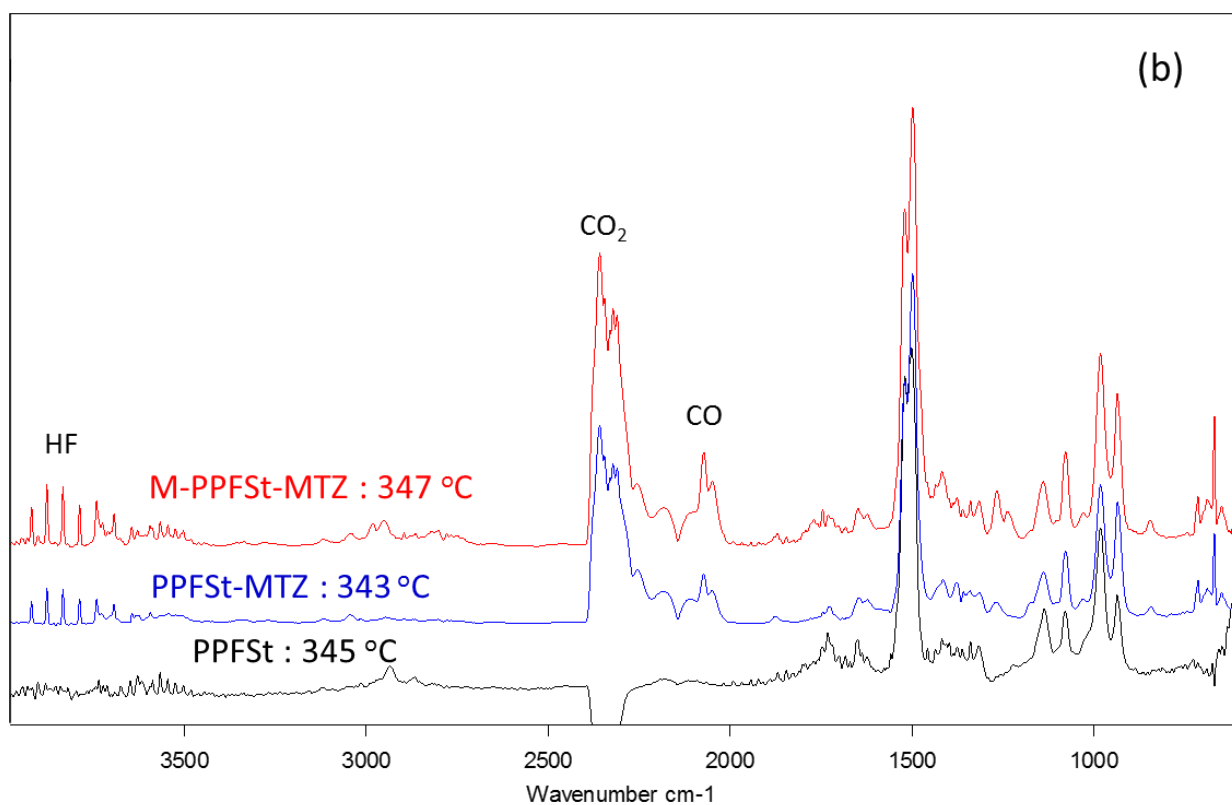


Figure S3. FT-IR spectrum of decomposed gases from first degradation step (a) and polymer main chain degradation (b).