

Supporting Information

Synthesis of sheet-coil-helix and coil-sheet-helix triblock copolymers by combining ROMP with palladium-mediated isocyanide polymerization

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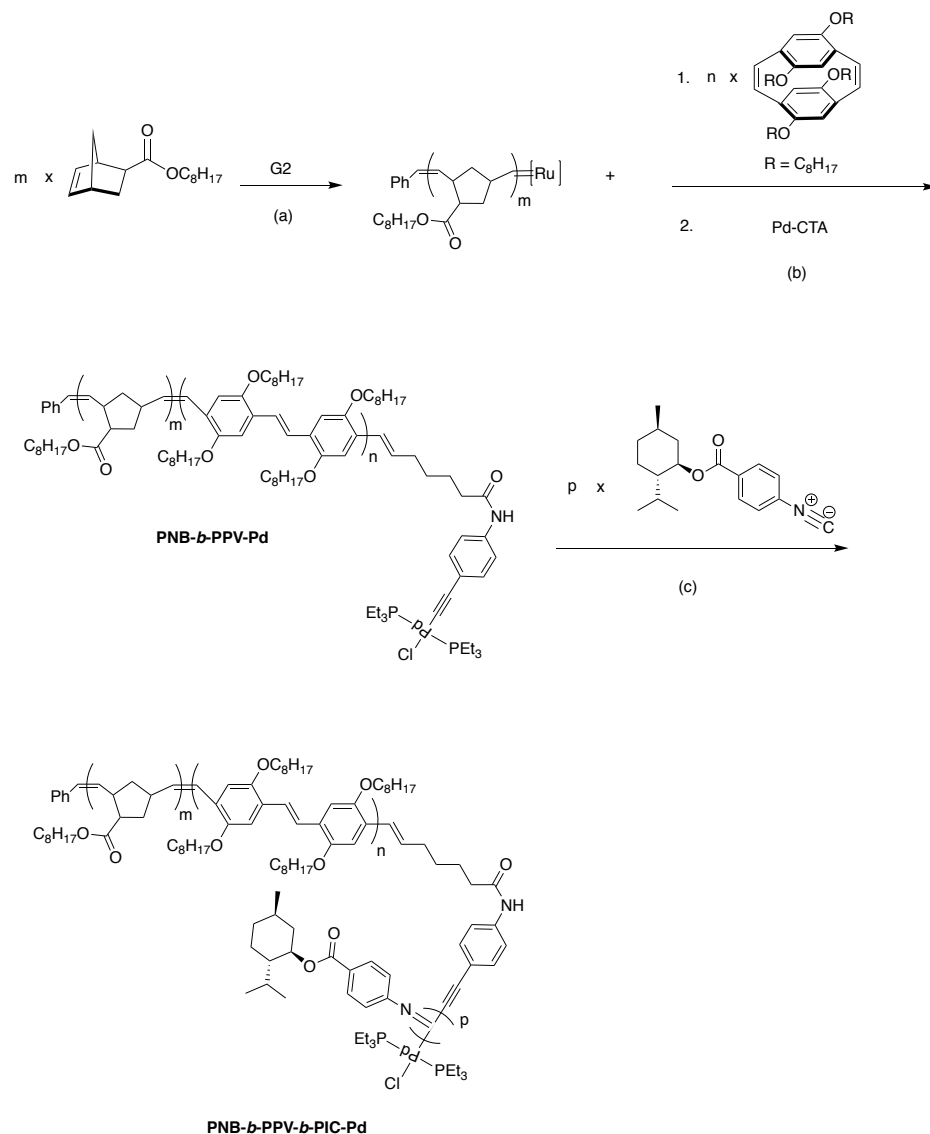
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Materials and Methods

All reactions were carried out under an inert atmosphere of either nitrogen or argon using standard vacuum and Schlenk techniques. All reagents were purchased from Sigma Aldrich or Alfa Aesar Chemicals and used without further purification unless indicated. ¹H NMR spectra were recorded at 25 °C on a Bruker AC 500 and Bruker AC 600 (¹H: 500.1 MHz, 600.1 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) with reference to solvent residual nuclei in deuterated solvents. Molecular weights and dispersity indices were measured using an Agilent 1200 GPC (Agilent Technologies) and operated using a ChemStation program equipped with ASTRA V program. An Agilent 1200 series isocratic pump coupled with a UV detector and the Optilab rEX differential refractive index detector (Wyatt Technology Corporation; Santa Barbara, CA) were calibrated with poly(styrene) standards. The column and guard column utilized were pre-packed (AM GPC Gel, CHCl₃; American Polymer Standards) and the column temperatures were maintained at 25 °C. Samples were measured with a mobile phase consisting of CHCl₃. The injection volume was 100 µL and the flow rate was 1 mL min⁻¹. The concentrations utilized for GPC measurements are ca. 1-3 mg mL⁻¹. *M_w*, *M_n*, and *D* represent the weight-average molecular weight, number-average molecular weight, and dispersity, respectively. Fluorescence spectra were recorded on a Horiba Quantamaster 40 spectrofluorometer (Photon Technology International) in a 10 mm quartz fluorometer cell at 25 °C with 5 nm excitation and 5 nm emission slit widths at intervals of 1 nm/s. Polymer samples (50 nM in CHCl₃) were excited at 365 nm and fluorescence emission was measured from 475 - 700 nm. Circular dichroism spectra were collected using a Jasco J-1500 CD Spectrometer. Spectra were obtained using a 2-mm path length Hellma Analytics quartz suprasil cell at around 5.50 µM in CHCl₃. Polymer samples were prepared in dry and micro filtered HPLC/UV grade CHCl₃ at 5.50 µM.

PNB-*b*-PPV-*b*-PIC-Pd (Coil-Sheet-Helix Triblock Copolymer)



Scheme S1. Synthesis of coil-sheet-helix **PNB-*b*-PPV-*b*-PIC-Pd** (target block ratio: $m:n:p = 100:50:100$).

(a) ROMP to form the coil block was performed under an inert nitrogen atmosphere (glove box) with a monomer-to-initiator ratio of 100:1. The norbornene octyl ester monomer and Grubbs' 2nd generation catalyst (G2) were dissolved in dry CHCl_3 in separate vessels. The resulting solutions were then combined, and the reaction mixture was allowed to stir at room temperature for 45 minutes; (b) The sheet-forming [2.2]paracyclophane-1,9-diene monomer was then taken up in dry CHCl_3 under an inert nitrogen atmosphere (glove box) and added to the solution containing the PNB block. Polymerization to form the diblock copolymer was run at 68 °C and monitored by ^1H NMR spectroscopy wherein a trace of the nonreactive monomer isomer was used as a standard.¹ The monomer-to-initiator ratio for this polymerization was chosen to be 50:1 (2 repeat units per monomer for an effective block length of 100 units after polymerization) as compared to initial

catalyst concentration. Finally, the polymerization mixture was added to a CHCl_3 solution containing Pd-CTA^2 , which was allowed to stir at room temperature for 12 hours. (c) To complete the triblock synthesis, the (-)-menthol isocyanide monomer was dissolved in dry CHCl_3 and added to the diblock macroinitiator in CHCl_3 . The chain-extension polymerization was run for 16 hours at 55 °C under an argon atmosphere. The targeted monomer-to-initiator ratio for this helical block was 100:1 as compared to initial catalyst concentration. The final block copolymer was purified by precipitation in cold MeOH and collected by filtration. ^1H NMR spectroscopic analysis was conducted after purification (Figure S4).

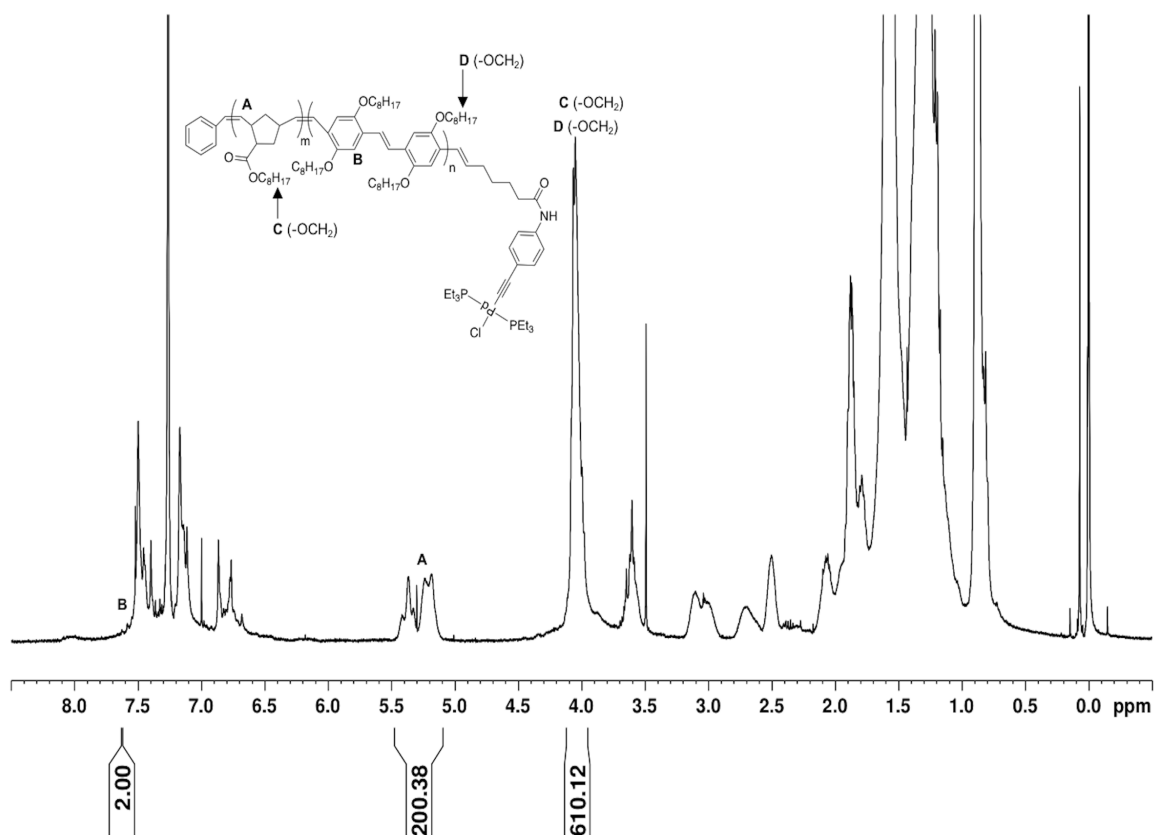


Figure S1. ^1H NMR spectrum (CDCl_3) of $\text{PNB-}b\text{-PPV-Pd}$.

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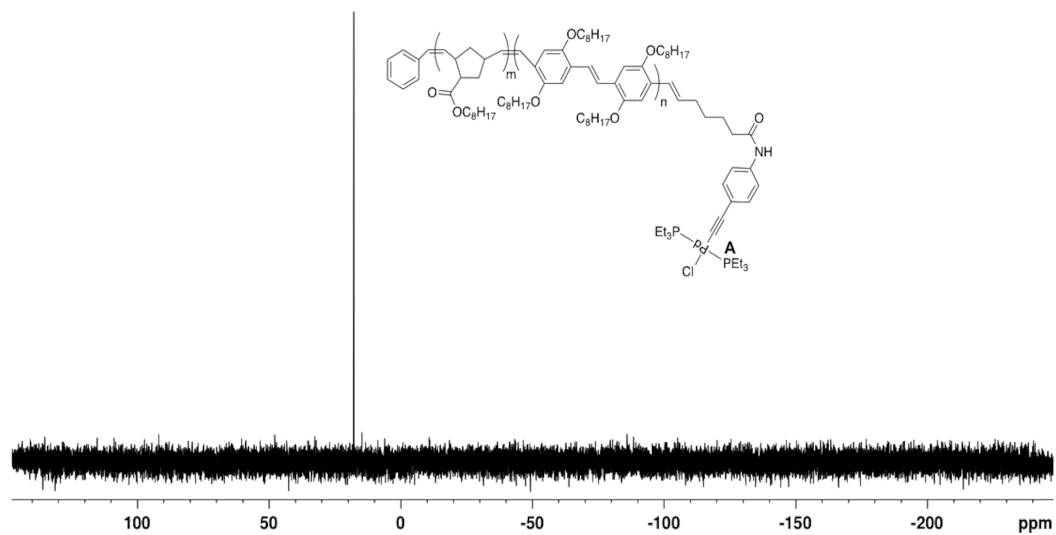


Figure S2. ^{31}P NMR spectrum (CDCl_3) of **PNB-*b*-PPV-Pd**.

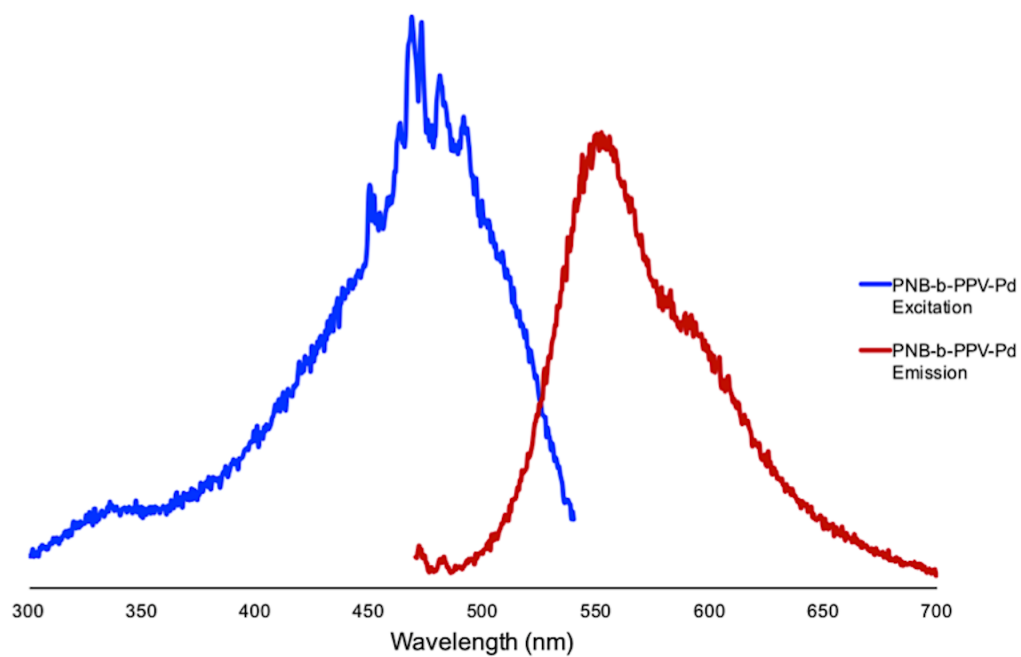


Figure S3. Fluorescence data of excitation and emission spectra for **PNB-*b*-PPV-Pd**.

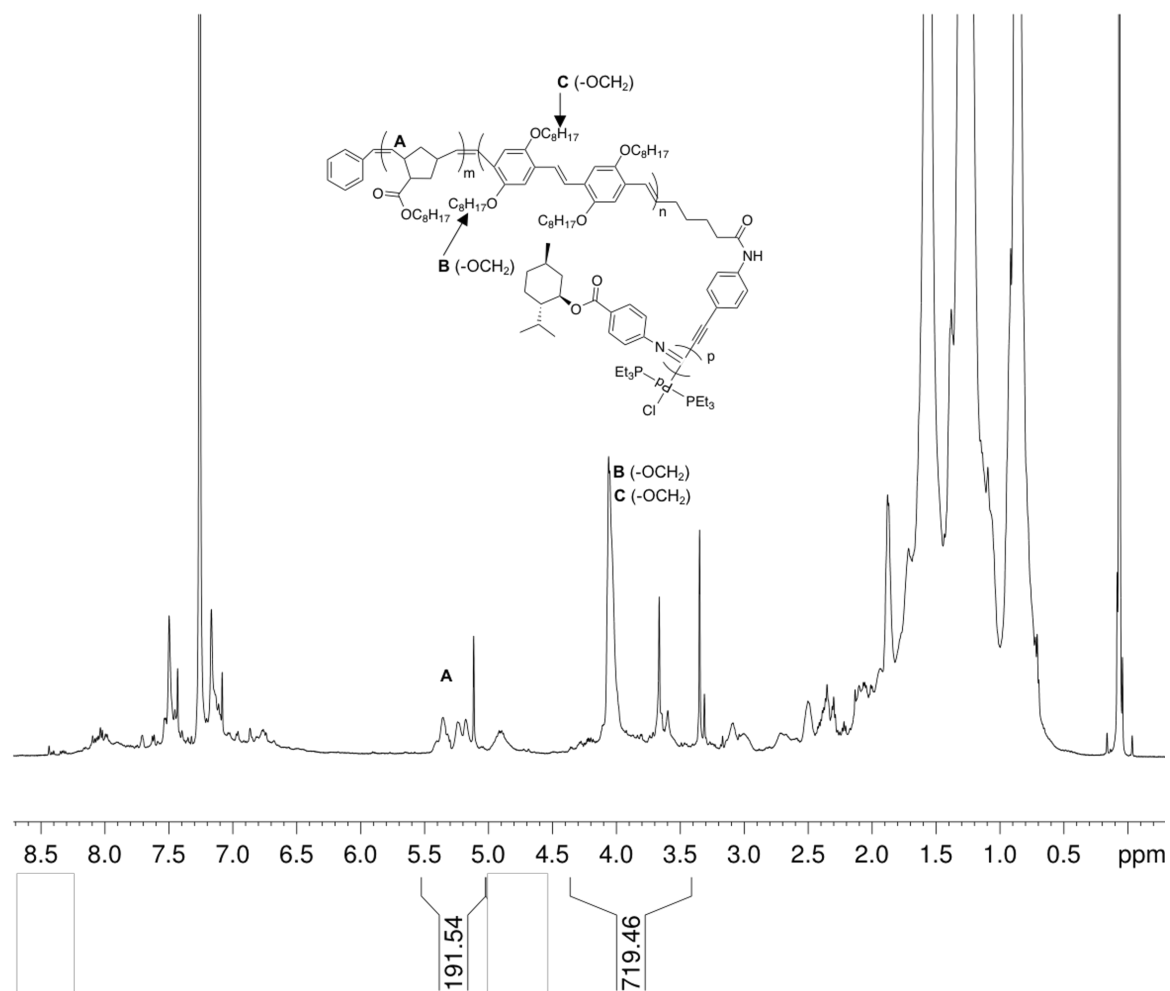


Figure S4. ^1H NMR spectrum (CDCl_3) of **PNB-*b*-PPV-*b*-PIC-Pd**.

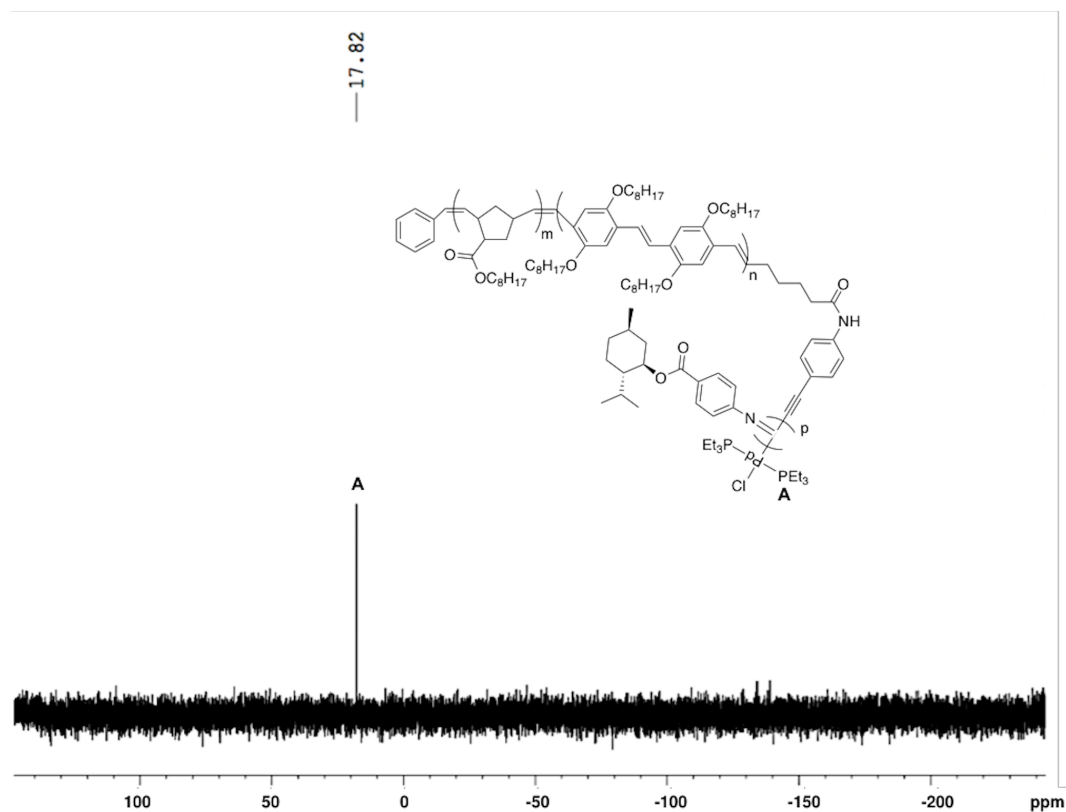


Figure S5. ^{31}P NMR spectrum (CDCl_3) of **PNB-*b*-PPV-*b*-PIC-Pd**.

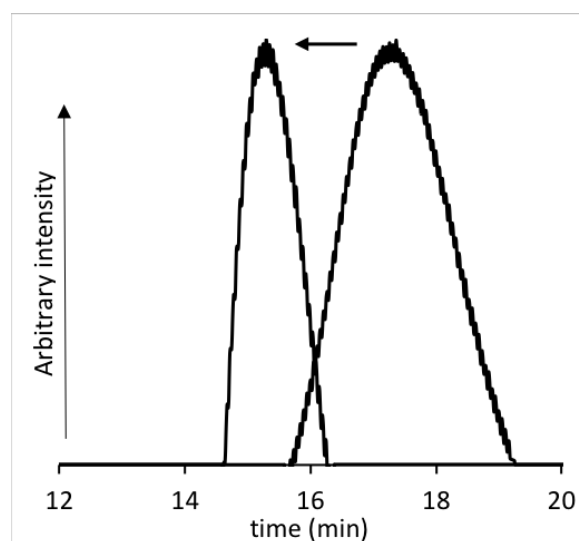


Figure S6. GPC traces (CHCl_3 , PS standards) of **PNB-*b*-PPV-Pd** (right; M_n , 16,000 g/mol, $D = 1.14$) and **PNB-*b*-PPV-*b*-PIC-Pd** (left; M_n = 45,500 g/mol, $D = 1.51$)

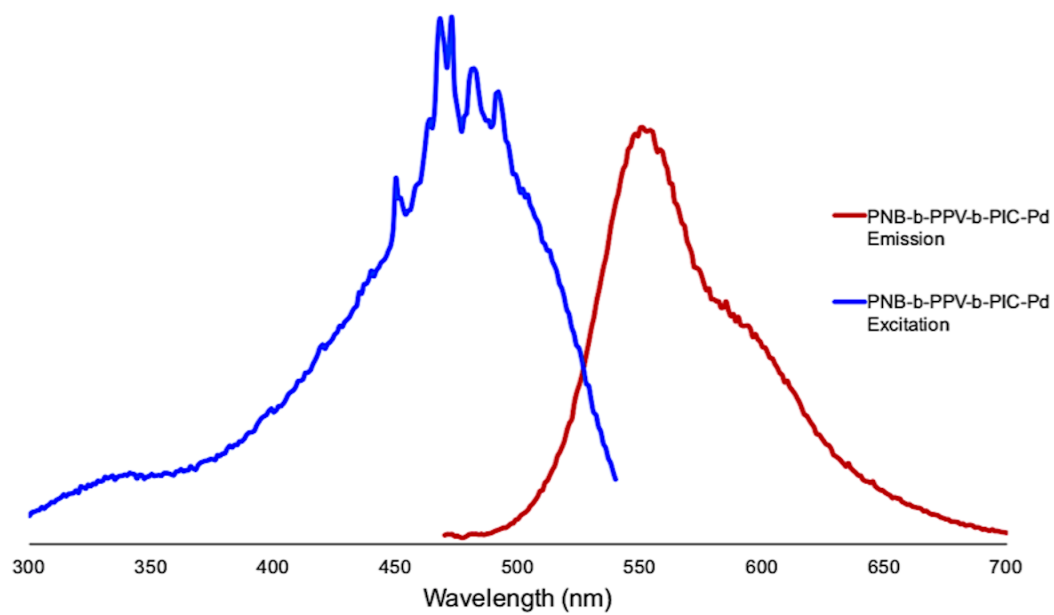
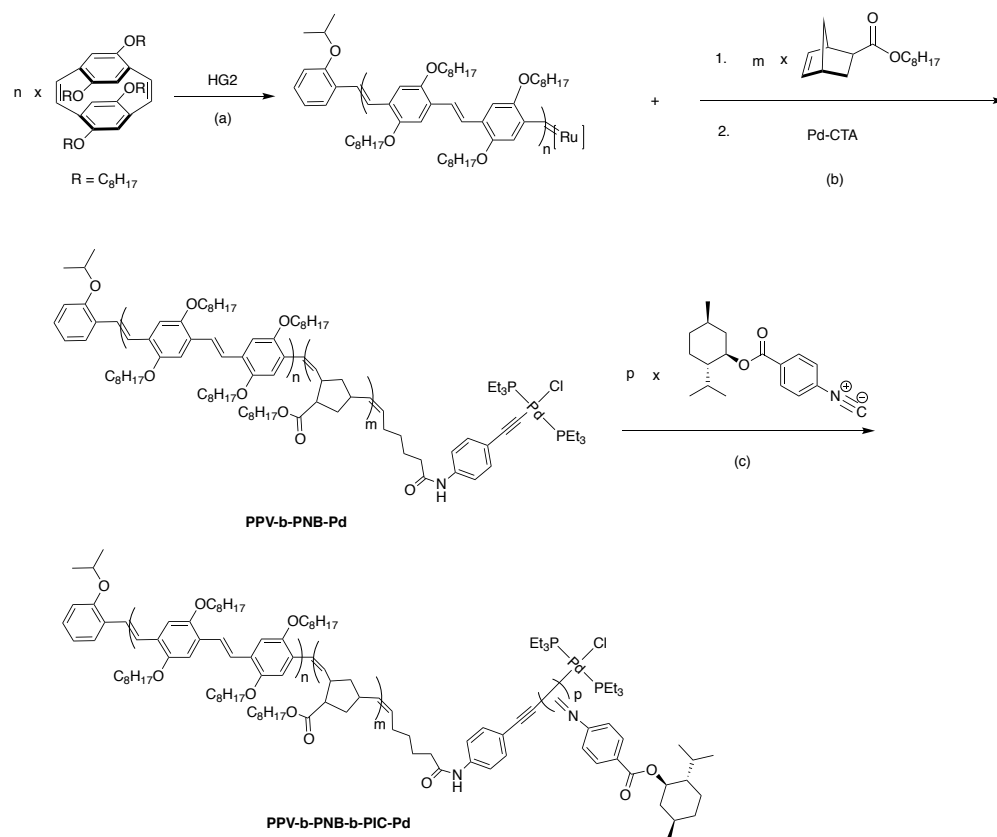


Figure S7. Fluorescence data of excitation and emission spectra for **PNB-*b*-PPV-*b*-PIC-Pd**.

PPV-*b*-PNB-*b*-PIC-Pd (Sheet-Coil-Helix Triblock Copolymer)



Scheme S2. Synthesis of sheet-coil-helix **PPV-*b*-PNB-*b*-PIC-Pd** (target block ratio: $n:m:p = 50:100:100$).

(a) ROMP to form the PPV block was performed under an inert nitrogen environment (glove box) with a monomer-to-initiator ratio of 50:1 (2 repeat units per monomer for an effective block length of 100 units after polymerization). The [2.2]paracyclophane-1,9-diene monomer and Hoveyda-Grubbs 2nd generation catalyst (HG2) were dissolved in dry $CDCl_3$ in separate vessels. These solutions were combined, and the reaction mixture was subsequently heated to 68 °C. The polymerization was monitored by 1H NMR spectroscopy wherein a trace of the nonreactive monomer isomer was used as a standard;¹ (b) The norbornene octyl ester monomer was then taken up in $CHCl_3$ and added under an inert atmosphere (glove box) to the previous reaction mixture containing the PPV block. Polymerization of the coil-forming block was allowed to run for 45 minutes at room temperature. For the PNB block, the monomer-to-initiator ratio targeted was 100:1 (as compared to initial catalyst concentration). Finally, the polymerization mixture was added to a dry $CHCl_3$ solution containing Pd-CTA¹, which was allowed to stir at room temperature for 12 hours; (c) To complete the synthesis of the sheet-coil-helix triblock copolymer, the (-)-menthol isocyanide monomer was dissolved in dry $CHCl_3$ added to the diblock macroinitiator in $CHCl_3$. The polymerization was run for 16 h at 55 °C under an argon atmosphere. For the helical block, the targeted monomer-to-initiator ratio was 100:1 as compared to initial catalyst concentration. After 16 hours, the final triblock copolymer was purified by precipitation in cold

MeOH and collected by filtration. ^1H NMR spectroscopic analysis was conducted after purification (Figure S11).

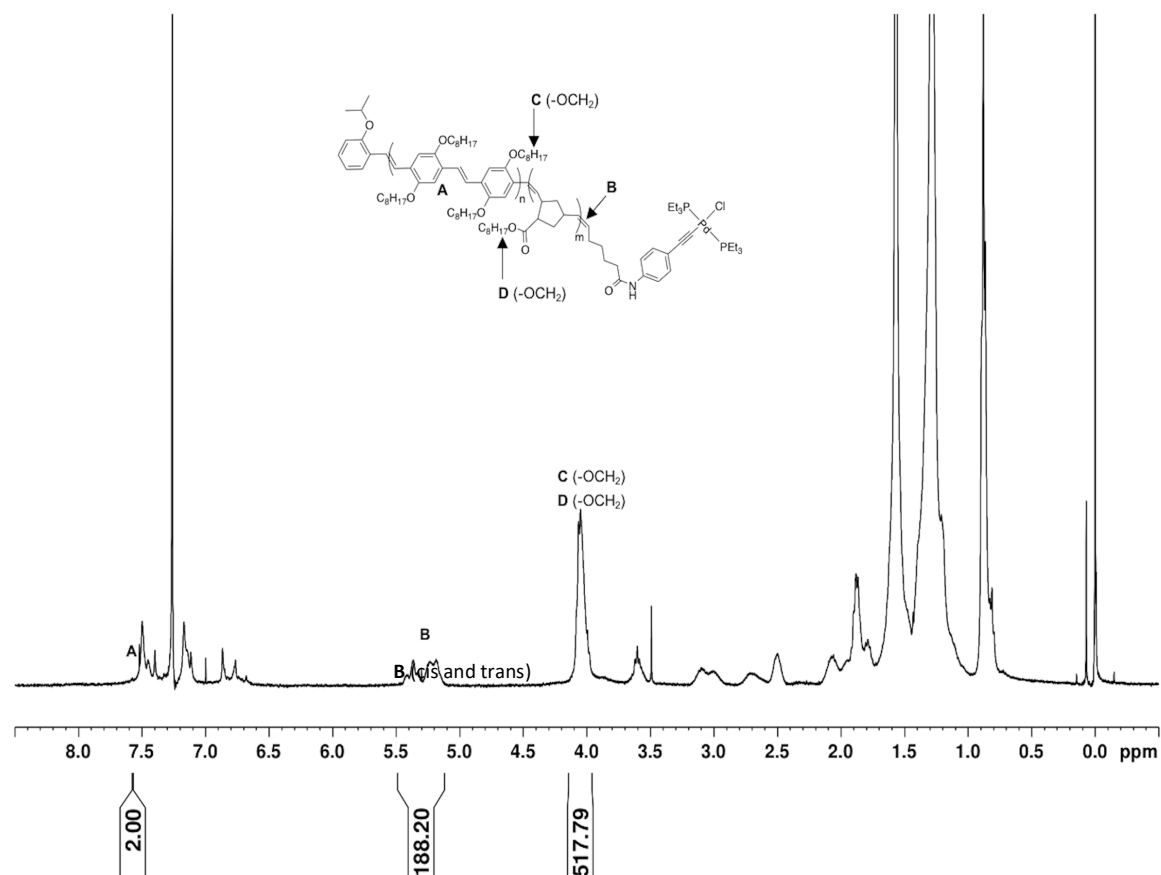


Figure S8. ^1H NMR spectrum (CDCl_3) of **PPV-*b*-PNB-Pd**.

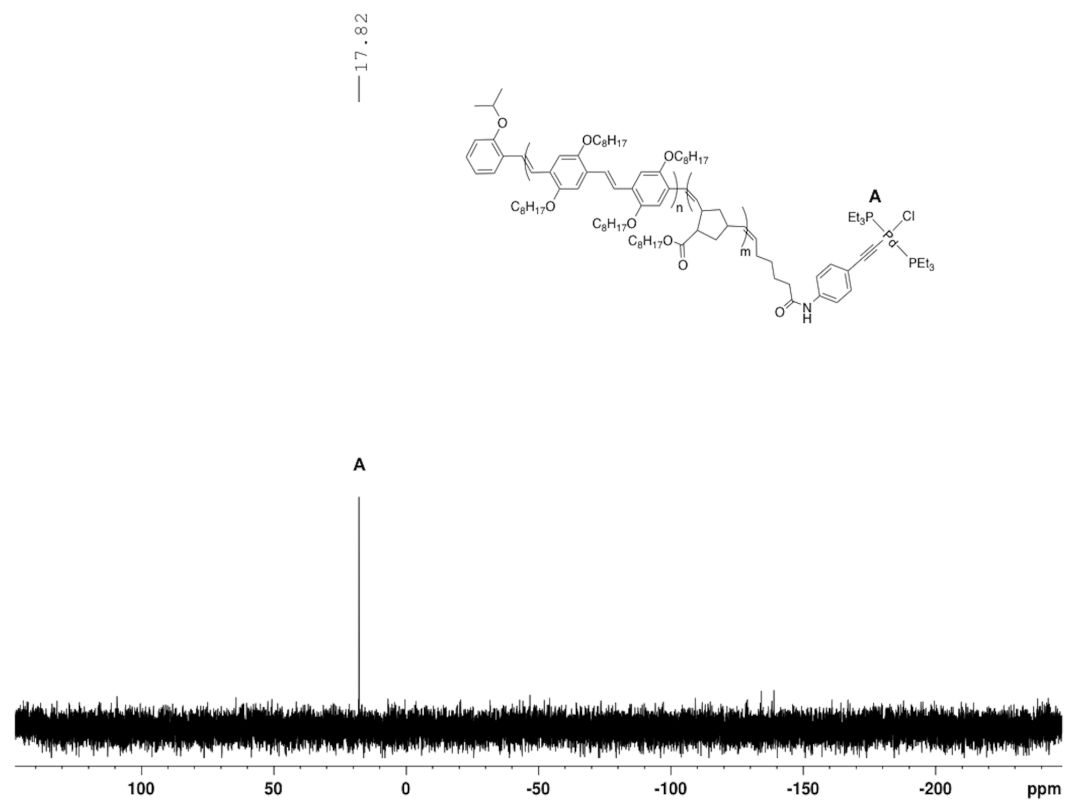


Figure S9. ^{31}P NMR spectrum (CDCl_3) of PPV-*b*-PNB-Pd.

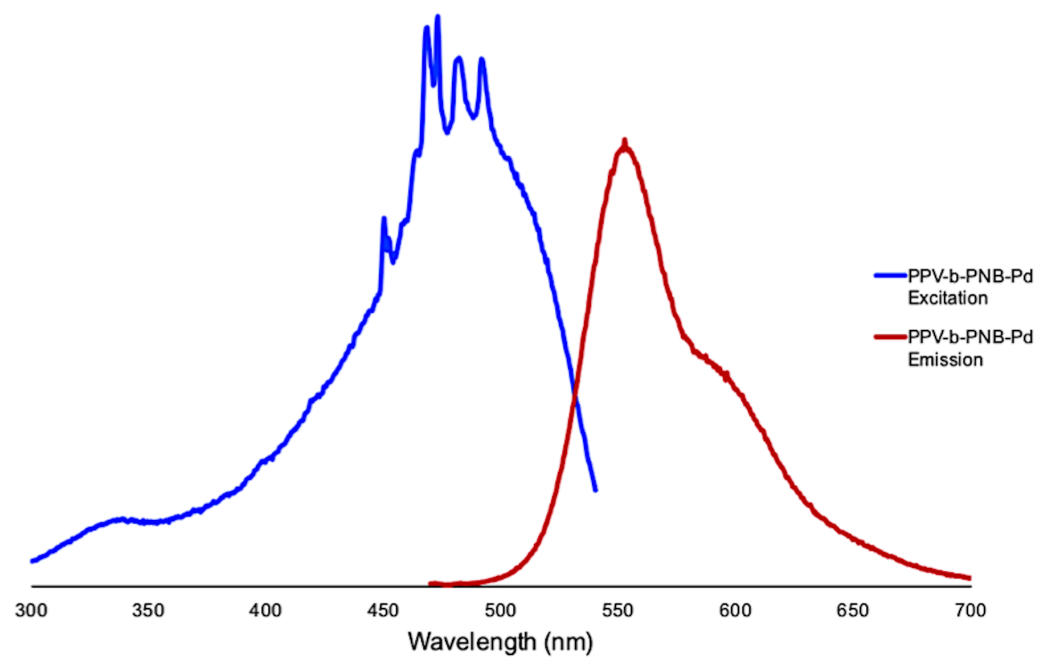


Figure S10. Fluorescence data of excitation and emission spectra for **PPV-*b*-PNB-Pd**.

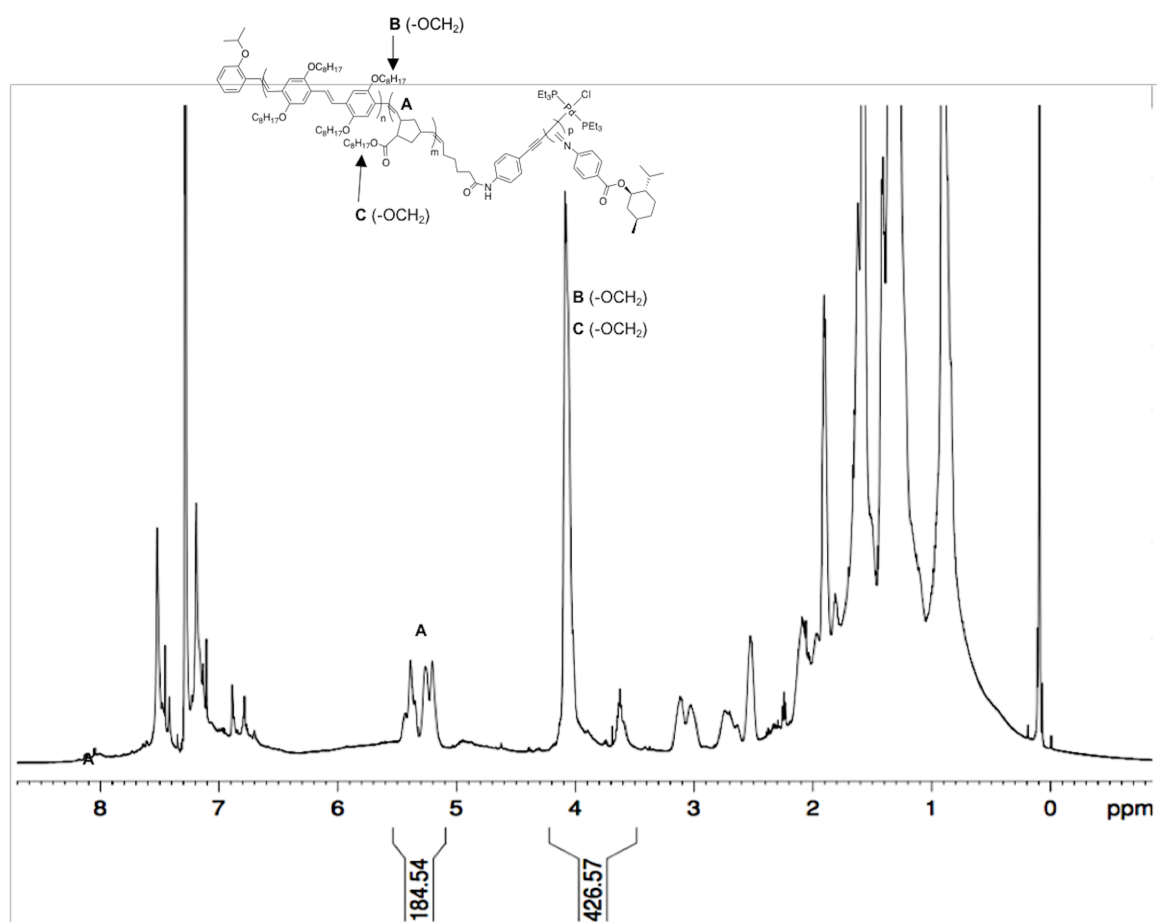


Figure S11. ^1H NMR spectrum (CDCl_3) of $\text{PPV-}b\text{-PNB-}b\text{-PIC-Pd}$.

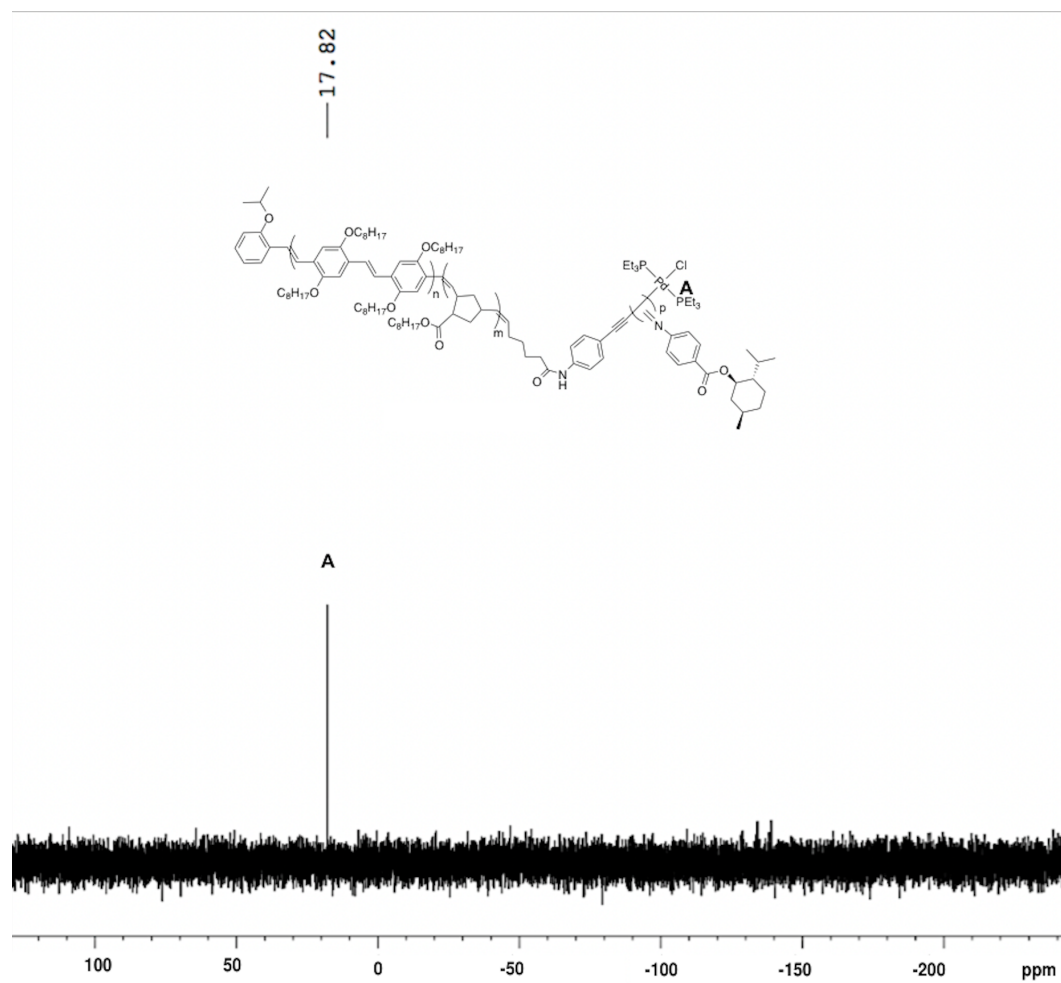


Figure S12. ^{31}P NMR spectrum (CDCl_3) of $\text{PPV-}b\text{-PNB-}b\text{-PIC-Pd}$.

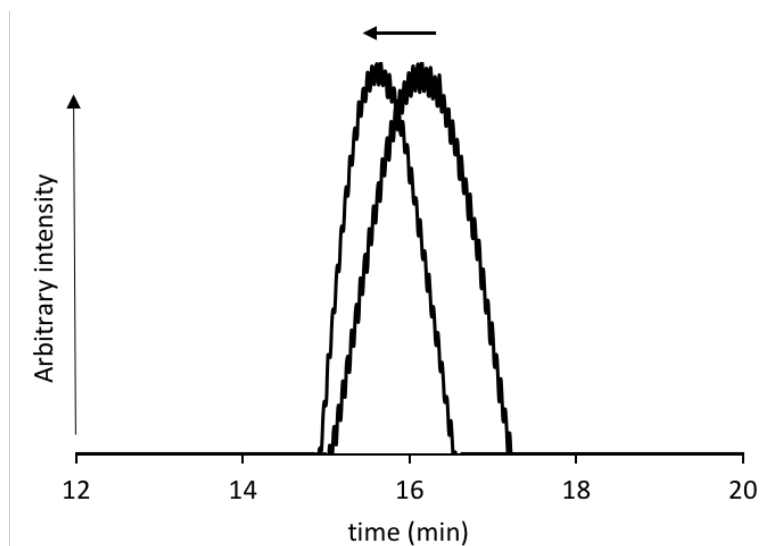


Figure S13. GPC traces (CHCl_3 , PS standards) of **PPV-*b*-PNB-Pd** (right; M_n , 25,500 g/mol, $D = 1.47$) and **PPV-*b*-PNB-*b*-PIC-Pd** (left; $M_n = 39,000$ g/mol, $D = 1.30$).

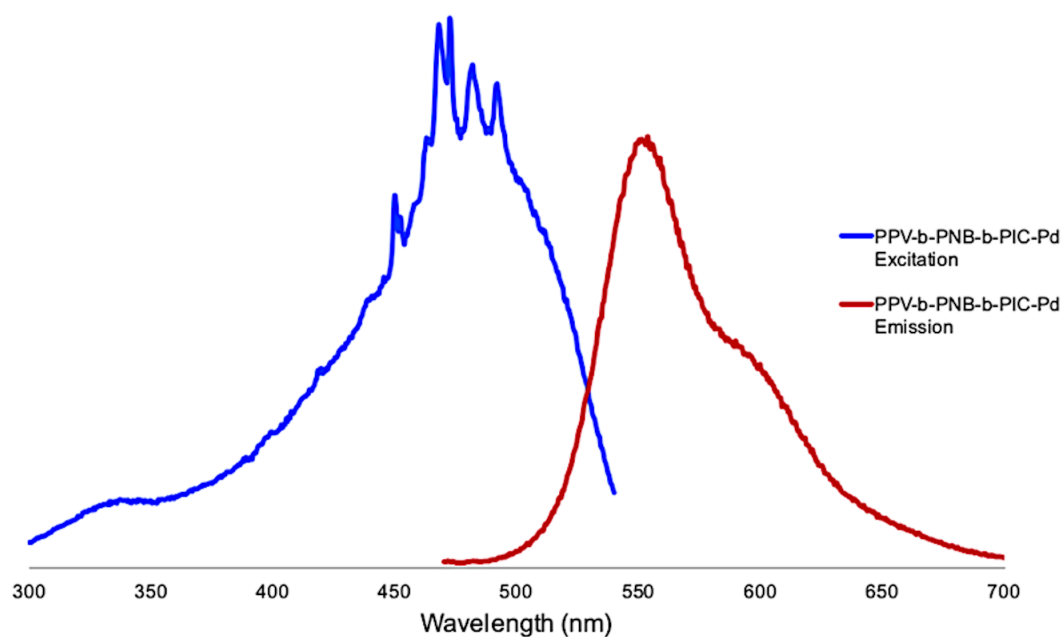


Figure S14. Fluorescence data of excitation and emission spectra for **PPV-*b*-PNB-*b*-PIC-Pd**.

References

1. E. Elacqua and M. Weck, *Chem. Eur. J.*, 2015, **21**, 7151-7158.
2. E. Elacqua, A. Croom, D. S. Lye and M. Weck *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2991-2998.