SUPPORTING INFORMATION

First Preparation of Low Band Gap Fulvene-Modified Polynorbornene via Ring-Opening Metathesis Polymerization

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General Methods and Materials

Solvents, starting materials, and reagents were purchased either from Sigma-Aldrich, TCI America, or Alfa Aesar as reagent grade or higher quality and used as received unless otherwise noted. HPLC grade THF was dried and deoxygenated by passage through a Pure-Solv solvent purification system equipped with Cu/Al columns from Innovative Technologies. Premium grade silica gel used for column chromatography was purchased from Sorbent Technologies (60Å, 40-63 nm (230 X 400 Mesh)). All reactions and solvent transfers were carried out under an atmosphere of nitrogen unless otherwise noted. All glassware was oven-dried prior to use. Compounds 1,3-diphenyl-6-(3-vinylphenyl)fulvene¹ (1), 1,3-diphenylcyclopentadiene² (3), and third generation Grubb’s catalyst³ (G3) were synthesized according to previously reported procedures.

Instrumentation

All ¹H and ¹³C NMR spectra were obtained under ambient conditions using an Agilent Technologies 400 MHz instrument, and chemical shifts were reported in parts per million (δ). All NMR spectra were internally referenced to CDCl₃ (¹H-NMR: δ = 7.26 ppm. ¹³C-NMR: δ = 77.0 ppm).

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected under ambient conditions using a Thermo Nicolet-FTIR Spectrometer iS10.

GCMS experiments were performed using an Agilent Technologies 7890A GC System interfaced with a 5975C EI mass spectrometer. Dichloromethane was used as a solvent and the sample was injected in 2 μL portions onto a HP5-MS column (30 m X 0.25 mm X 0.25 μm). The operating method was programmed with a 2.00 min solvent delay. The initial temperature was set at 90 °C and held for 2 min. The temperature was ramped at 20 °C per min to 325 °C and was held for 4.00. The injector and source temperatures were set to 250 °C and 230 °C, respectively. The sample was injected using split mode after 3 pre-injection solvent cycles with a He flow rate of 1 mL/min.

Gel permeation chromatography (GPC) data in THF were collected using polystyrene as a standard (Polymer Labs Easical PS-H) using a Polymer Laboratories GPC 200 with a RI detector whereby samples were eluted in series through Polymer Labs PLgel Mixed-B LS columns.

Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q200 and TA Q500 instrument, respectively. Glass transitions temperatures (Tₜg) of polymers were obtained from the third heating cycle using DSC analysis at a temperature ramp of 10 °C/min. The reported Tₜg values were taken as the midpoint of the Cp change.
Cyclic voltammetry was performed with a Metrohm Autolab PGSTAT101 potentiostat using a Ag/AgCl reference electrode, platinum wire counter electrode, and a glassy carbon working electrode. All electrochemical experiments were performed at 5 mM in nitrogen sparged 100 mM tetrabutylammonium hexafluorophosphate (CH$_2$Cl$_2$) at 25 °C.

General absorbance and emission spectra were collected using a Varian Cary 50 Bio ultraviolet visible (UV–vis) spectrophotometer and a Varian Cary Eclipse spectrofluorometer. Samples for absorbance and emission spectra were collected in THF using a path length of 1 cm in Spectrosil quartz cuvettes (3 mL).

**Materials Synthesis**

![Chemical structure](image)

**Bis(1,3,6-triphenylfulvene) (2).** 1,3-diphenyl-6-(3-vinylphenyl)fulvene (1) (255 mg, 767 μmol) and second generation Grubbs’ catalyst (33 mg, 38.4 μmol) were dissolved in dichloromethane (10 mL) and heated to refluxing solvent for 16 h. The reaction mixture was cooled to room temperature and solvent was concentrated under reduced pressure. The crude reaction mixture was passed through a plug of silica (80:20, hexanes/ethyl acetate), and removal of solvent under reduced pressure afforded a maroon solid (234 mg, 96%, (Z:E, 1:9)). $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.73-7.76 (m, 2H, fulvene ring CH) 7.69-7.72 & 7.54-7.60 (2 m, 8H, styrene ring CH), 7.27-7.53 (m, 20H, Ph), 7.21 & 7.16 (s, 2H, olefin CH, E and Z, respectively), 7.05 (m, 2H, fulvene ring CH), 7.02 (d, 2H, fulvene exocyclic CH). $^{13}$C-NMR (400 MHz, CDCl$_3$): 147.0, 144.8, 141.7, 138.1, 137.6, 135.2, 129.8, 129.4, 129.1, 129.0, 128.9, 128.7, 128.4, 128.2, 128.0, 127.1, 127.0, 126.2, 114.5. Anal. Calcd for C$_{50}$H$_{36}$: C, 94.30; H, 5.70. Found: C, 94.22; H, 5.69.
**1,3-Diphenyl-6-norborneylfulvene (4).** To a stirred suspension of 1,3-diphenylcyclopentadiene (3) (2.00 g, 9.2 mmol) in absolute ethanol (15 mL) were added freshly distilled 5-norbornene-2-carboxaldehyde (mixture of isomers, 1142 μL, 9.6 mmol) and pyrrolidine (842 μL, 10.1 mmol). The reaction mixture gradually fades from pale yellow to bright orange. The reaction mixture was stirred at room temperature for 16 h, and then placed in an ice bath. The resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum dried to afford a bright orange powder (1.77 g, 60%). $^1$H-NMR (400 MHz, CDCl$_3$): (mixture of isomers) δ 7.27-7.71 (m, 10H, Ph), 6.89-6.97 (m, 2H, fulvene ring CH), 6.60 and 6.09 (d, 1H, exo and endo, fulvene exocyclic CH), 6.10 and 6.17-6.26 (m, 2H, vinyl CH), combined 3.48-3.55, 2.80-3.06, 2.12-2.20, 1.39-1.58, and 0.95-1.01 (8 m, 7H, norbornene alkyl CH, mixture of isomers). $^{13}$C-NMR (400 MHz, CDCl$_3$): 149.6, 148.7, 144.6, 144.5, 143.7, 143.6, 140.4, 140.3, 138.2, 135.6, 135.5, 132.4, 129.1, 129.0, 128.6, 128.4, 128.3, 127.9, 127.6, 126.8, 126.7, 113.8, 113.7, 50.0, 49.4, 45.6, 43.2, 42.5, 40.7, 40.3, 3.46. MS (EI, 70 eV): m/z (% relative intensity) 322 (M$^+$, 49), 256 (47), 255 (62), 239 (96), 228 (64), 215 (67), 207 (100), 202 (88), 165 (58), 152 (62), 115 (68), 77 (59), 66 (89).

![Image](image-url)

**1,3-Diphenyl-6-isopropylfulvene (5).** To a stirred suspension of 1,3-diphenylcyclopentadiene (3) (2.58 g, 11.8 mmol) in absolute ethanol (50 mL) were added isobutylraldehyde (1400 μL, 15.3 mmol) and pyrrolidine (1600 μL, 19.2 mmol). The reaction mixture gradually fades from pale yellow to dark orange. The reaction was stirred at room temperature for 4 h, and the resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum dried to afford a bright orange powder (2.15 g, 67%). The filtrate was placed in a refrigerator (4 °C) overnight, and a second batch of precipitate was collected (0.23 g, total combined yield 2.38 g, 74%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.2-7.8 (m, 10H, Ph), 6.94 (d, 1H, fulvene ring CH), 6.89 (dd, 1H, fulvene ring CH), 6.33 (d, 1H, fulvene exocyclic CH), 3.15 (m, 1H), 1.18 (d, 6H, CH(CH$_3$)$_2$). $^{13}$C-NMR (400 MHz, CDCl$_3$): 150.2, 144.4, 142.3, 140.5, 136.1, 135.4, 129.6, 128.6, 128.4, 128.1, 127.7, 126.8, 126.0, 113.6, 30.6, 23.2. MS (EI, 70 eV): m/z (% relative intensity) 272 (M$^+$, 71), 257 (100), 242 (34), 229 (22), 217 (19), 215 (21), 179 (27), 165 (26), 115 (24), 91 (28).
General Preparation of Homopolymer (P4) and Copolymers (P(4-co-6)). A solution of catalyst (6.2 μmol or 0.62 μmol) in CH₂Cl₂ (2 mL) was rapidly added to a flame dried vial containing 4 (and norbornene (6)) (620 μmol) in CH₂Cl₂ (8 mL) under argon atmosphere. The reaction mixture was stirred at the desired temperature for 4 h, and excess butyl vinyl ether was added to stop the reaction. The polymer was precipitated into methanol, collected via vacuum filtration, washed with excess methanol, and dried under vacuum at 60 °C overnight. Samples were collected in THF for GPC analysis.
Figure S1. GPC (vs polystyrene) traces at 1% catalyst loading for P4 [A: G1, B: G2, C: G3] and P(4-co-6) [G3, 50:50 (4:6)].
Figure S2. $^1$H-NMR spectra for: Bottom: 1,3-diphenyl-6-isopropylfulvene (5). Top: equimolar mixture of 5 and third generation Grubbs’ catalyst (G3).
Figure S3. $^1$H-NMR spectra for: Bottom 1,3-diphenyl-6-isopropylfulvene (5). Middle: equimolar mixture of 5 and third generation Grubbs’ catalyst (G3). Top: G3.
Figure S4. $^1$H-NMR spectra for: Bottom: 1,3-diphenyl-6-norbornenylfulvene (4). Top: polyfulvene (P4) (Table 1, Entry 4: $M_n = 107400$).
Figure S5. Infrared spectra for: Bottom: 1,3-diphenyl-6-norbornenylfulvene (4). Top: polyfulvene (P4) (Table 1, Entry 4: $M_n = 107400$).
Figure S6. Solution (0.4 – 0.6 mM, THF) emission spectra for 1,3-diphenyl-6-norbornenylfulvene (4) and polyfulvene (P4) (Table 1, Entry 4: $M_n = 105400$) excited at 370 nm.
References

