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Photoinduced Synthesis of Poly(N-ethylcarbazole) from Phenacylium Salt without Conventional Catalyst and/or Monomer

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1. Materials

All solvents (dichloromethane, n-hexane, ethanol, methanol) were purified according to literature before use. N-ethylcarbazole (97%, Sigma-Aldrich) was purified by recrystallization in hot ethanol. Sodium hexafluorophosphate (98%, Sigma-Aldrich) and 2-bromoacetophenone (98%, Sigma-Aldrich) were used as received.

Experimental Procedures

Polymerization Procedure. 1 mmol (460 mg) of ECPPhAc was dissolved in 2 mL of dry dichloromethane and then transferred into a Schlenk tube which was previously degassed by three freeze-pump-thaw cycles. The mixture was irradiated with a light source emitting light nominally at 350 nm. After irradiation for 60 min, the resultant dark blue polymer solution was precipitated by pouring it to 20 mL n-hexane. The precipitated polymer was then filtered and dried for 24 h under vacuum at 40°C. The polymer powder was stirred in 100 mL of hydrazinium hydroxide: methanol (1:1; v: v) solution for 1 h for the dedoping process. After dedoping, the dark blue colour of the solution turned into light brown and finally filtered and dried for 24 h under vacuum at 40°C. Two successive polymerizations under identical experimental conditions yielded polymers with 62 and 58 % conversions, 6.8 and 5.3 kg mol⁻¹ Mw (D= 1.2-1.5) values, respectively.

NMR Measurements. ¹H-NMR and ¹³C-NMR spectra were recorded in deuterated chloroform (CDCl₃ with tetramethylsilane as an internal standard) at 500 MHz and 125 MHz, respectively on an Agilent VNMR 500 spectrometer at 25°C.

IR and UV Measurements. Fourier-transform infrared (FTIR) spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride (MCT) detector. 32 scans were averaged. UV–visible spectra were recorded with a Shimadzu UV-1601 double-beam spectrometer equipped with a 50W halogen lamp and a deuterium lamp which can operate between 190nm-1100nm.

GPC Measurements. Gel permeation chromatography measurements were performed on a TOSOH EcoSEC GPC system equipped with an auto sampler system, a temperature controlled pump, a column oven, a refractive index (RI) detector, a purge and degasser unit and TSKgel superf2000, 4. 6mm ID x 15 cm x 2cm column. Tetrahydrofuran was used as an eluent at flow rate of 1.0 mL.min⁻¹ at 40 °C. Refractive index detector was calibrated with poly (methyl methacrylate) standards having narrow molecular-weight distributions. GPC data were analyzed using Eco-SEC Analysis software.

Mass Spectroscopy. Mass spectra were measured on a Bruker Microflex LT MALDI-TOF MS in THF solvent.

Electrochemical Measurements. The electrochemical measurements were carried out by using CH Instruments 617D potentiostat–galvanostatic system. The electrochemical cell containing a Ag wire as a reference electrode (RE), a Pt wire as counter electrode (CE) and glassy carbon as a working electrode (WE) immersed in 0.1 M tetrabutylammonium hexafluorophosphate TBAPF₆ as the supporting electrolyte under argon atmosphere. In addition, oxidation potential onsets determined from the cyclic voltammetry (CV) and differential puls voltammetry (DPV) measurements were used for the HOMO level calculations by using the equation EHOMO = –e (Eox – EFc) + (–4.8 eV) according to the ferrocene oxidation E₀(Fc/Fc+) = 0.41 V as internal standard. The optical band gap (Eg) of PEC was calculated by using its absorption edges (Eg: 1241/λons) of the UV-Vis spectra.

AFM Measurements. The polymer films of PEC were prepared on glass surface by using spin casting technique from the %2 polymer solution in chloroform with applying 2000 rpm spin rate for 1 min. Morphology of the polymer films was investigated by Atomic Force Microscope (AFM, Nanosurf Naio). The measurements were carried out in non-contact mode (wave mode) at ambient conditions scanned in a 10µm x 10µm measurement area. The AFM system was covered with an acoustic chamber to protect from the electromagnetic noise.
Figure S1. $^1$H-NMR spectrum of ECPhAc (CDCl$_3$, 500MHz).

Figure S2. $^{13}$C-NMR spectrum of ECPhAc (CDCl$_3$, 125MHz).
Figure S3. FT-IR spectrum of ECPhAc.

Figure S4. $^1$H-NMR (left) and $^{13}$C-NMR (right) spectra of PEC (CDCl$_3$, 125MHz).
Figure S5. FT-IR spectra of PEC before (red) and after (black) dedoping.

Figure S6. MALDI-TOF spectra of dedoped PEC in THF solvent. (1st (upper) and 2nd run (lower))
Figure S7. GPC traces of PEC after dedoping.

Figure S8. TGA thermogram of PEC after dedoping.