Supporting Information

Supramolecular Architecture of Molecular-Level-Ordered 1,1'-Ferrocenedicarboxylic acid with Poly(4-vinylpyridine) for Bulk Magnetic Coupling

Hong-Joon Lee[1], Won-Jeong Shin[1], Nakheon Sung[1], Wonbin Kim[1], Beongki Cho[1,2], Mohammad Changez[1,3]* and Jae-Suk Lee[1]*

[1]School of Materials Science and Engineering, [2]Grünberg Center for Magnetic Nanomaterials, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61005, Korea

[3]Department of Basic Sciences, College of Applied Sciences, A'Sharqiyah University, Ibra 400, Oman

* Corresponding Authors. E-mail: jslee@gist.ac.kr; mchangej@asu.edu.om

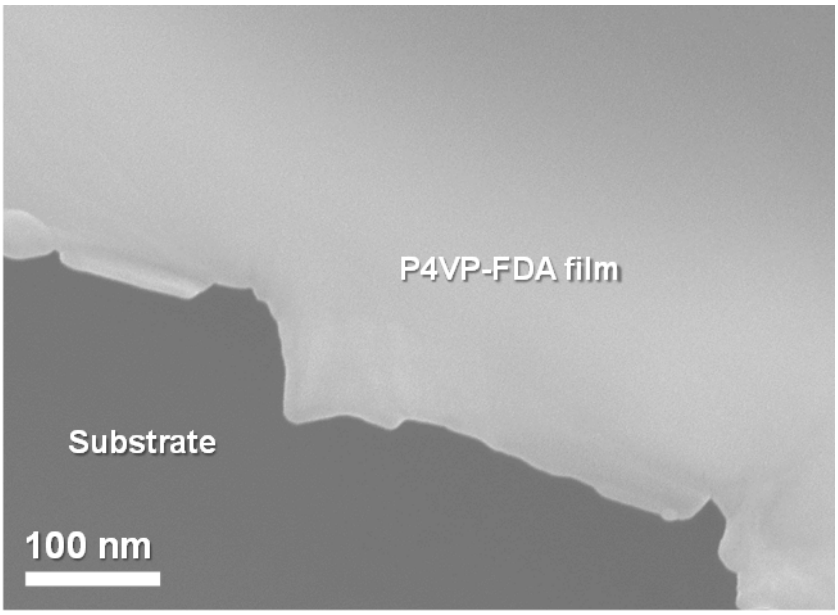

Figure S1. SEM micrograph of the hydrogen-bonded P4VP film with FDA. The morphology shows a uniform, smooth surface of P4VP-FDA on the Si wafer.

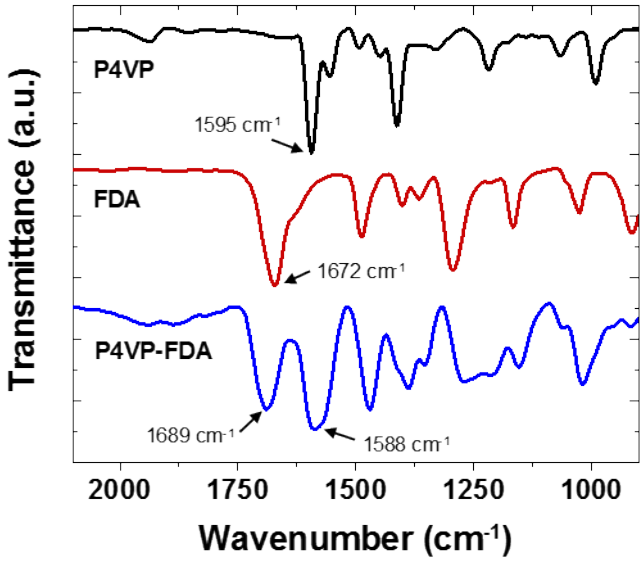

Figure S2. FT-IR spectra of P4VP, FDA and P4VP-FDA. Coexistence of P4VP and FDA is confirmed from FT-IR spectroscopy, which shows the absorptions of pyridine and carbonyl groups. Hydrogen-bonding interactions influences the absorption of each participating functional group in the interaction.

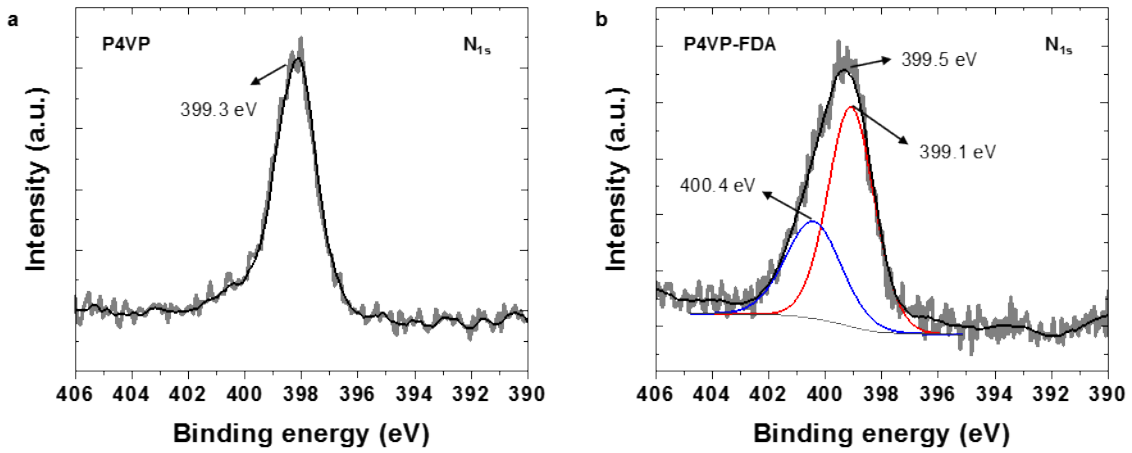

Figure S3. Comparison of the N_{1s} signals in XPS after hydrogen bonding. XPS spectra of the N_{1s} signals of P4VP (a) and P4VP-FDA (b).

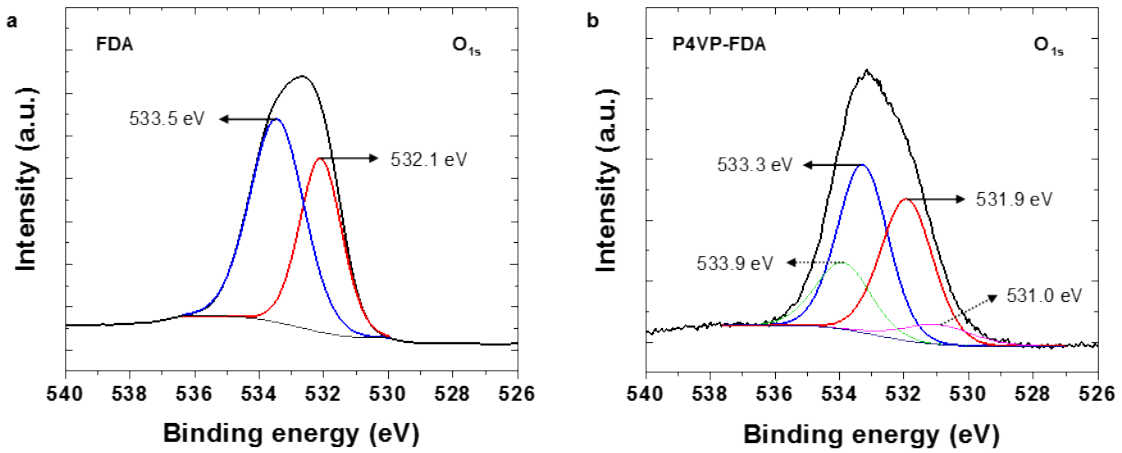

Figure S4. Comparison of the O_{1s} signals in XPS after self-assembly. XPS spectra of the O_{1s} signals of (a) FDA and (b) P4VP-FDA. In the spectrum of FDA, two components are observed corresponding to the carbonyl (532.1 eV) and hydroxyl (533.5 eV) groups. After self-assembly of FDA with P4VP, these peaks are also observed and slightly shifted to 531.9 and 533.3 eV, respectively. A low percentage of a H_2O peak (533.9 eV) is also detected along with a small peak corresponding to carboxylate groups (531.0 eV).

Presence of a low percentage of H_2O detected in the XPS spectrum is not unexpected. Pyridine units in P4VP can easily absorb moisture in air. This is attributed to poly(4-vinylpyridine) being a weakly hydrophilic polymer, which can be simultaneously crosslinked and quaternized, a property utilized for humidity sensor applications (Li, Y.; Yang, M.; She, Y., Humidity Sensitive Properties of Crosslinked and Quaternized Poly (4-vinylpyridine-co-butyl methacrylate). *Sensors and Actuators B: Chemical* **2005**, *107*, 252-257. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M., A Humidity Sensor Using Cross-linked Quaternized Polyvinylpyridine. *J. Electrochem. Soc.* **1989**, *136*, 171-174.). It is possible that a small amount of the hydrogen bonded structure (N…HOCO) undergoes proton transfer leading to quaternization of pyridine N and onset of ionic interaction

(NH^+ COO^-). The presence of a small amount of the carboxylate group in the XPS further supports this possibility.

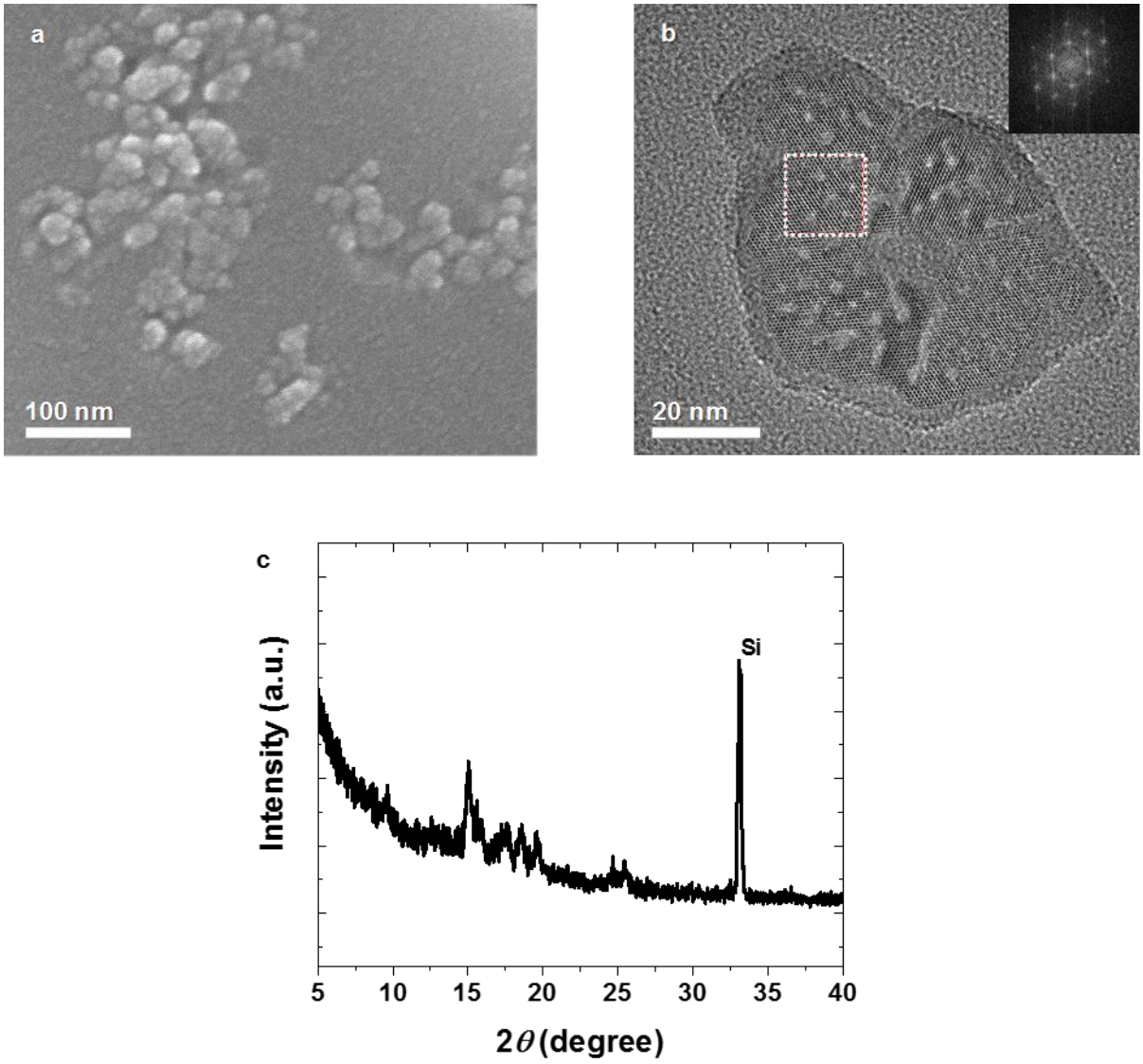

Figure S5. Morphology and HRTEM studies of pure FDA. a) SEM image of pristine FDA. b) HRTEM micrograph (inset: FFT image of the white square box in the HRTEM image) of FDA. c) XRD pattern of the FDA film. For SEM and XRD, FDA is drop-cast on Si wafers.

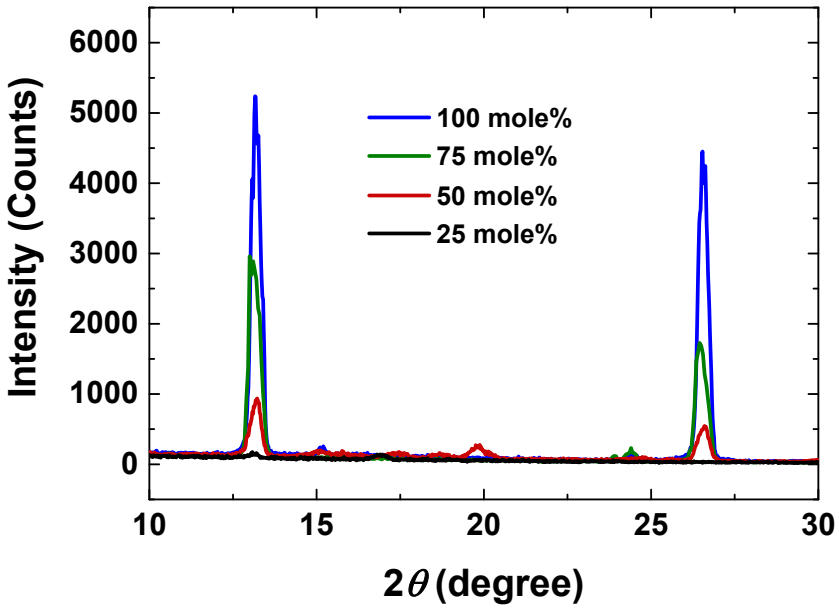

Figure S6. XRD spectra of P4VP-FDA varying the ratio between FDA and pyridine repeating unit of P4VP.

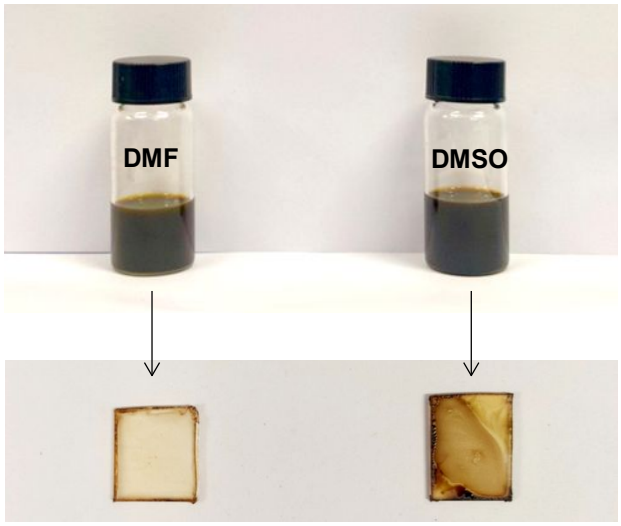

Figure S7. Color of the solution and drop-cast film of P4VP-FDA prepared using DMF and DMSO as a solvent.

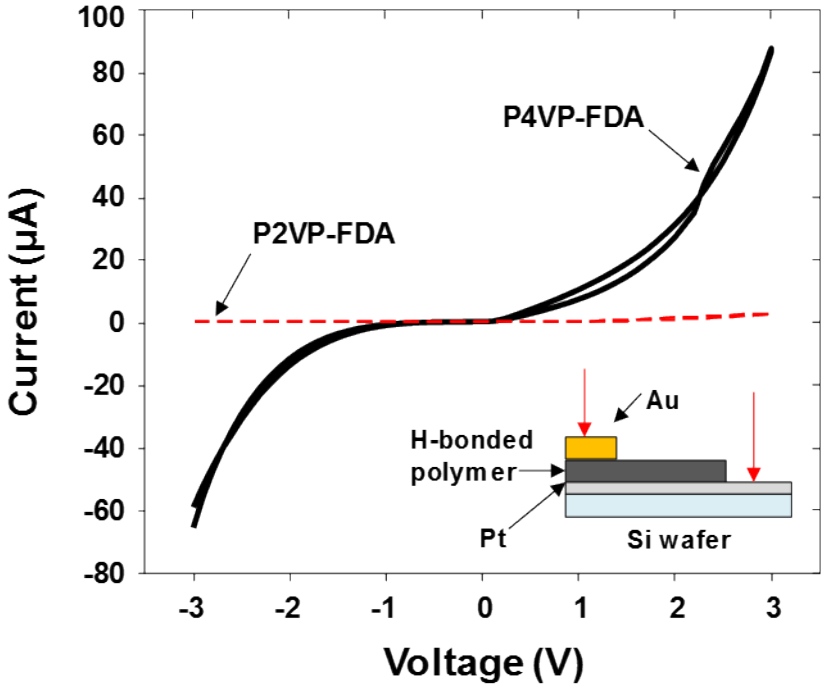

Figure S8. I-V curves of P4VP-FDA and P2VP-FDA. P2VP and P4VP both are insulating polymers. Thus, the P2VP-FDA film, which has a nearly amorphous nature, shows low electrical current; however, the P4VP-FDA film shows much higher current than that of P2VP-FDA. This indicates the self-assembled structures facilitate electron transfer.

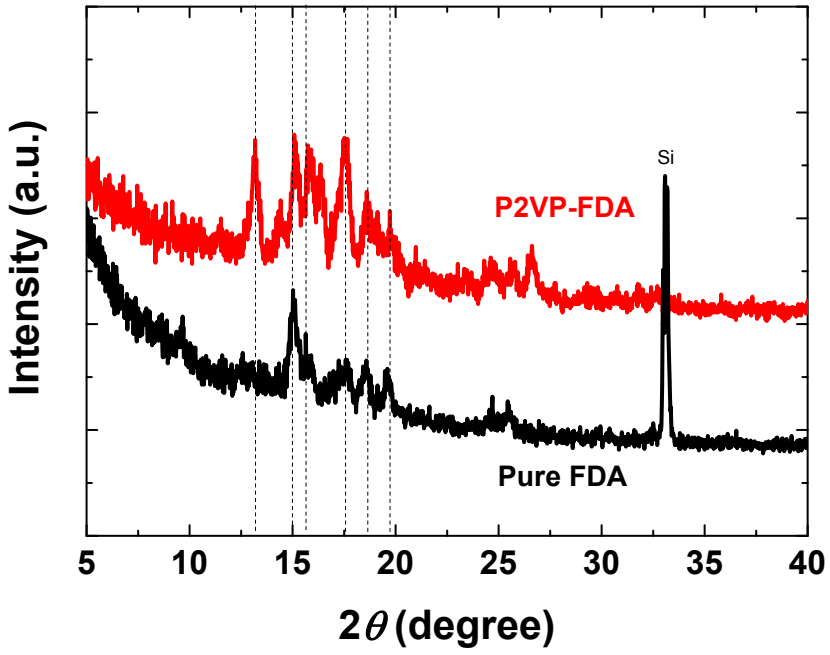

Figure S9. XRD spectrum of P2VP-FDA and pure FDA. The spectrum shows the crystal peaks of the unreacted FDA in P2VP-FDA and the amorphous nature of P2VP polymer in P2VP-FDA.