Supporting Information

Tuning self-healing properties of stiff, ion-conductive polymers

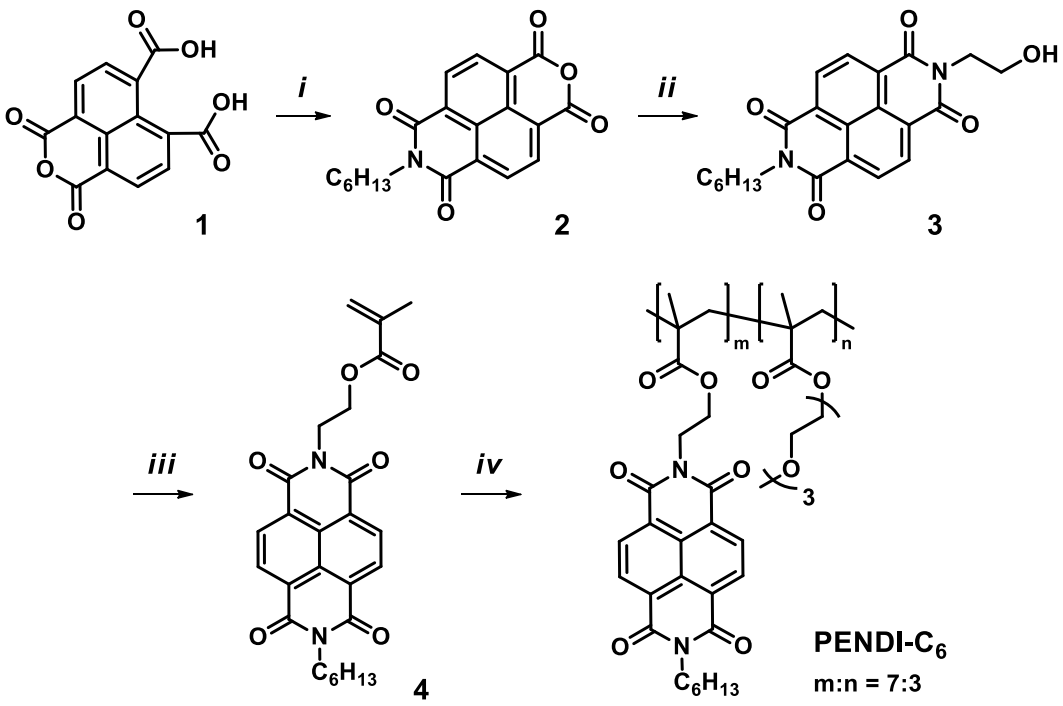
Jiaxu Qin[a], Francis Lin[b], Dion Hubble[a], Yujia Wang[b], Yun Li[c], Ian A. Murphy[b], Sei-Hum Jangb[c], Jihui Yang[c] and Alex K.-Y. Jen[*abcd]

a. Molecular Engineering & Science Institute, University of Washington, Seattle, Washington, 98195, United States.

b. Department of Chemistry, University of Washington, Seattle, Washington, 98195, United States.

c. Department of Materials Science and Engineering, University of Washington, Seattle, Washington, 98195, United States.

d. Department of Chemistry, and Department of Materials Science & Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong.



Scheme S1. Synthetic routes of PENDI. Reagents and conditions: i) a) 1-Hexylamine, H_2O, 0 °C, then refluxed; b) 10% $HCl_{(aq)}$, 0 °C; c) THF/$HCl_{(conc.)}$, (v/v=1:2). ii) Ethanolamine, EtOH, 80 °C. iii) Methacryloyl chloride, Et_3N, DCM/THF (v/v=1:1), 40 °C. iv) Triethylene glycol methyl ether methacrylate, AIBN, THF, 70 °C. All chemical reactions were conducted under the protection of argon. TriPy linker and dbNDI were prepared according to literature procedures with modifications.[1],[2]

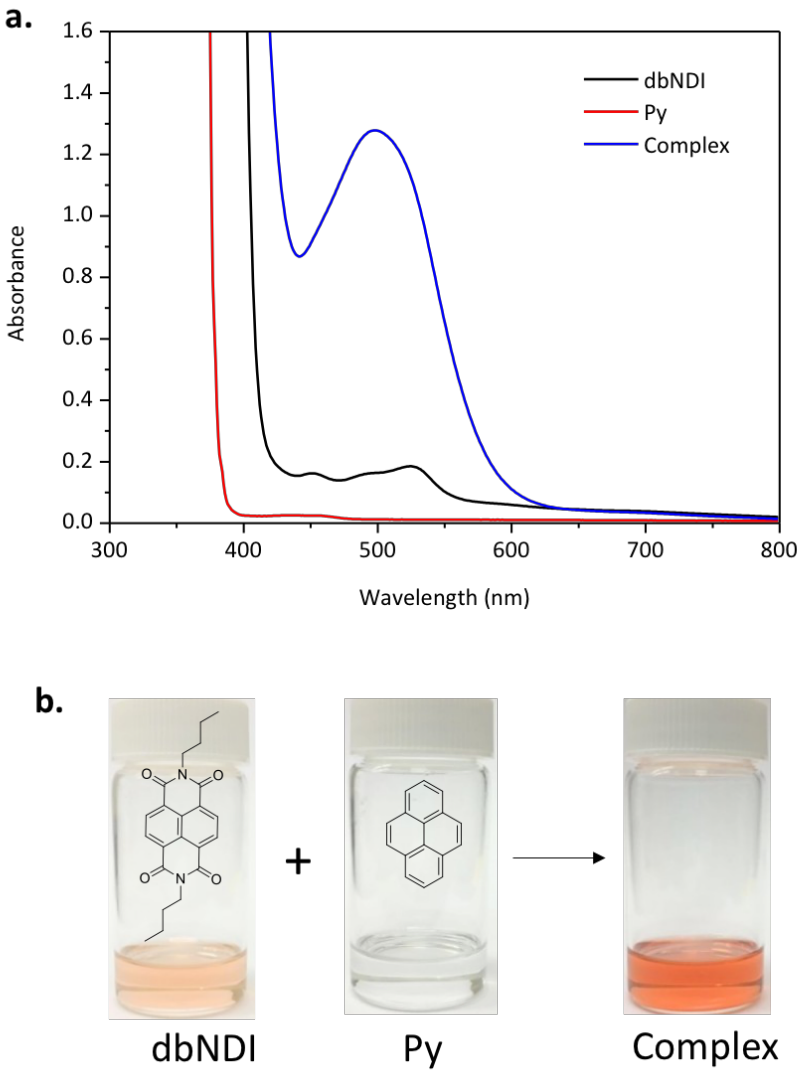


Figure S1. a) UV-Vis spectra and b) optical images of Py (0.03 M), dbNDI (0.03 M), and their equimolar complex (0.03 M) solutions in dichloromethane (25 °C).

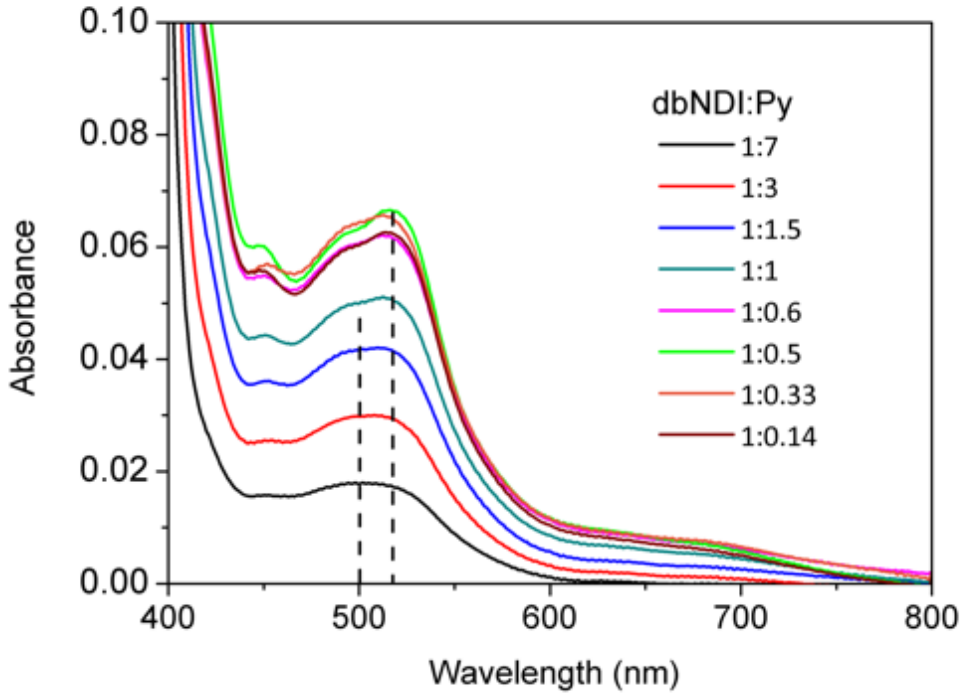


Figure S2. UV-Vis spectrum of dbNDI-Py mixture in DCM with various molar ratio (total concentration of dbNDI and Py was kept constant as 0.004 mol/L). By changing the molar ratio between dbNDI and Py while maintaining the same overall molar concentration, we found that another characteristic absorbance peak emerges at 514 nm when dbNDI is added in excess. This absorbance peak reaches a maximum with a dbNDI : Py ratio of 2:1, suggesting that the new complex consists of a 2:1 (dbNDI:Py) structure.

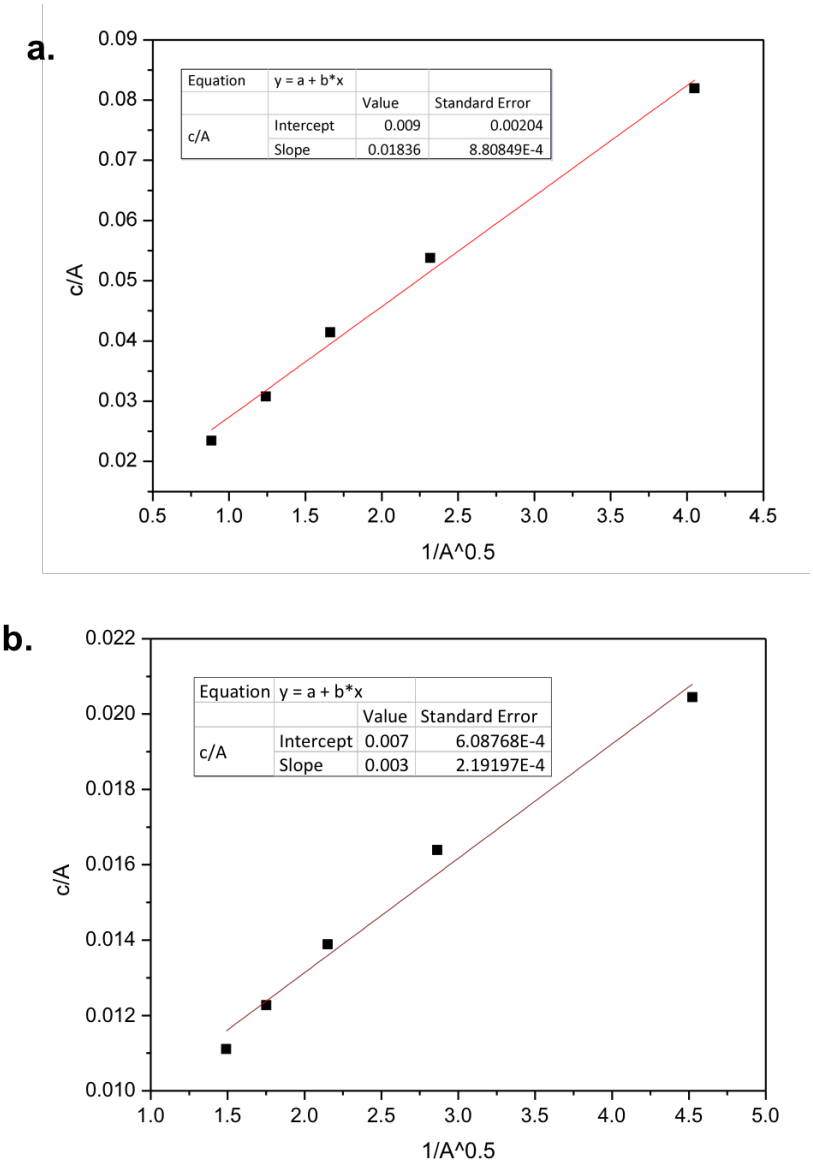


Figure S3. UV-Vis dilution method plot of 1:1 complex a) and 2:1 complex b).

Table S1. Association Constant and Free Energy of Complexation

Different binding modes	Association constant	Free energy of complexation
1 : 1 complex	26.7 M^{-1}	-8.19 KJ/mol
2 : 1 complex	777.8 M^{-1}	-16.49 KJ/mol

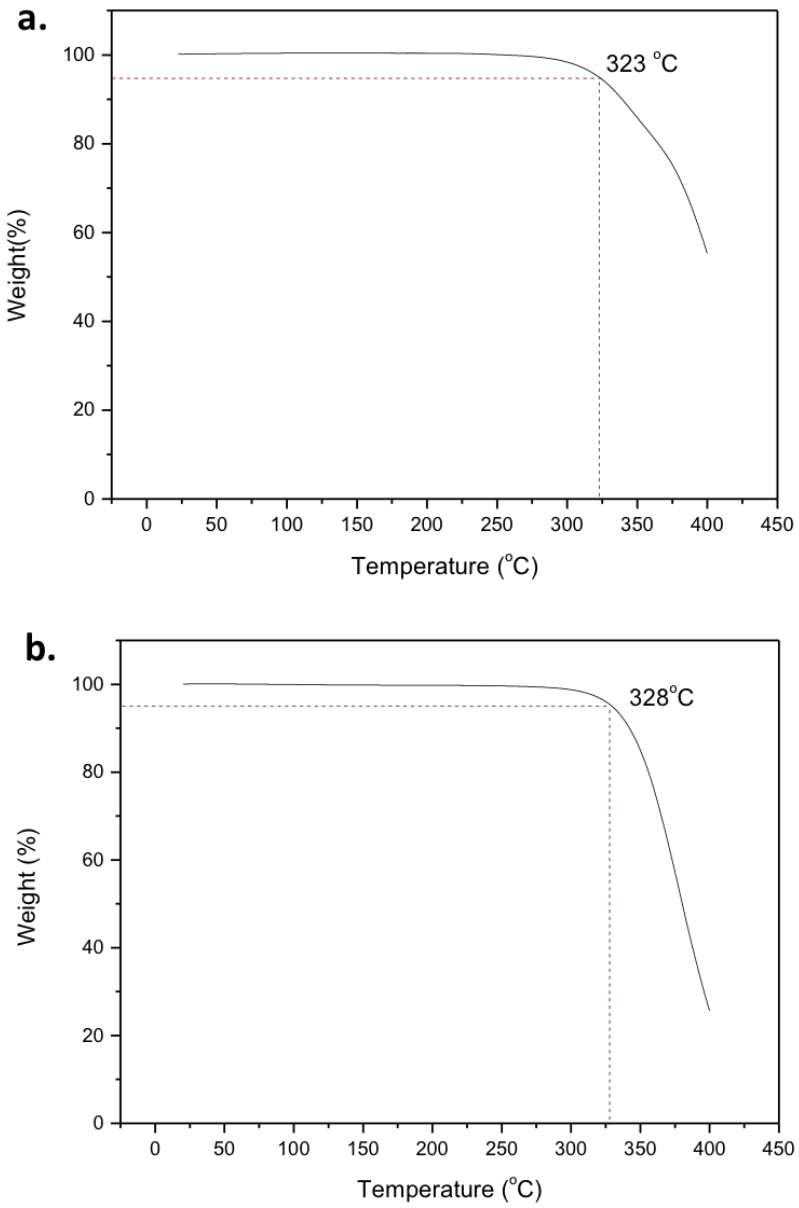


Figure S4. TGA test for a) PENDI and b) triPy.

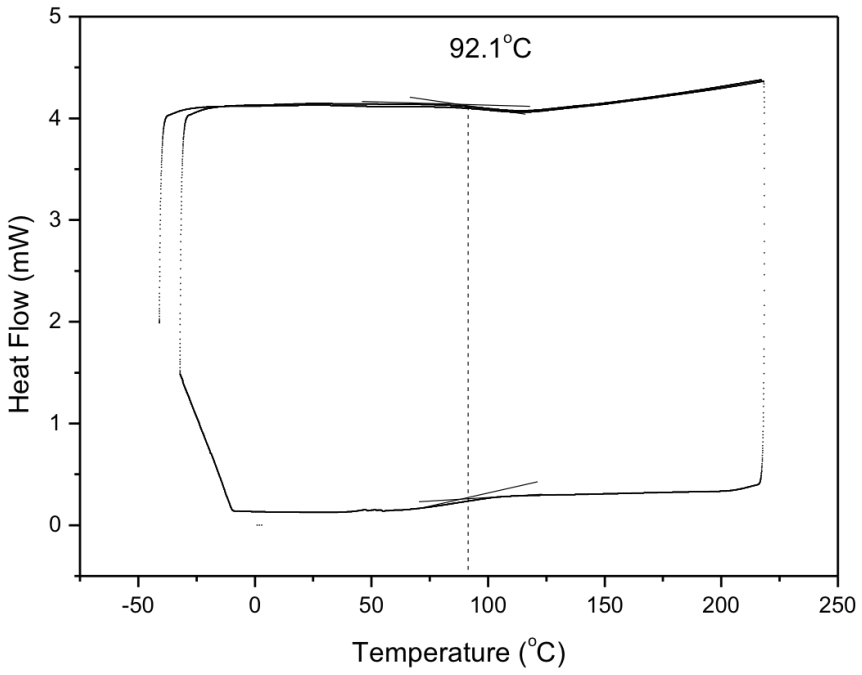


Figure S5. DSC test of PENDI. DSC measurements were performed in a heat-cool-heat cycle (-40 to 220 ºC, 10 ºC/min; 220 to -40 ºC, -10 ºC/min; -40 to 220 ºC, 10 ºC/min).

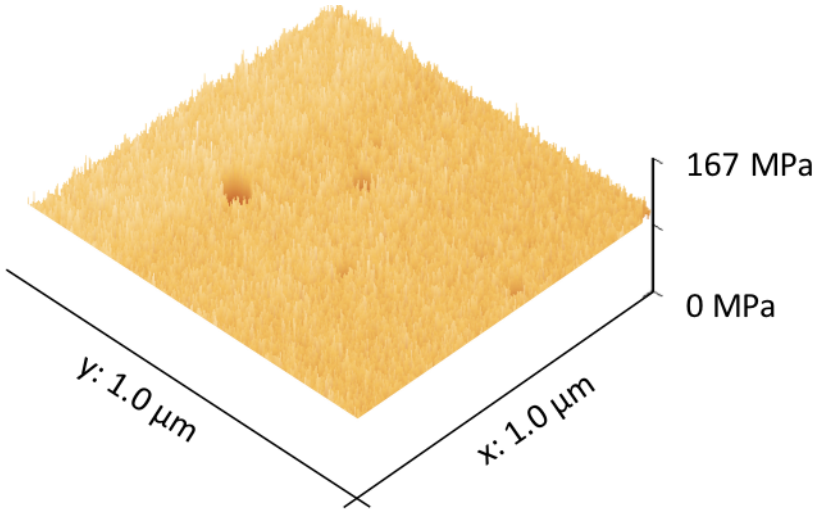


Figure S6. AFM Young's modulus 3D map of PENDI.

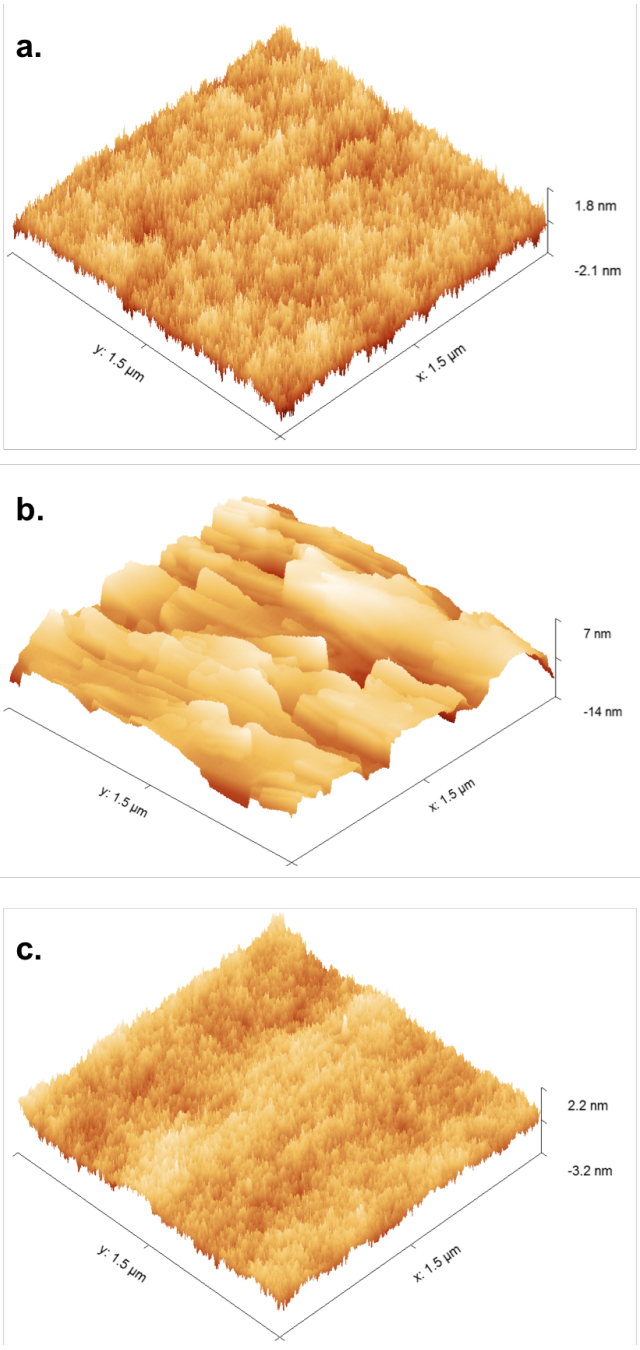


Figure S7. The AFM 3D height profile of PP-1 a), PP-dbNDI b), and PP-Py c).

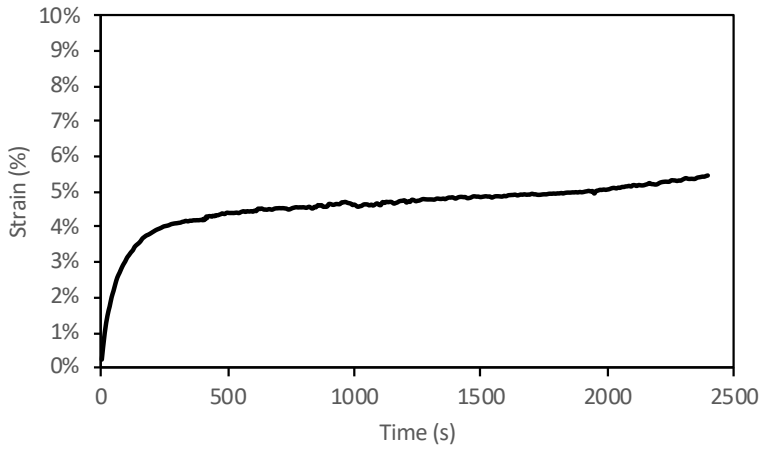


Figure S8. Strain-time curve of PP-1 under constant stress around 1 MPa.

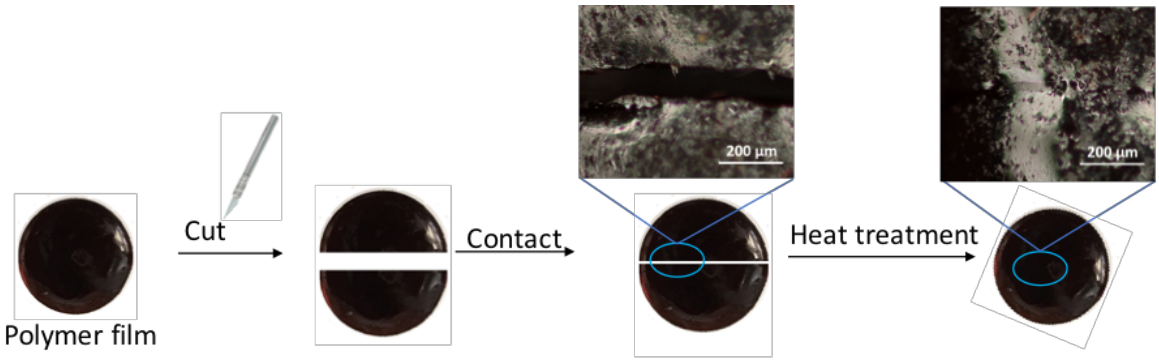


Figure S9. Self-healing property tests of PP polymer films.

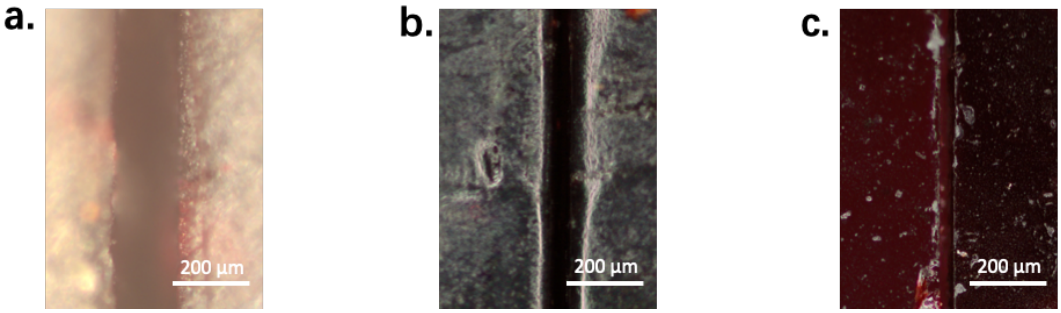


Figure S10. Optical images of PP polymer films after cutting of PP-dbNDI a), PP-1 b), and PP-Py c).

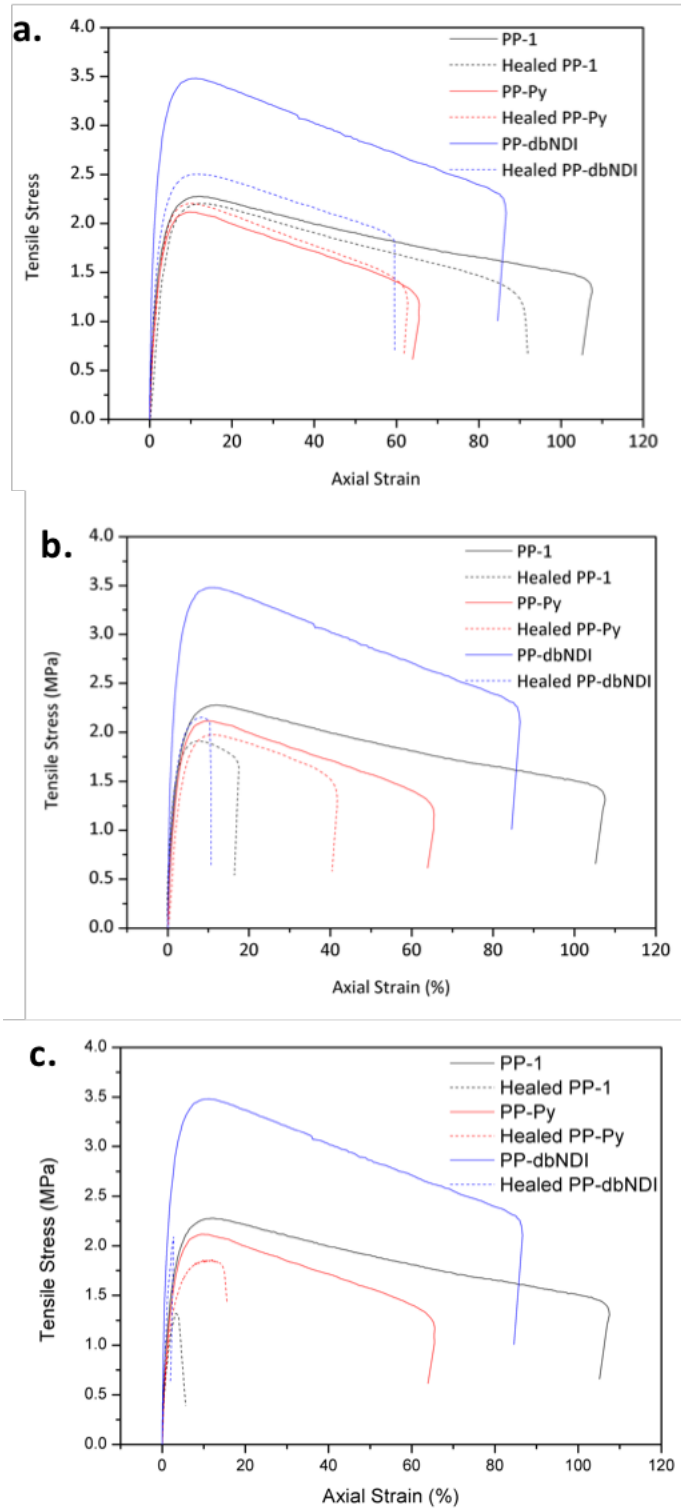


Figure S11. Stress-strain tests prior to damage (solid line) and after healing (dotted line) by heat treatment for 12 hours at different temperature. a) 60 ºC. b) 50 ºC, c) 40 ºC.

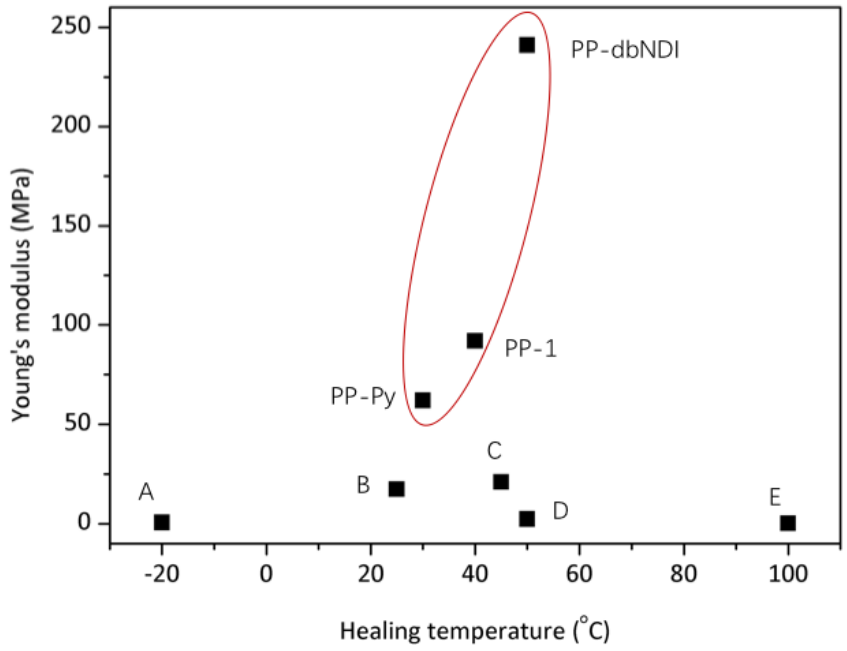


Figure S12. Comparison between our design and previous studies (A,[3] B,[3] C,[4] D,[5] E[6]).

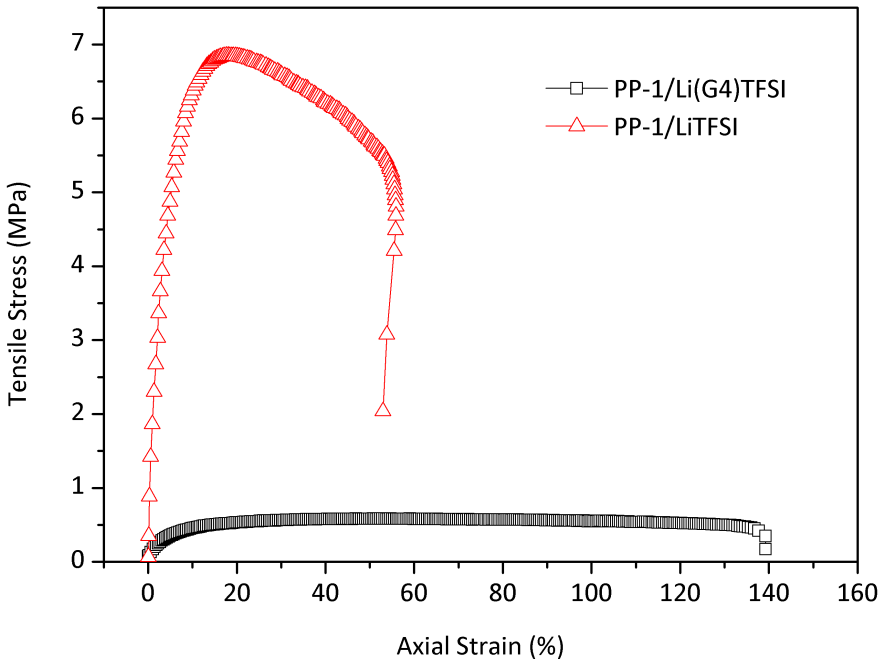


Figure S13. Stree-strain tests of PP-1/LiTFSI and PP-1/Li(G4)TFSI.

REFERENCE:

[1] L. R. Hart, J. H. Hunter, N. A. Nguyen, J. L. Harries, B. W. Greenland, M. E. Mackay, H. M. Colquhoun, W. Hayes, *Polym. Chem.* **2014**, *5*, 3680.

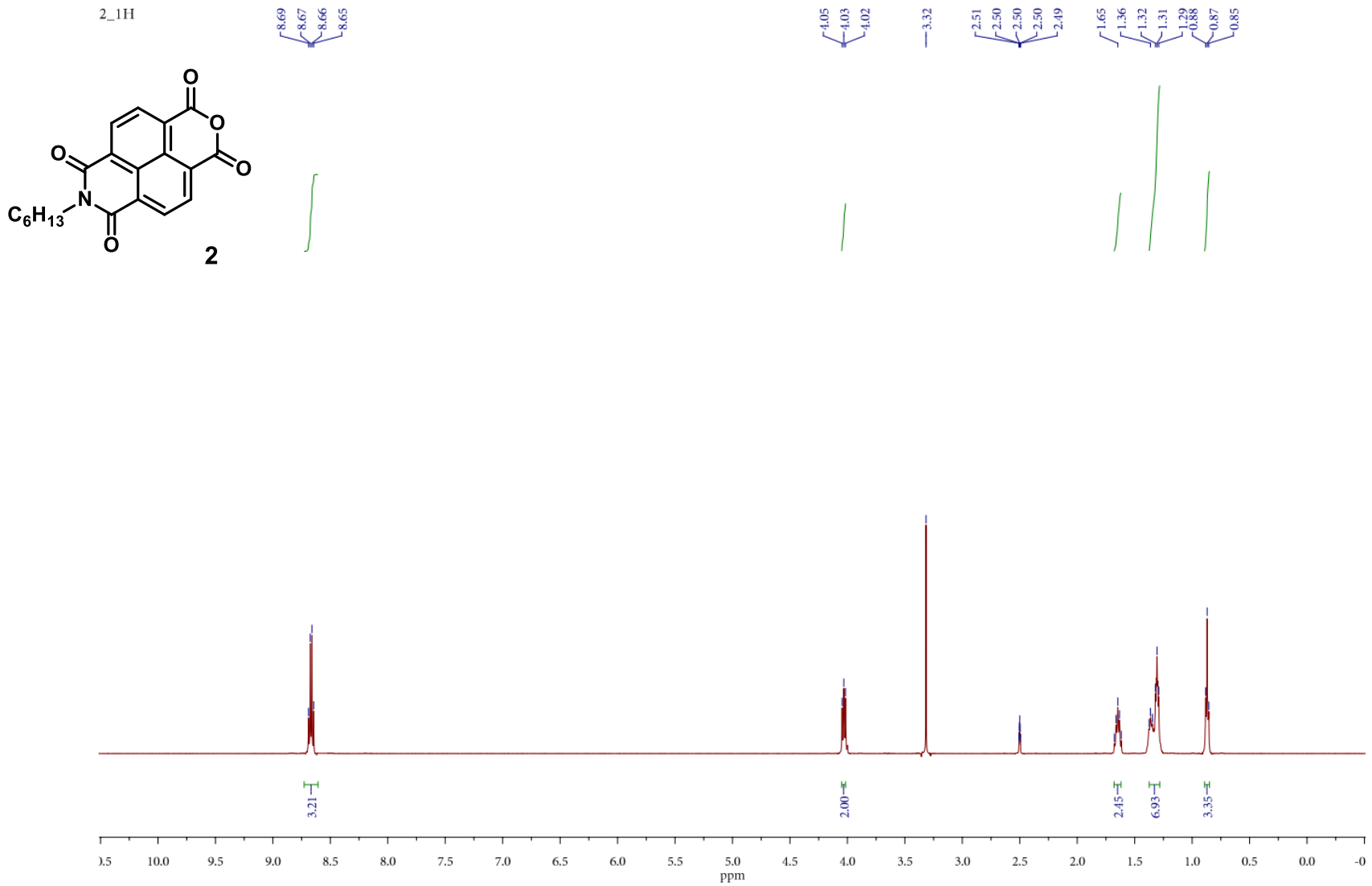
[2] G. S. Vadehra, R. P. Maloney, M. A. Garcia-Garibay, B. Dunn, *Chem. Mater.* **2014**, *26*, 7151.

[3] C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.-Z. You, Z. Bao, *Nat. Chem.* **2016**, *8*, 618.

[4] J. Hentschel, A. M. Kushner, J. Ziller, Z. Guan, *Angew. Chemie Int. Ed.* **2012**, *51*, 10561.

[5] J. A. Neal, D. Mozhdehi, Z. Guan, *J. Am. Chem. Soc.* **2015**, *137*, 4846.

[6] S. Burattini, B. W. Greenland, D. H. Merino, W. Weng, J. Seppala, H. M. Colquhoun, W. Hayes, M. E. Mackay, I. W. Hamley, S. J. Rowan, *J. Am. Chem. Soc.* **2010**, *132*, 12051.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2.50
2.49
1.65
1.36
1.32
1.31
1.29
0.88
0.87
0.85
O
O
O
O
O
N
C6H13
2
3.21
2.00
2.45
6.93
3.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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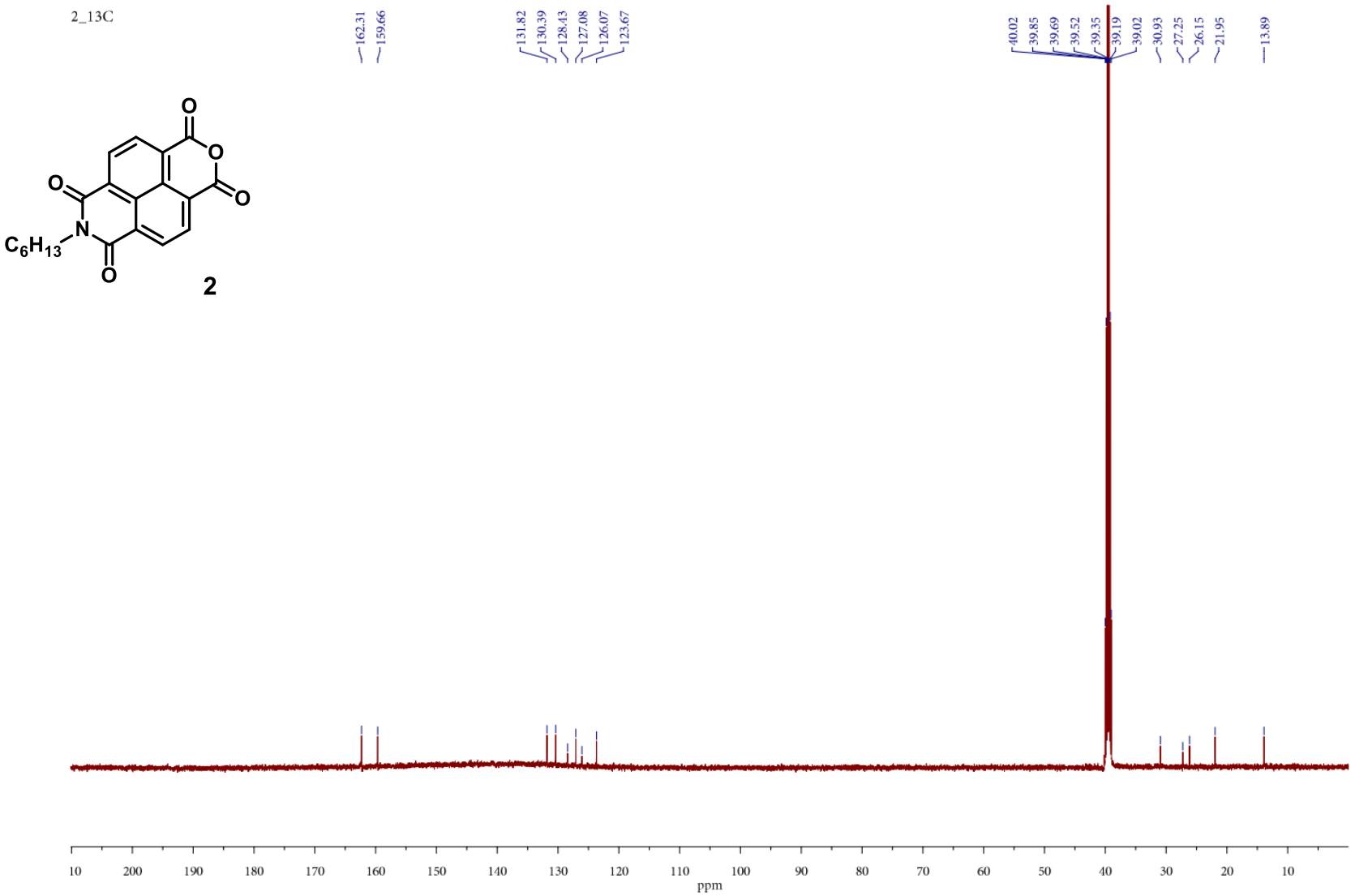
0.0
ppm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39.35
39.19
39.02
30.93
27.25
26.15
21.95
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O
O
O
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O
C6H13
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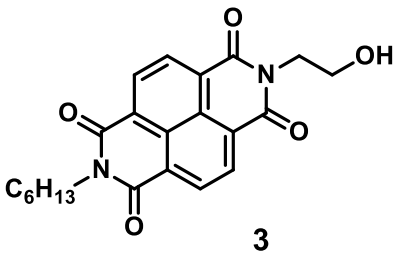
ppm

3_1H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C_6H_{13}
O

3

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4.12
4.02
4.00
3.99
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3.62
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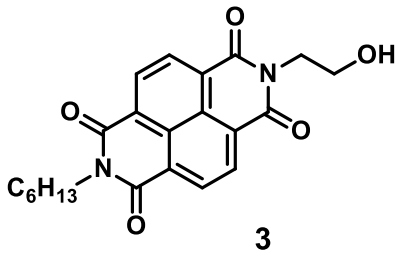
3_13C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3

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125.74
57.56
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21.69
13.58
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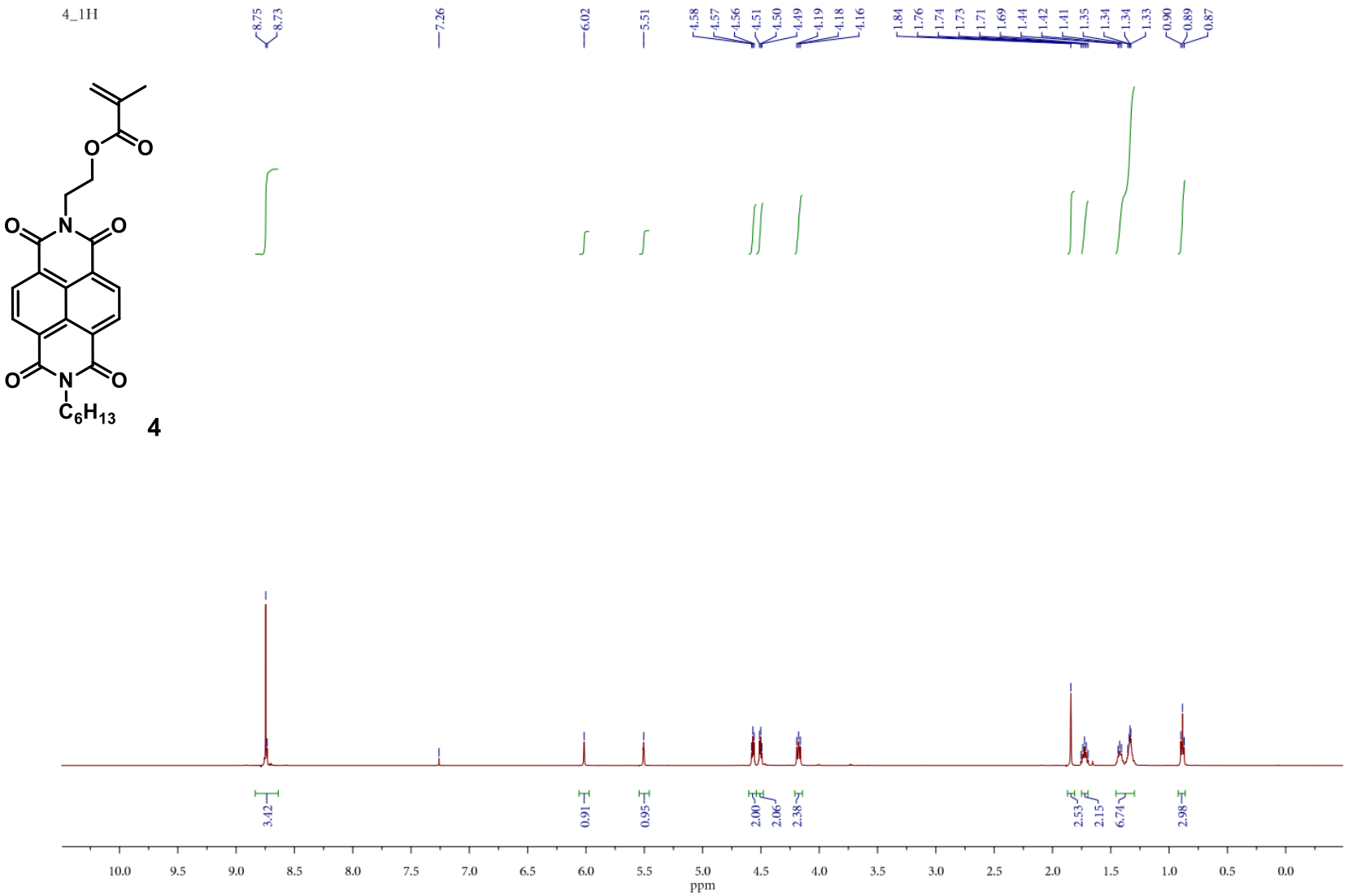
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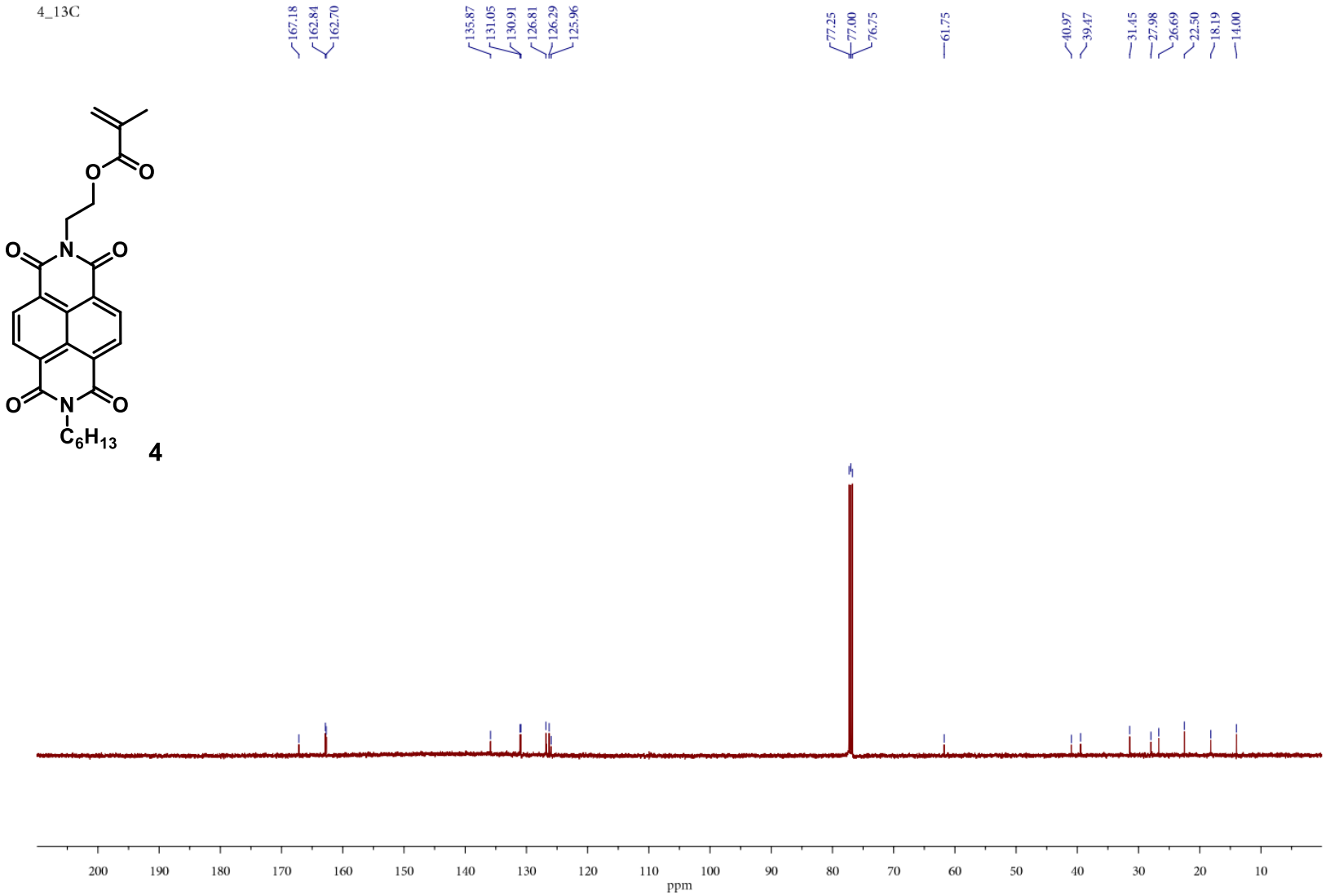
4_13C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4