

## Supporting Information

### Postpolymerization Modification Based on Dynamic Imine Chemistry for Synthesis of Functional Polyacetylenes

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Table S1 The reaction between PVM and 1-phenylethanamine at 30 °C.<sup>a</sup>

| Solvent <sup>b</sup> | CD <sub>3</sub> CN | THF             | CDCl <sub>3</sub> |
|----------------------|--------------------|-----------------|-------------------|
| Ad <sup>c</sup> %    | 100 <sup>d</sup>   | 88 <sup>d</sup> | 59 <sup>d</sup>   |

<sup>a</sup> The concentration of all the reagents was 60 mmol/L. <sup>b</sup> Water content below <sup>1</sup>HNMR detection limits. <sup>c</sup> Reaction advancement degree (%) calculated as  $(I_t/I_e) \times 100$ , where  $I_t$  and  $I_e$  are the normalized intensity of the CH=N signal at  $t = 30$  min and at equilibrium, respectively. <sup>d</sup>PVEM at equilibrium was 28.5 mmol/L.

Table S2. Synthesis of **P1a-P1e** through transimination of **P1** with various amines.<sup>a</sup>

| Amine  | Product    | Yield (%) | $M_n^b \times 10^{-3}$ | $M_w/M_n$ |
|--|------------|-----------|------------------------|-----------|
| ( <i>S</i> )-1-phenylethanamine              | <b>P1a</b> | 96.5      | 26.2                   | 2.6       |
| ( <i>R</i> )-1-phenylethanamine              | <b>P1b</b> | 95.2      | 24.1                   | 2.5       |
| ( <i>S</i> )-2-amino-2-phenylethanol         | <b>P1c</b> | 90.5      | 29.1                   | 2.8       |
| ( <i>S</i> )-1-(naphthalen-2-yl)ethanamine   | <b>P1d</b> | 91.7      | 32.7                   | 2.7       |
| 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl | <b>P1e</b> | 91.5      | - <sup>c</sup>         | -         |

<sup>a</sup> Reactions were carried out in THF at 30 °C for 12 h under nitrogen, 2.0 equiv of amine relative to the imine units in **P1**. <sup>b</sup> Estimated by GPC eluted with THF on the basis of polystyrene calibration. <sup>c</sup> insoluble in THF.

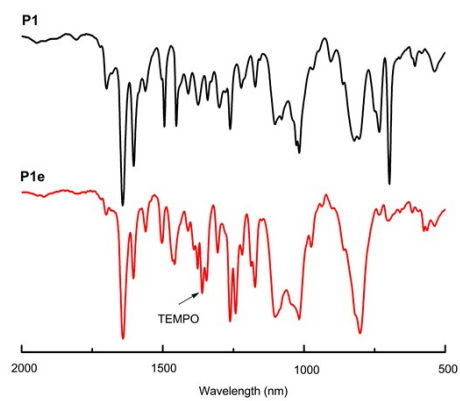


Figure S1. IR spectra of **P1** and **P1e**.

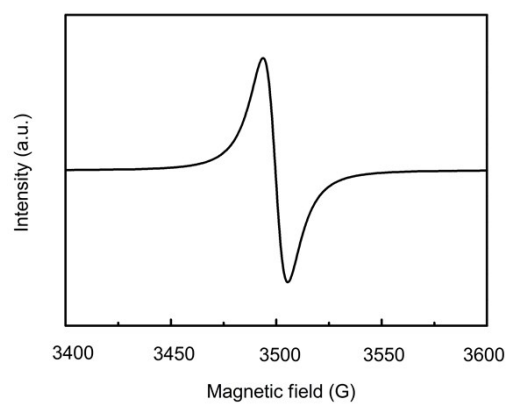


Figure S2. ESR spectrum of **P1e** measured in the powder state.

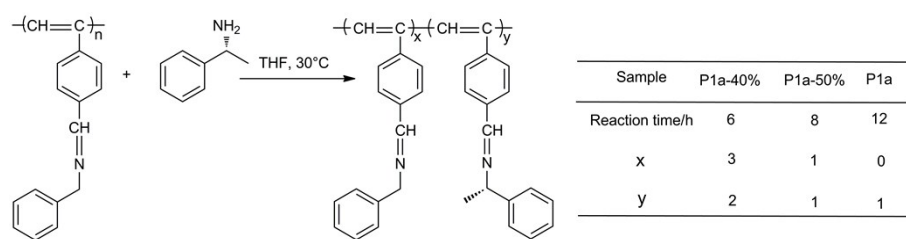


Figure S3. Synthesis of **P1a-40%**, **P1a-50%**, and **P1a**

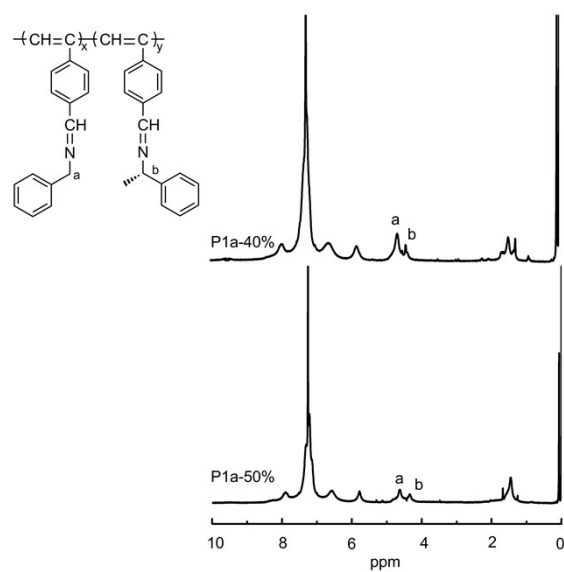


Figure S4.  $^1\text{H}$  NMR spectra of **P1a-40%** and **P1a-50%**

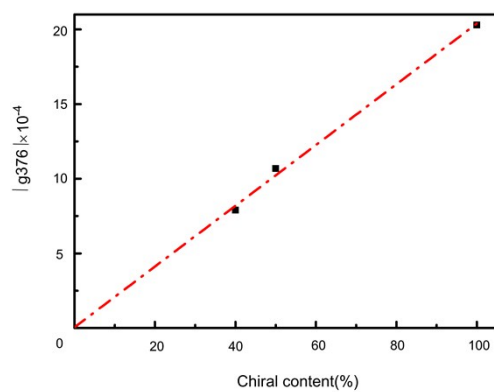


Figure S5. Plot of Kuhn dissymmetry factor ( $g = [\theta]/(3300 \times \epsilon)$ ) at 376 nm of **P1a-40%**, **P1a-50%** and **P1a** in THF against chiral content. The dotted line is shown simply to guide the eye.



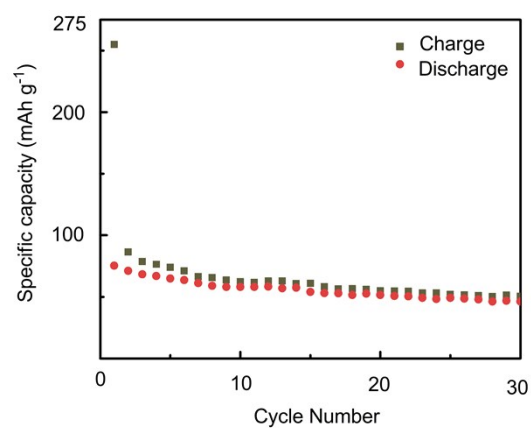


Figure S6. Dependence of capacity on the cycle number of **P1e**. Charging and discharging were repeated at a 50 mA/g current density in a range of 3.3-4.4 V cell voltage.