Supporting Information

Synthesis of Indole-Based Functional Polymers with Well-Defined Structures via Catalyst-free C-N Coupling Reaction

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I. Synthesis of 3,3’-diindolylmethane [1]

To a mixture of indole (10 mmol) and formaldehyde (5 mmol) was added the bentonitic clay (5 g). The reaction mixture was IR irradiated with a commercial IR lamp (250 W), according to the methodology reported by Pool and Teuben, [2] for 15 minutes (after this reaction time no changes were detected by thin layer chromatography), and the temperature reached during the reaction was 180 °C. Then, to the produced reaction mixture a 1 : 1 water–methanol mixture was added for recrystallization purpose.

\(^{1}\text{H-NMR (600 MHz, DMSO-}d_{6}\text{): } \delta = 4.14 \text{ (s, 2H), 6.90 (t, } J = 10.2 \text{ Hz, 12.0 Hz, 2H), 7.02 (t, } J = 10.8 \text{ Hz, 12.0 Hz, 2H), 7.13 (d, } J = 2.4 \text{ Hz, 2H), 7.31 (d, } J = 12.0 \text{ Hz, 2H), 7.52 (d, } J = 12.0 \text{ Hz, 2H), 10.73 (s, 2H) ppm; } ^{13}\text{C-NMR (150 MHz, DMSO-}d_{6}\text{): } \delta = 20.9, 111.3, 114.2, 118.0, 118.6, 120.7, 122.7, 127.2, 136.4 \text{ ppm; MS (ESI) } m/z: 246 \text{ [M]+; Anal.Calced for } C_{17}H_{14}N_{2}: \text{ C, 82.90; H, 5.73; N, 11.37; Found: C, 81.75, H, 5.77, N, 11.04.}

\[\text{Scheme S1. Synthesis of 3,3’-diindolylmethane}\]


II. Optical properties of model compounds

Figure S1. UV spectra of model compounds 3-5 in NMP solutions. Solution concentration: $10^{-5}$ M.

Figure S2. Fluorescence spectra of 3, 4 and 5 in NMP ($\lambda_{\text{exc}} = 340$ nm, 340 nm, 320 nm, respectively; excitation and emission slits = 5.0 nm and 2.5 nm, respectively).
III. IR spectra of model compounds (3-5) and PMDINs

**Figure S3.** The IR spectrum of model compound 3.

**Figure S4.** The IR spectrum of model compound 4.
**Figure S5.** The IR spectrum of model compound 5.

**Figure S6.** The IR spectrum of polymer PMDIN-1.
Figure S7. The IR spectrum of polymer PMDIN-2.

Figure S8. The IR spectrum of polymer PMDIN-3.
Figure S9. The IR spectrum of polymer cross-linked PMDIN-3.
IV. The SEM of the dip coated PMDIN-3 film

Figure S10. The SEM of the dip coated PMDIN-3 film.
V. Copies of $^1$H and $^{13}$C NMR spectra of 3,3'-diindolylmethane, model compounds (3-5) and PMDINs